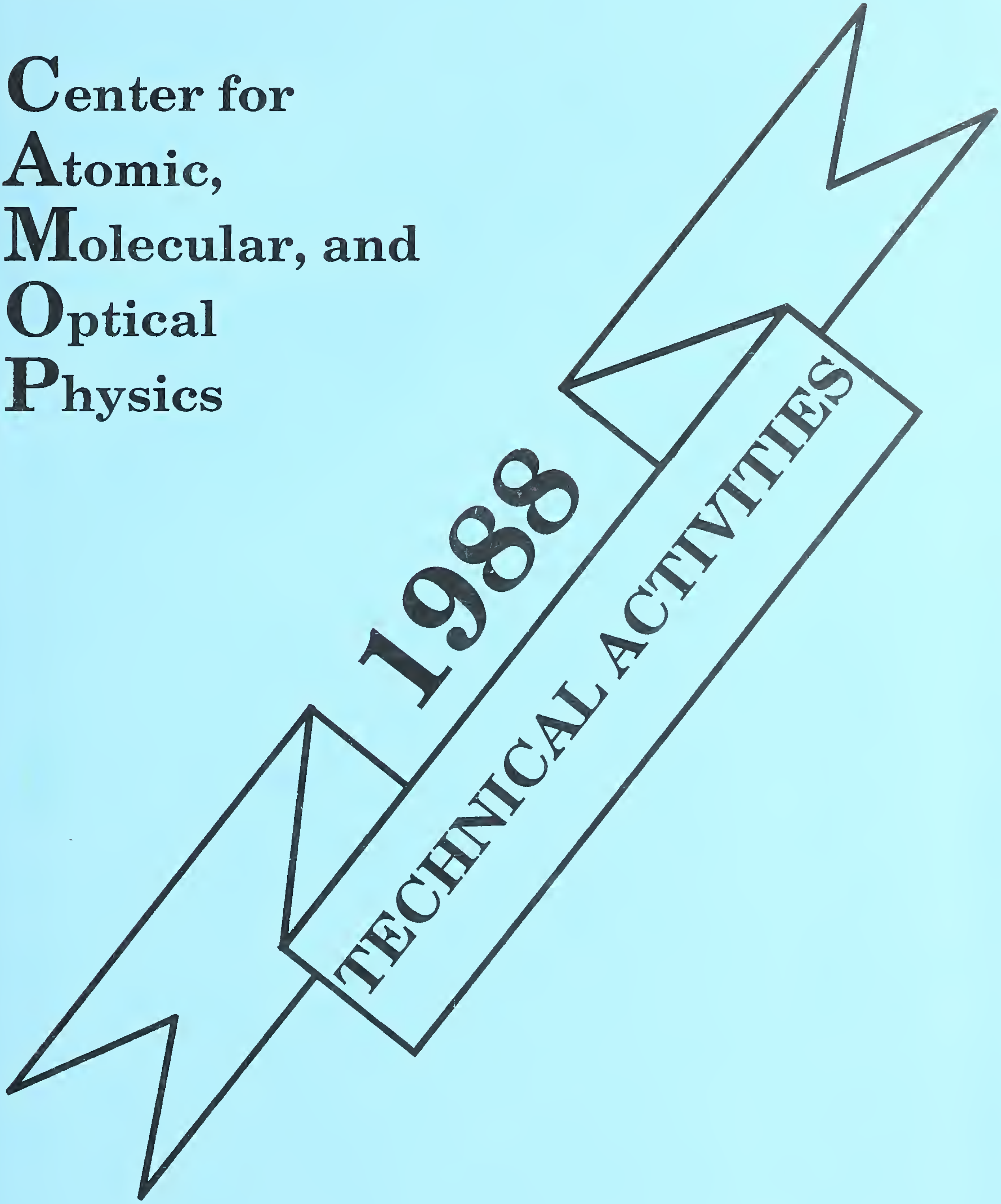
NISTIR 88-3881

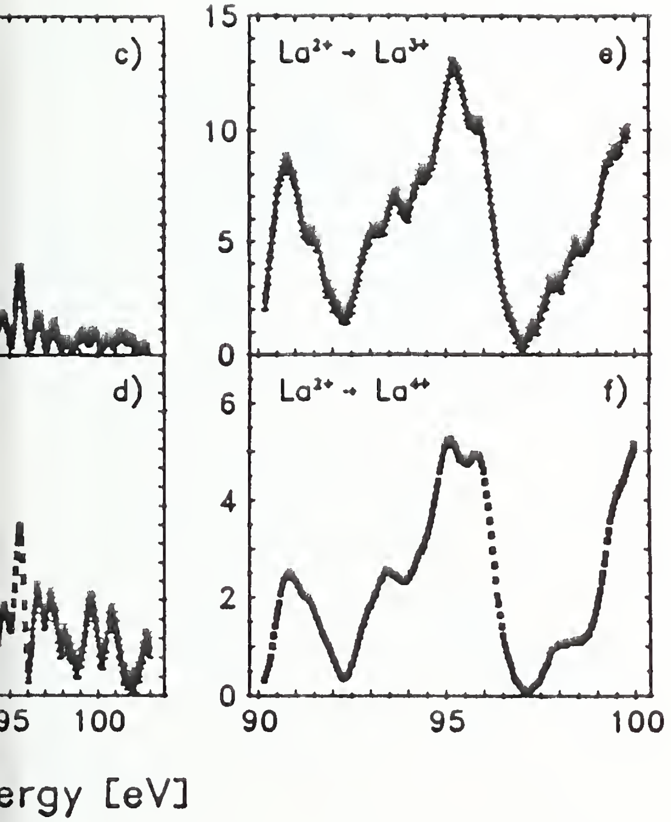
Center for
Atomic,
Molecular, and
Optical
Physics



1988

TECHNICAL ACTIVITIES

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards and Technology



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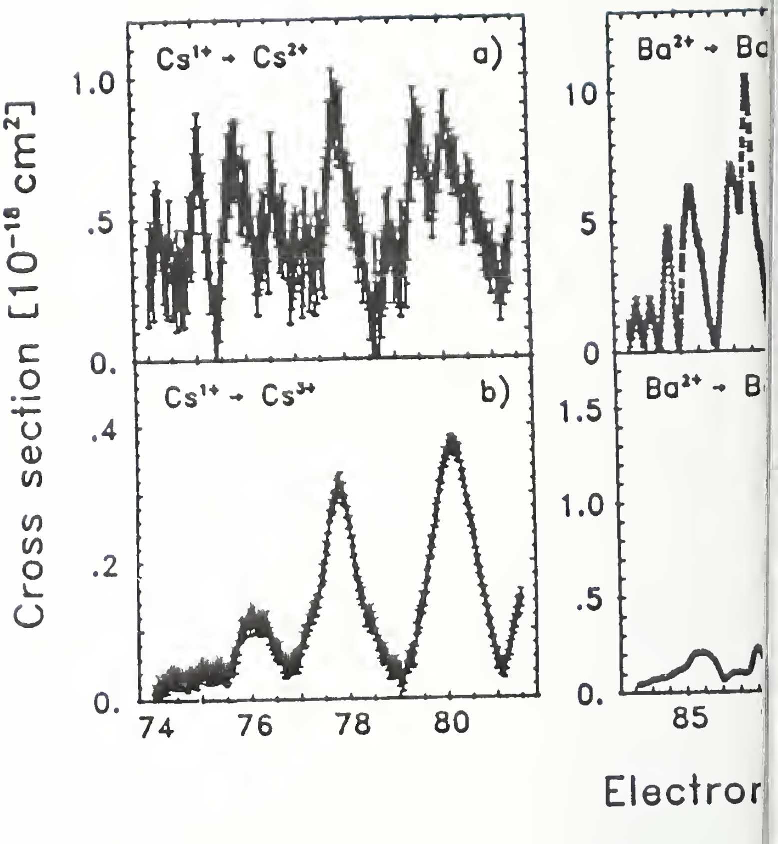

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NISTIR 88-3881

Center for Atomic, Molecular, and Optical Physics

1988
Technical Activities

December 1988

Katharine Gebbie, Acting Director
Center for Atomic, Molecular, and Optical Physics
National Measurement Laboratory

U.S. Department of Commerce, C. William Verity, Secretary
National Institute of Standards and Technology, Ernest Ambler, Director

ABSTRACT

This report summarizes the research and technical activities of the Center for Atomic, Molecular and Optical Physics during the Fiscal Year 1988. These activities include work in the areas of fundamental constants, radiation physics, surface science, molecular spectroscopy, electron and optical physics, atomic and plasma spectroscopy, time and frequency, quantum metrology, and quantum physics.

Keywords: Astrophysics; atomic physics; calibrations; chemical physics; fundamental constants; gravity; laser physics; molecular physics; optical physics; plasmas; radiation; solid state physics; spectroscopy; standards; surface science; time and frequency; wavelength standards.

INTRODUCTION

This report is a summary of the technical activities of the National Institute of Standards and Technology (NIST) Center for Atomic, Molecular and Optical Physics (CAMOP) for the period October 1, 1987 to September 30, 1988. The Center is one of the four technical operating units in the National Measurement Laboratory. It is a new Center formed from two Divisions of the Center for Radiation Research, three Divisions of the former Center for Basic Standards, and two Divisions of the former Center for Chemical Physics.

The summary of activities is organized into eight sections, one for the technical activities of the Center office staff, and one each for the seven divisions of the Center. Each division tells its own story in its own way. In general, there is an overview followed by a series of short reports on current projects. Then the publications, invited talks, committee participation, and some of the technical interactions during the year are listed. In the case of the two Divisions from the Center for Chemical Physics (the Molecular Spectroscopy Division and the Surface Science Division), this report includes activities from both FY 87 and FY 88. Their panel was on a biennial meeting schedule and did not meet last year.

To obtain more information about particular work, the reader should address the individual scientists or their division, c/o Center for Atomic, Molecular and Optical Physics, B160 Physics Building, National Institute of Standards and Technology, Gaithersburg, Maryland 20899.

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INTRODUCTION

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FUNDAMENTAL CONSTANTS DATA CENTER

B. N. Taylor

OBJECTIVES: To provide an international information center within the U.S. for work in the general area of precision measurement and fundamental constants (PMFC), to analyze the consistency of measured values of the fundamental physical constants resulting from different experiments, and to obtain recommended values of fundamental constants for international use.

This is an important field for NIST because of the close relationship between the fundamental constants and precision measurements, basic measurement units such as the ampere, volt, and ohm, fundamental physics, and state-of-the-art measurement technology. One of the purposes of this project is to provide assistance and guidance in the PMFC area to both NIST staff and university scientists, in particular, to advise them on the potential impact of the experiments they are considering carrying out and to keep them informed of related work currently underway in various laboratories throughout the world.

CURRENT ACTIVITIES: These include: (1) keeping apprised of and maintaining a complete reprint collection of the latest accomplishments throughout the world in PMFC; (2) carrying out least-squares adjustments of the fundamental constants to obtain sets or subsets of recommended values; (3) participating in the work of national and international groups, for example, the CODATA Task Group on Fundamental Constants, the NAS/NRC Advisory Committee on Fundamental Constants and Standards, and the Josephson Effect and the Quantum Hall Effect Working Groups of the Consultative Committee on Electricity (CCE); (4) organizing PMFC conferences or PMFC sessions at conferences; and (5) answering inquiries from both within and without NIST relating to the PMFC field.

ACCOMPLISHMENTS: A major activity of the Center during the past year was to continue the wide dissemination of information on the 1986 least-squares adjustment of the fundamental constants and its associated set of recommended values first published in 1987. The latter set replaces the obsolete set resulting from the 1973 adjustment. The 1986 effort, like its 1973 predecessor, was carried out by B. N. Taylor in collaboration with E. R. Cohen, Rockwell International, under the sponsorship and guidance of the CODATA Task Group on Fundamental Constants.

A short article on the new adjustment appeared in *Physics Today* along with the recommended values. An improved version of a more detailed report on the adjustment, CODATA Bulletin 63, was published in *Reviews of Modern Physics*. A wallet card giving most of the recommended values was published as NBS Special Publication 731. A short, popular article on the adjustment was published in *Physics News* of the American Institute of Physics. Finally, a table of fundamental constants was prepared for publication in the 1988 Review of Particle Properties.

Another major activity was to review all of the data available relating to the determination in SI units of values of the Josephson frequency to voltage quotient or Josephson constant K_J, and voltage to current quotient of the quantum Hall effect or von Klitzing constant R_K; and to prepare initial versions of the reports of the Working Group (WG) on the Josephson Effect (JE) and the WG on the Quantum Hall Effect (QHE) of the Consultative Committee on Electricity (CCE) of the International Committee of Weights and Measures (CIPM).

These reports recommended values of K_J and R_K to be adopted by the CCE upon the approval of the CIPM for use by the national standards laboratories and others in realizing practical representations of the volt and ohm based on the JE and QHE, respectively. As part of this effort, extensive new computer programs were written to analyze data that have correlated uncertainties by the standard least-squares method. The programs were applied to the available K_J *and* R_K data, including the results of the Electricity Division's several experiments relating to SI values of K_J and R_K. We chaired a joint meeting of the two Working Groups at the time of the 1988 Conference on Precision Electromagnetic Measurements (CPEM) in Tsukuba, Japan, during which the WG reports were intensively discussed and revised. Two talks relating to the fundamental constants were also presented at the conference.

FUTURE PLANS: The principal focus of the Fundamental Constants Data Center during the coming year will be (1) completing final versions of the CCE Working Group reports; (2) preparing articles on the new representations of the volt and ohm resulting from the CCE adopting the values recommended in the reports; (3) organizing the Data Center's extensive collection of reprints; and (4) beginning to develop computer programs to treat correlated discrepant fundamental constants data by the least-squares method.

These last two items are motivated by a request of the CODATA Task Group on Fundamental Constants. At its meeting on 8 June 1988, the Task Group asked E. R. Cohen and B. N. Taylor to prepare a status report on the fundamental constants which will update their 1986 effort (but new recommended values of the constants are not to be given). This report is to be completed by the time of the 1990 CPEM (11-14 June 1990) and is to be presented at the conference.

PRECISION MEASUREMENT GRANTS

[NIST Precision Measurement Grants Committee: R. D. Deslattes, J. L. Hall, B. N. Taylor (Chairman), D. J. Wineland]

OBJECTIVES: To award each year two new $30 k Precision Measurement Grants (PMGs) and to renew each year four existing PMGs. (The PMGs are renewable for two additional years beyond the initial year, at NIST's option.)

The NIST PMG program was initiated in 1970 and is funded by the NIST Director. PMGs are awarded to scientists in U.S. academic institutions in order to (1) promote and encourage fundamental research in the field of precision measurement and fundamental constants and train future measurement-oriented scientists, and (2) foster contacts between NIST scientists and those researchers in the academic community who are actively engaged in such work. While NIST has much research underway in this field, there is considerable expertise and relevant work in U.S. colleges and universities. It is the purpose of this project to tap this reservoir and to foster the training of students who might eventually become NIST staff by awarding grants to a selected number of outstanding academic researchers.

CURRENT ACTIVITIES: Proposals were openly solicited via an advertisement in Physics Today, announcements in appropriate trade journals and newsletters, and the mailing of a brochure to the physics departments of all of the colleges and universities in the U.S. which grant bachelor and higher degrees in physics (about 850). PMG candidates are requested to submit a biographical sketch and pre-proposal summary outlining the objective of their proposed research, why they believe it to be important, and the general approach to be used, including some indication of what they expect to accomplish in the three year time period covered by the grant. On the basis of this material, four to eight candidates are selected by the NIST Precision Measurement Grants Committee and the Outside Advisory Committee (consisting of four senior university professors) to submit more detailed proposals. The same committees evaluate these and, on the basis of this evaluation, the two recipients are selected. The criteria used to evaluate the pre-proposals and full proposals include the importance of the proposed research to science, the feasibility of the research, and the past accomplishments of the applicant.

ACCOMPLISHMENTS: Excellent proposals were received from 21 candidates, five of whom were chosen to submit final, full proposals. The following are the two recipients selected:

Edward A. Hinds and Malcolm G. Boshier, Yale University
Two-Photon Spectroscopy of H and He^+

Randall G. Hulet, Rice University
Measurement of the Recombination Rate of Spin-Polarized Ultra-Cold Atoms

Hinds and Boshier will test quantum electrodynamics (QED) by using two photon laser spectroscopy to compare the frequency of the 1S - 2S transition in hydrogen with the 2S - 4S transition to a precision of 20 kHz; and then with the 2S - 4S transition in the He^+ ion to a precision of 100 kHz. The first comparison will result in the best measurement of the Lamb shift in any atomic system, the second in tests of certain higher order QED corrections. In combination, the two measurements will yield a new precise value of the proton radius.

Hulet will study collision dynamics at ultra-low temperatures by measuring the rate of recombination of laser-cooled, spin-polarized lithium atoms interacting via the attractive van der Waals potential, and probing spectroscopically the vibrational structure of the resulting weakly bound triplet state molecules. An atomic beam of lithium atoms will be collimated and cooled using the strong dipole force of a near resonant laser beam and then confined in a high magnetic field gradient from permanent magnets. The latter techniques should lead to trapped atom densities considerably greater than previously achieved.

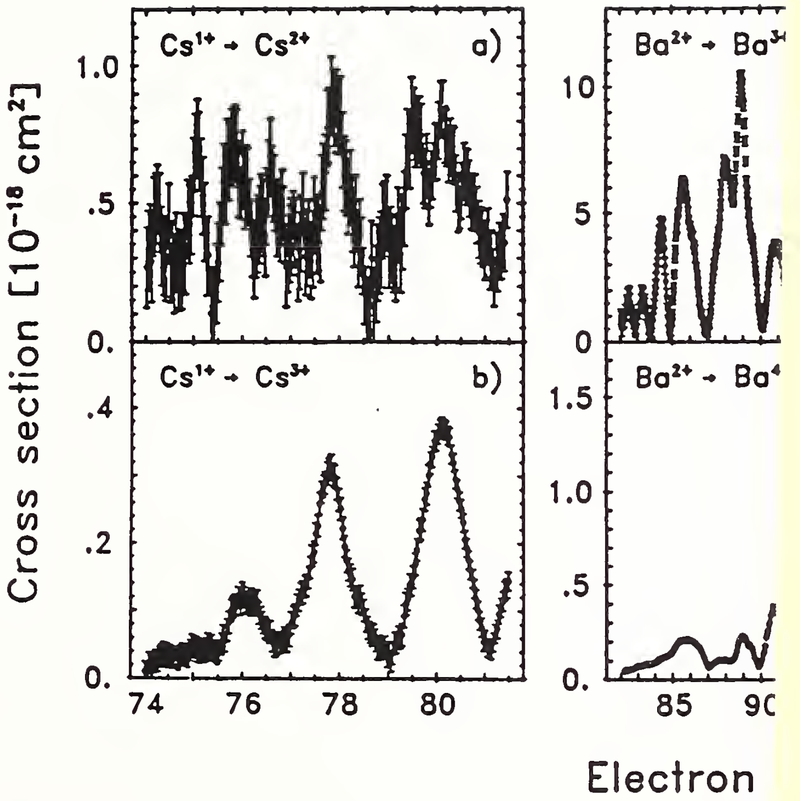
For FY 88, the Outside Advisory Committee consisted of Professors Crampton, Fairbank, Larson, and Metcalf.

The following grants were renewed in FY 88: Frederick R. Raab, University of Washington, Atomic Physics Tests of Gravity and the Equivalence Principle; Daniel R. Stinebring, Princeton University, High Precision Timing of Millisecond Pulsars; W. P. Kirk, Texas A&M University, Quantized Hall Resistance and Fine-Structure Constant Investigations: A Study of Uncertainty Contributions; J. D. Morgan III, University of Delaware, High Precision Calculation of Helium Atom Energy Levels.

There were significant accomplishments by a recent and a current grant recipient during the year. R. W. Dunford (with M. S. Dewey), Princeton University, reported the result of his atomic beam/microwave resonance measurement of the $n = 2$ Lamb shift in $^4He^+$. D. R. Stinebring (and collaborators), also at Princeton University, reported the discovery of a previously unknown dwarf star that is orbiting -- and periodically eclipsing -- an unusual pulsar. A new high-precision timing system developed by Stinebring facilitated the discovery.

FUTURE PLANS: FY 89 plans naturally focus on renewing the four eligible current grants and awarding two new grants. Current and past recipients will be invited to visit NIST and to present talks as appropriate, and visits to current and past recipients will be made by NIST staff in conjunction with other travel.

Figure 2



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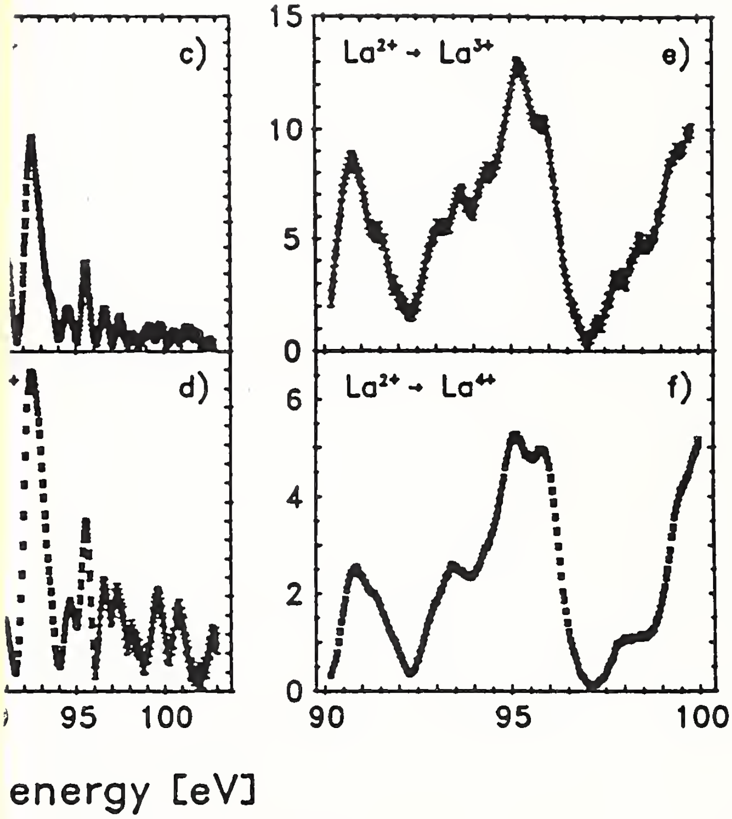

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PUBLICATIONS - FY 88

1. In Print

E. R. Cohen and B. N. Taylor, "The fundamental physical constants," Physics Today 40, No. 8, Pt. 2, pp. BG11-BG15 (August 1987); *ibid.* 41, pp. BG9-BG13 (August, 1988).

E. R. Cohen and B. N. Taylor, "The 1986 adjustment of the fundamental physical constants," Rev. Mod. Phys. 59, No. 4, pp. 1121-1148 (Oct. 1988).

E. R. Cohen and B. N. Taylor, "Fundamental physical constants, 1986 CODATA recommended values" (a wallet card giving values of selected constants from the 1986 CODATA set of recommended values), Natl. Bur. Stand. (U.S.), Spec. Publ. 731 (Oct. 1987). Also published as CODATA and Rockwell International wallet cards.

B. N. Taylor, "New values for the constants of physics," in Physics News in 1987, P. F. Schewe, Ed. (American Institute of Physics, N.Y., Jan. 1988), pp. 29-30; and Phys. Today 41, No. 1, pp. S29-S30 (Jan. 1988).

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R. Kaarls, B. P. Kibble, B. N. Taylor, and T. J. Witt, "Report to the Comite Consultatif d'Electricite from the Working Group on the Josephson Effect," Bur. Intl. Poids Mes. Rapport.

F. Delahaye, T. Endo, O. C. Jones, V. Kose, B. N. Taylor, and B. M. Wood, "Report to the Comite Consultatif d'Electricite from the Working Group on the Quantum Hall Effect," Bur. Intl. Poids Mes. Rapport.

F. Delahaye, T. Endo, O. C. Jones, V. Kose, B. N. Taylor, and B. M. Wood, "Technical guidelines for the reliable measurement of the quantized Hall resistance," Bur. Intl. Poids Mes. Rapport.

B. N. Taylor, "Basic standards and fundamental constants," IEEE Trans. Instrum. Meas. IM-38, 1989.

M. E. Cage, R. F. Dziuba, R. E. Elmquist, B. F. Field, G. R. Jones, Jr., P. T. Olsen, W. D. Phillips, J. Q. Shields, R. L. Steiner, B. N. Taylor, and E. R. Williams, "NBS determination of the fine-structure constant, and of the quantized Hall resistance and Josephson frequency to voltage quotient in SI units," IEEE Trans. Instrum. Meas. IM-38, 1989.

TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

B. N. Taylor, liason member, Advisory Committee on Fundamental Constants and Standards of the Division of Chemistry and Chemical Technology, Numerical Data Advisory Board, National Academy of Sciences/National Research Council/National Academy of Engineering.

B. N. Taylor, Chairman, NBS Precision Measurement Grants Committee.

B. N. Taylor, NBS representative, Consultative Committee on Electricity (CCE), International Committee of Weights and Measures (CIPM).

B. N. Taylor, member, ANSI C-42, American National Standards Institute Committee on Definitions of Electrical Terms.

B. N. Taylor, member, CODATA (Committee on Data for Science and Technology) Task Group on Fundamental Constants.

B. N. Taylor, NBS representative to the Executive Committee, Conference on Precision Electromagnetic Measurements (CPEM), and Comptroller of CPEM.

B. N. Taylor, Coordinator, Consultative Committee on Electricity (CCE) Working Group on the Quantum Hall Effect and member, CCE Working Group on the Josephson Effect.

B. N. Taylor, Vice Chairman, American Physical Society Topical Group on Precision Measurement and Fundamental Constants.

B. N. Taylor, member, editorial board of Metrologia and of J. Phys. Chem. Ref. Data.

INVITED TALKS - FY 88

B. N. Taylor, "Basic Standards and Fundamental Constants," 1988 Conference on Precision Electromagnetic Measurements (CPEM 88), Tsukuba, Japan, June 1988.

B. N. Taylor, "Changes in the Representations of the Volt and Ohm: Report from the CCE," 1988 National Conference of Standards Laboratories (NCSL) Workshop and Symposium, Washington, DC, August 1988.

B. N. Taylor, "Practical Implementation of the New Representations of the Volt and Ohm: A New Unit or a New Physical Quantity?," NCSL Ad Hoc Committee 91.4 on Change in the Volt and Ohm, Washington, DC, August 1988.

COLLABORATIONS, CONSULTING, MISCELLANEOUS ACTIVITIES

B. N. Taylor is collaborating with E. R. Cohen, Rockwell International, and the CODATA TAsk Group on Fundamental Constants, on various aspects of data analysis relevant to the fundamental physical constants.

Laser-Cooled and Trapped Neutral Atoms

W. D. Phillips, P. D. Lett, R. N. Watts, C. I. Westbrook, S. Rolston; Guest Scientists: P. L. Gould, H. J. Metcalf, J. Weiner, H. Thorsheim

Objectives: To study the basic physics of laser-cooling and electromagnetic trapping of neutral atoms and the application of these techniques to new physical measurements. Areas of interest include high resolution spectroscopy, ultra-low energy-collisions, ultra-low-energy atom-surface interactions, Bose-Einstein condensation, and atomic beam manipulation. This work is complementary to work in the Time and Frequency Division on cooling and trapping of ions.

Current Activities: We have a laser-cooled atomic sodium beam capable of producing a continuous beam of atoms with velocities as low as tens of m/s. This has been used to load atoms into optical molasses, (a laser cooling region formed at the intersection of three orthogonal pairs of counterpropagating laser beams), an optical trap, and a magnetic trap. Focussing, deflection, and collimation of the beam is also possible.

Accomplishments: Last year we made the first, continuously loaded optical molasses, and performed experiments which suggested some problems with the usual theoretical understanding of molasses. In particular, we found that the confinement time was much longer than was expected from the usual theory. We also operated the first, hybrid, radiation pressure-dipole force laser trap. During the past year, we have discovered that one reason for the discrepancy with the molasses theory is that the temperature of atoms in optical molasses is much lower than the lowest temperature that was believed to be possible. We have used our laser trap to perform the first measurement of a collision cross section at sub-millikelvin temperatures.

Cooling below the cooling limit: The lowest temperature expected from laser cooling (the Doppler cooling limit) can be derived simply from the balance between the cooling provided by the laser and the heating arising from the random nature of absorption and emission. For sodium, this cooling limit is 240 μK. In fact, however, we have measured the temperature of Na atoms in optical molasses to be about 40 μK, six times lower than the cooling limit. The result was so surprising and unexpected that we insisted on confirming it with four independent methods of temperature measurement. After the results were reported, groups at Stanford and Ecole Normale Superieur confirmed the achievement of below-cooling-limit temperatures.

We also found that the low temperatures are destroyed by the presence of a magnetic field or by deviating from the standard practice of using orthogonal linear polarizations in the three pairs of laser beams used in the molasses. These observations suggested that degenerate magnetic sublevels are responsible for the extra cooling. Indeed, colleagues at Ecole Normale and at Stanford have suggested a mechanism whereby the differing laser-induced dynamic stark effect in the different sublevels is used to extract kinetic energy from the atoms. The properties of this new laser cooling mechanism are at least in qualitative agreement with our observations.

Collisions at millikelvin energy: Our tiny optical trap (10^{-6} cm^3), embedded in the optical molasses, provides a potential well into which the very cold atoms of the molasses fall, becoming concentrated so that the excited state atomic density is about 10^{10} cm^{-3}. At this density, collisions between excited atoms are important and the associative ionization reaction $Na^* + Na^* \rightarrow Na_2^+ + e^-$ is easily seen. By measuring the number and distribution of excited atoms with a video camera, the rate of ionization with an electron multiplier, and deducing the atomic temperature (0.75 mK) from the distribution in the known trap potential, we were able to measure the cross section for this process. We obtained about 10^{-13} cm^2, a value about three orders of magnitude bigger than what had been measured at temperatures from 20 K to 2000 K. The extremely large cross section is due to the long deBroglie wavelength of the atoms at these ultra-low temperatures.

Our colleague, Paul Julienne of the Molecular Spectroscopy Division, has shown theoretically that at these low energies the cross section for associative ionization is strongly reduced unless the atom is in a strong laser field. This is due to the decay of the excitation needed for associative ionization before the atoms are close enough for association to occur. In a strong laser field, the transition is power broadened sufficiently that the atoms can be re-excited even when close together. Preliminary results indicate that this is indeed the case experimentally, and that most of our observed associative ionization is from periods when the strong trap laser is on.

Future Plans: We intend to continue measurements on super cold optical molasses to discover basic properties such as the ultimate low temperature achievable, the degree to which the experiments agree quantitatively with theory, and the relationship of the new discoveries about the temperature to the previous observations of long confinement times in molasses. We will also be exploring other collision experiments, particularly measuring the associative ionization cross section in the range between 1 mK and 20 K. We are continuing the study of laser cooling atomic hydrogen, the construction of a diode laser cooling laboratory for laser cooling of heavier alkalis, and the construction of apparatus for the laser cooling of atoms having interest as optical frequency standards. We are also continuing the study of experiments on the reflection of ultra-cold atoms from surfaces.

PUBLICATIONS - FY 88

W. Phillips, P. Gould, and P. Lett, "Electromagnetic Manipulation of Atomic Hydrogen," in Proceedings of the Cooling, Condensation and Storage of Hydrogen Cluster Ions Workshop, Menlo Park, CA, January 8-9, 1987, J. T. Bahns, ed. (University of Dayton, 1987) p. 157.

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R. Blatt, G. Lafyatis, W. Phillips, S. Stenholm, and D. Wineland, "Cooling in Traps," Physica Scripta T22, 216-223 (1988) (Section 3).

W. D. Phillips, "Summary of the Physics in Traps Panels," ed. by R. S. VanDyck, Jr., Physica Scripta T22, 228-237 (1988) (Section 6).

P. L. Gould, P. D. Lett, P. S. Julienne, W. D. Phillips, H. R. Thorsheim, and J. Weiner, "Observation of Associative Ionization of Ultra-Cold Laser-Trapped Sodium Atoms," Phys. Rev. Lett. 60, 788 (1988).

P. Lett, R. Watts, C. Westbrook, W. D. Phillips, P. Gould, and H. Metcalf, "Observation of Atoms Laser Cooled Below the Doppler Limit," Phys. Rev. Lett. 61, 169 (1988).

INVITED TALKS - FY 88

W. D. Phillips, "Laser Cooling and Trapping," University of Indiana, Bloomington, Indiana, Physics Department Colloquium, November 1987.

W. D. Phillips, "Laser Cooling of Neutral Atoms," NBS, Gaithersburg, Maryland, Research Advisory Committee Colloquium on Laser Cooling, November 1987.

P. D. Lett, "Associative Ionization of Ultra-Cold Sodium," University of Nebraska, Lincoln, Nebraska, Physics Department Colloquium, February 1988.

W. D. Phillips, "Cooling, Stopping, and Trapping Atoms," Naval Research Laboratory, Washington, DC, Physics Colloquium, February 1988.

P. D. Lett, "Associative Ionization of Ultra-Cold Sodium," University of Oregon, Eugene, Oregon, Physics Department Colloquium, February 1988.

P. D. Lett, "Associative Ionization of Ultra-Cold Sodium," Yale University, New Haven, Connecticut, Atomic Physics Seminar, March 1988.

P. D. Lett, "Laser Cooling Below the Doppler Cooling Limit," University of Michigan, Ann Arbor, Michigan, Physics Department Seminar, April 1988.

W. D. Phillips, "Cooling, Stopping, and Trapping Atoms," Ohio University, Athens, Ohio, Physics Department Colloquium, April 1988.

W. D. Phillips, "Laser Cooling Below the Doppler Cooling Limit," AT&T Bell Laboratories, Murray Hill, New Jersey, Seminar, June 1988.

P. L. Gould, "Associative Ionization of Ultra-Cold, Laser-Trapped Na," Eleventh International Conference on Atomic Physics, Paris, France, July 1988.

P. D. Lett, "Associative Ionization of Ultra-Cold Na," International Quantum Electronic Conference, Tokyo, Japan, July 1988.

P. D. Lett and R. N. Watts," Laser Cooling Below the Cooling Limit," NEC Corporation, Central Research Laboratories, Kawasaki City, Japan, Research Seminar, July 1988.

C. I. Westbrook, "Laser Cooling Below the Cooling Limit," University of Bonn, Bonn, West Germany, Atomic Physics Seminar, July 1988.

C. I. Westbrook, "Laser Cooling Below the Cooling Limit," Max Planck Institute, Garching, West Germany, Quantum Optics Seminar, July 1988.

C. I. Westbrook, "Laser Cooling Below the Cooling Limit," University of Hamburg, Hamburg, West Germany, Atomic Physics Seminar, July 1988.

W. D. Phillips, "Laser Cooling Below the Cooling Limit," Fourth Symposium on Frequency Standards and Metrology, University of Ancona, Ancona, Italy, September 1988.

W. D. Phillips, "Experiments with Laser-Cooled Atoms," University of Maryland, College Park, Maryland, Analytic and Nuclear Chemistry Seminar, September 1988.

TECHNICAL ACTIVITIES

Division 571, Radiation Physics

The Radiation Physics Division focuses on measurement programs related to the use of electron, laser, ultraviolet, and soft x-ray radiation in the energy range from about 5 eV (250 nm) to 1 keV (1.3 nm).

In support of this mission, radiation standards and advanced measurement techniques are developed. Through our standards program, the Division provides the central national basis for the measurement of far ultraviolet and soft x-ray radiation. The NIST synchrotron radiation facility and a detector calibration facility based upon well-characterized photoionization chambers serve as national radiation standards. Measurement services are available for the calibration of the quantum efficiency of uv photodiodes and the spectral responsivity of vacuum ultraviolet spectrometer systems.

Through our electron measurements program, new types of electron sources and detectors are developed to investigate the properties of matter on an atomic scale. For example, specially designed spin-polarized electron sources and detectors are used to determine fundamental atomic scattering properties and to measure surface magnetism. A scanning tunneling microscope is being used to provide "images" of surfaces on an atomic scale and to study relationships between macroscopic material properties and surface microstructure.

With the goals of improving standards and understanding the fundamental physical phenomena upon which they are based, the Division also conducts theoretical and experimental research on the electronic structure of atomic and molecular systems, the interaction of the systems with photon and electrons, and radiation deposition and energy transfer processes. Theories are developed for the scattering and transport of electrons in materials of fundamental and technological interest. New techniques and instrumentation are developed to study radiative reactions with matter, including photoexcitation and photoionization processes and non-linear effects in intense laser fields. Studies are underway to relate the behavior of condensed matter systems to their fundamental atomic and molecular properties.

The Division has two major research facilities: a dedicated synchrotron ultraviolet radiation facility (SURF-II), and a polarized electron research facility.

SURF-II is a dedicated synchrotron radiation facility, consisting of a 300 MeV electron storage ring, a 10 MeV microtron injector, and associated synchrotron radiation beamlines. It produces radiation in a narrow, intense, highly polarized beam with a continuous and accurately known spectrum from the infrared, through the visible and the far ultraviolet, and into the soft x-ray region. SURF-II is unique among synchrotron light sources by virtue of its uniform and precisely known circular orbit. This allows accurate determination of all the spectral and geometrical properties of the radiation and hence its use as an absolute radiometric standard.

This facility serves staff from our own Division, users from other NIST Divisions, and outside users in radiometric standards and calibration work, optical physics research, surface science, biochemistry, spectroscopy, and other research areas utilizing far ultraviolet radiation. It helps to fill a growing demand for radiation in the ultraviolet and soft x-ray region of the electromagnetic spectrum. Of the 11 light ports at SURF, 6 are now instrumented for user applications and for calibration of optical instruments and transfer standard photodiodes. Some of these ports are shared by more than one experimental station. Three of the remaining ports are utilized for beam current monitoring, electron counting, and machine diagnostics. Most experiments and calibrations can run simultaneously, unless they require special beam parameters.

The polarized electron scattering facility is used to produce and measure beams of spin polarized electrons. It is available for collaborative research by NIST and outside scientists in areas of mutual interest on a time-available basis. Three separate, ultra-high vacuum instruments are available. The polarized electron beams have currents in excess of 1 μA, with an optically reversible polarization at energies less than 1 keV and with an energy resolution of $\approx$0.15 eV.

These electrons are used to probe spin dependent scattering interactions between polarized electrons and surfaces or polarized electrons and atoms. The electron-surface scattering parameters can be used to determine surface structure or study surface magnetic phenomena and the dependence on temperature, composition, adsorption, etc. The electron-atom scattering parameters can be used to probe spin-orbit and exchange interactions in electron scattering and to completely describe the selected collision process.

In relatively new research directions, several innovative electron measurement techniques pioneered at NIST are being further developed in cooperative programs with industry to study the atomic and magnetic microstructure of advanced materials. Magnetic microstructure can be measured with a spatial resolution approaching 100 Angstroms (0.01 microns) by a technique called Scanning Electron Microscopy with Polarization Analysis (SEMPA). An ultra-high vacuum scanning tunneling microscope has also been constructed to investigate, on an atomic scale, the nucleation and growth of thin films on clean metallic and semiconductor surfaces.

Division staff are also collaborating on two projects at the National Synchrotron Light (NSLS) facility at Brookhaven. The first involves radiation probing of exotic materials with soft x-rays. With colleagues from the U. of Tennessee and Oak Ridge National Labs, we are studying core-hole excitation and soft x-ray fluorescence in solid materials of fundamental and industrial significance such as GaAs, quasi-crystals, and high Tc superconductors. This is being done using an IR-100 award-winning, high sensitivity, soft x-ray emission spectrometer with an efficiency 1000 to 10,000 higher than conventional spectrometers in the energy range 20 eV to 1 keV.

In the second project, Division staff are part of a consortium of 11 principal investigators from 8 major laboratories representing industry, universities, and government. This "Materials Research Group", funded principally by NSF, is studying surface magnetism using spin polarized photoemission techniques on materials prepared with molecular beam epitaxy methods. This work is being done on an undulator beamline at NSLS.

As can be seen in the following sections, the Division staff have been active in publishing research papers, providing calibration services, presenting invited talks, sponsoring conferences, providing consultation services, and participating in technical and professional committees. We have also been very active in technical collaborations within NIST and with universities, industry, and other government agencies. Some highlights of the past year include:

1. A new, greatly improved SEMPA instrument for measuring magnetic microstructure with greater speed, sensitivity, and reliability is operational. The development was featured in several corporate magazines, and a major new collaboration was initiated with Perkin-Elmer.

2. Our scanning tunneling microscope has been used to measure unusual "atomic chains" formed with a low coverage of Cs adsorbate on GaAs(110). The vertical resolution of the ultra-low noise instrument is about .01 Angstroms.

3. SURF-II had a record, stored-beam current of 258 mA in May, 1988, and a record quarterly average of 200 mA during Apr-Jun, 1988, about 20% higher than last year's record. Increased current means increased flux. Experiments can be done faster, more sophisticated measurements can be made, and the quality of the work is higher.

4. There were a number of new users at SURF-II this year, including industrial users. Some of the new users were from U. California (Berkeley), U. Nebraska, ARACOR, Lockheed, and KMS Fusion Corporation. In addition, we are collaborating with United Detector Corporation and Science Applications Inc to develop new uv and soft x-ray detectors for radiometric applications, including silicon photodiodes with enhanced uv response and stability.

5. High Tc superconductors were investigated using x-ray fluorescence from photon- and electron-irradiated samples as a measure of the local, partial density of states. There were eight publications on this project, a collaboration between NIST, U. of Tennessee, U. Uppsala, and Oak Ridge National Labs.

6. A new "competence" project for "Advanced Studies in Laser Cooling and Trapping" is being initiated as a collaboration between three Divisions with expertise in atomic, molecular, and optical physics.

The Radiation Physics Division will develop a vuv laser radiation source to cool hydrogen atoms to within a few °K.

7. Thirty major visiting scientist collaborations were active in FY88: nine in the Far UV Physics Group; seven in the Electron Physics Group; and fourteen in the Photon Physics Group.

FAR UV PHYSICS GROUP

Far UV Detector Calibrations (L.R. Canfield, N. Swanson, and J. Kerner)

Calibrated transfer standard detectors for the far ultraviolet continue to be made available to the scientific community and industry, and recalibrations of detectors already in use are performed as requested. Two facilities with coverages of 5-50 nm and 50-254 nm are used. A beamline at the SURF-II facility is dedicated to this activity in the shorter wavelength region. During FY88, 39 calibrations of user photodiodes were provided, a significant increase over last year's total of 21.

The NIST far uv detector calibration competence forms the basis for the radiometric needs of the space research community. In addition, nearly any measurement activity making use of far ultraviolet photons e.g. for plasma diagnostics, remote sensing, or irradiation applications, requires a determination of the magnitude of the flux incident on the experiment. Such a measure has been provided by NIST transfer standard photodiodes for almost two decades.

Windowless photoemissive diodes are fabricated within NIST for use in the region 5-122 nm. Working standards of this type are calibrated by direct comparison with the photoionization current from a rare gas ionization "chamber". A special windowless thermopile is used to transfer these calibrations to the longer wavelengths, where commercially available MgF_2-windowed photodiodes fabricated to our specifications are used as working standards. Intercomparison calibrations with both types of these working standards are then used to arrive at calibrations of detectors to be supplied to outside users.

In a collaboration with industry, the radiometric characteristics of newly-developed Si photodiodes that may serve as future standards in the far uv have begun to be studied. Silicon photodiodes are used in numerous applications to measure visible and infrared radiation and are normally opaque to shorter wavelength radiation. The special silicon detectors developed in this collaboration were designed to optimize sensitivity to uv and soft x-ray radiation. Our measurements indicate that they are the most efficient photodiodes ever measured in this wavelength region, having an efficiency of about 3000 percent at 10 nm, about 300 times greater than commonly used photodiodes. These highly efficient solid state detectors could be used for calibrating radiation measurement instrumentation, but may also be sensitive enough that they can be used as active elements in remote sensing and other applications. If tests of stability and homogeneity also give positive results, this development could lead to a new, high-efficiency radiometric standard and form the technical basis for a new generation of high-efficiency array detectors for uv and soft x-ray imaging applications.

SURF-II Operation (L. Hughey, A. Hamilton, R. Madden, and W. Wooden)

The performance of SURF-II continues to improve. The average beam current over the past year is about 170 mA (last year it was 90 mA), while the average over the last five months is over 200 mA. A new record beam of 258 mA was recorded during this period. In addition to this, the beam lifetime has been improved. The half-life of a 200 mA beam is now about 2 1/2 hours as compared to 1 1/2 hours a year ago for similar operating conditions. SURF-II has also operated very reliably this year. Beam was provided to users more than 90% of the scheduled beam time (nine hours/day; 4 days/week) in FY88.

A number of improvements at SURF have been responsible for the higher current and longer lifetime. The output of the injector accelerator (a 10 MeV microtron) was improved by 25-30%, resulting in more electrons injected into the storage ring. Improvements in the magnetic field gradient profile as a function of electron energy have resulted in an increase in the ratio of full energy electrons to injected electrons. Additional increases in the ratio of full energy electrons to injected electrons are due to the development of automatic systems for controlling the r.f. power in the storage ring cavity and the vertical beam expansion (fuzz) as functions of electron energy. These automatic systems are also responsible for achieving more consistency in full energy beam current.

Another improvement was: (1) finding one length of r.f. transmission line, for use during the energy ramp, to promote a resonant beam oscillation that provides an even greater ratio of full energy to injection energy electrons; and (2) finding a second transmission line length, for use at full energy, to promote another stable, self-stimulated beam oscillation that results in a significant beam lifetime increase.

SURF-II User Programs (R. Madden)

SURF-II was utilized by a variety of NIST and outside users in FY88 for spectrometer and detector calibrations and for research in surface science, atomic and molecular physics, and uv and soft x-ray optical physics. The heaviest use was seen on the Surface Science beamline, BL-1, and the Spectrometer Calibration beamline, BL-2, followed closely by activity on the Angle-Resolved Photoelectron Spectroscopy (ARPES) beamline, BL-5, and the Detector Calibration beamline, BL-9. The High Resolution Spectrometer beamline, BL-3, was commissioned. Staff of the Photon Physics Group and the University of Maryland are now characterizing the high resolution, 6.65 m spectrometer and initiating an experimental program in atomic and molecular physics.

A. Surface Science Beamline, BL-1 (R. Kurtz, T. Madey, and R. Stockbauer, all from NIST Center for Chemical Physics)

We have supported at SURF-II the establishment by the NIST Surface Science Division of an experimental capability to study well- characterized surfaces. These studies use several SURF-II monochromators and an ultrahigh vacuum system. Photon stimulated desorption (PSD) of ions is being studied to understand desorption mechanisms and energetics. Ion desorption mechanisms for ionically and covalently bonded adsorbates are investigated. Variable wavelength ultraviolet photoemission spectroscopy (UPS) is also utilized to study the electronic structure of metals, oxides, and chemical species adsorbed on these materials.

One of the techniques developed by this group is the measurement of electron attenuation lengths through molecular films. By measuring the decrease of a substrate photoemission peak as a molecular film is condensed and varying the photon energy, the attenuation length can be measured as a function of electron energy. These are the first measurements of their kind in the 20-200 eV energy range and are important in modeling the effects of ionizing radiation on materials and tissue.

The most exciting work this year was the study of the new, high temperature superconductors. Using UPS, this group, in collaboration with a group from the Naval Research Laboratory, investigated the electronic structure and surface chemistry of high Tc superconductors and related materials. Using resonant photoemission, they found the electrons to be highly correlated and almost covalent in nature. The controversy over the existence of Cu^{3+} in high Tc compounds was resolved by studying the Cu resonant satellites. Their behavior is indicative of Cu^{2+} rather than Cu^{3+}. Currently a unique O 2p satellite observed in these materials is under investigation.

Chemisorption studies of these materials showed that they react strongly with H_2O to form surface hydroxides. This is the first step in the degradation of these materials when exposed to air. The surfaces react less strongly with CO_2, but the reaction is significant.

Two new areas of research have been initiated by this group, again in collaboration with the Naval Research Laboratory. The first is a study of the electronic states and surface chemistry of prototype dispenser cathode materials. In a H_2O chemisorption study of Ba and BaO on W(110) and W(111), they observed that a thick layer of hydroxide was formed, indicating that the H_2O was able to penetrate the hydroxide layer and react with the underlying W. The second new area is the study of the electronic states of metal-on-metal systems, in which controlled amounts of one metal are deposited onto a single crystal of a different metal.
The resulting electronic energy states are not, as one might presume, simply a superposition of the individual states of the two materials. Rather, totally new states are observed for thin overlayers. This is an exciting result, suggesting the possibility of tailoring unique electronic structures for new materials applications.

Work is also continuing on the effects on molecular adsorption of surface defects in TiO_2. This is an important catalytic material and a model compound for the theory of ion desorption.

A new ellipsoidal mirror analyzer is now ready for installation on BL-1, the Surface Science beamline. This is a unique instrument, with only one other operational in the United States. It is capable of measuring kinetic energy and angular distributions simultaneously. It will be used for angular resolved photoemission and ion desorption measurements. A He-cooled sample stage, a side sample preparation chamber, and a sample transport mechanism are being constructed to produce single crystal thin films of the high T_c superconductors and of metal overlayers. The other Surface Science instrumentation has been moved to BL-8 to continue the electron attenuation length and photoemission measurements.

B. Radiometric Instrumentation Calibration Beam Line, BL-2 (M. Furst and R. Graves)

During FY88 there were 7 user groups who used the SURF-II calibration facility over a period of 39 weeks. Since the photon flux from the electron storage ring can be calculated from precisely measured parameters, the synchrotron radiation is used as a radiometric standard to characterize absolute instrument response over a range of wavelengths from 4-400 nm. Users were from NASA/Goddard Space Flight Center, Laboratory for Atmospheric and Space Physics/University of Colorado, North Carolina State University, Space Sciences Laboratory/U. California (Berkeley), Naval Research Laboratory, and Space Sciences Center/University of Southern California. NASA continues to provide partial support for the facility.

Two of the user groups were new to the facility. The group from Berkeley made radiometric measurements of components of the EUV Explorer satellite that will be used for stellar flux measurements. The group from the University of Southern California measured the efficiency of an EUV normal incidence spectrometer that will be used to measure the full solar disk emission spectrum over the range 15-60 nm.

The cryopumps have been upgraded on the large vacuum chamber that is used to simulate upper atmospheric vacuum conditions. The new pumps reduce down time for users since they have a larger pumping capacity and permit a longer time period between regenerations.

C. High Resolution Spectrometer Beamline, BL-3 (M. Ginter and D. Ginter, U. Maryland; and R. Morrison, Talladega College)

The High Resolution Spectrometer Facility installed on BL-3 has been put through a final set of tests in preparation for its use in two sets of experiments. The tests indicated that a resolving power of 80,000 is attainable and absolute absorption measurements with 2% accuracy should be possible. These characteristics make it one of a few instruments in the world capable of absolute measurements with such high resolution.

Our first experiments will exploit the very high resolution to measure the photoabsorption cross-section in the region of the 3s np window resonances in argon. Although the cross-sections of these resonances have been measured at lower resolution, our new studies of the absolute cross-sections at high resolution will enable theorists to compare their calculations with experiment in a more meaningful way.

The second experiments, which form the main objective of our new program, will study the Stark effect on the Rydberg levels of para-hydrogen. In this work we expect to uncover some of the "quantum chaos" observed in similar studies with high resolution laser spectroscopy (by K.H. Welge and others). The experiments will provide the first detailed look at the photon absorption of highly excited molecular states in an electric field at energies where the transition to chaos is just occurring. The work is closely correlated with theoretical work in our group that has successfully predicted the onset of chaos in atomic hydrogen in a magnetic field.

D. Angle-Resolved Photoelectron Spectroscopy Beamline for Molecular and Chemical Physics, BL-5 (T. Ferrett, J. Hardis, S. Southworth, and A. Parr, all from Radiometric Physics Division; J. Dehmer, Argonne National Lab)

Studies were made of resonant photoionization processes in N_2O and NO, motivated in both cases by recent developments in theory. The high resolution capability of the ARPES instrument was used to study vibrationally-dependent shape resonance effects in N_2O. Vibrationally-dependent effects in the resonant photoionization of polyatomic molecules are not well understood. New insight into these effects was obtained by comparison of the ARPES measurements with corresponding fluorescence measurements and with recent theoretical calculations.

Our previous ARPES measurements, along with recent theoretical developments, have led to the prediction of complex resonant states in NO which arise due to the interaction among several types of resonant excitations. In addition, the ionization dynamics may be further complicated by competition with neutral dissociation processes. In order to characterize these complex resonances, we have made new, more detailed ARPES measurements on NO.

The ARPES instrument was moved to the Daresbury storage ring during the summer to continue the research program with higher resolution irradiation capabilities, in collaboration with colleagues at Daresbury.

E. Optical Properties of Materials Beamline, BL-8 (R. Madden; R. Keski-kuha, GSFC; D. Husk, U. Virginia)

The 2.2m grazing incidence spectrometer on BL-8 was used with a reflectometer chamber at the exit slit for studies of optical properties of materials. The characteristics of multilayer reflectors for the 10-20 nm region were studied by R. Keski-Kuha of Goddard Space Flight Center, and by a group collaboration from the Laboratory for Atmospheric and Space Physics

(U. Colorado) and Lockheed. The beamline was also used by a U. Virginia group to measure the fluorescent yield of phosphors.

The measurement system was upgraded with a new sample manipulator and an improved vacuum system. In FY89 we intend to further improve the existing system and begin planning for a new monochromator and measurement chamber to support the newly developing vacuum ultraviolet and soft x-ray multilayer technology.

F. <u>Detector Calibration Beamline, BL-9</u> (R. Canfield and J. Kerner)

The recently activated SURF-II detector calibration facility continues to provide calibrations in the 5-50 nm spectral range. Refinements to the technology have been made as experience has been developed.

To extend measurements to shorter wavelengths, we are currently assembling a proportional counter module which will serve as an absolute standard for detector calibrations into the soft x-ray region (up to 1 keV). Initially the module will be mounted on BL-9 and be used to intercompare calibrations made with the standard ionization chamber in the 200-300 eV range.

The design puts the detector being calibrated behind a thin-windowed gas flow proportional counter so that both detectors view the same incident beam. Calibrated filters are used to reduce the beam intensity for the photon counting measurements. The module also features a thin window isolation from the UHV section of the beamline.

Several research activities have also been carried out with this facility during FY88.

Photoemission measurements of two classes of high temperature superconductors have been made, with emphasis on the copper/copper oxide features found in the 77 eV region. These measurements help in understanding chemical differences related to processing parameters and to the degree of superconductivity present. The work will continue as new materials and processing techniques become available.

A group of filters used in x-ray laser measurements were characterized in collaboration with personnel from Lawrence Livermore Labs and AT&T Bell Labs. Calibration of power density in laser research at Livermore was dependent on these measurements. Also, several special narrow-band detection devices were characterized in collaboration with staff from KMS Fusion Inc. These will be used in plasma diagnostics in the laser fusion program.

A variety of experimental silicon photodiodes were characterized in collaboration with staff from United Detector Technology Corporation in an attempt to optimize development parameters with a view toward radiometric applications. The measurements indicate that solid state photodiodes can be made to be very efficient and relatively stable in the region 10-200 nm.

Further testing will be done to determine their suitability for radiometric applications.

ELECTRON PHYSICS GROUP

The Electron Physics Group has ongoing research efforts in electron collision physics including electron-atom collisions, electron-surface interactions, surface magnetism, electron interaction theory, electron polarization phenomena, tunneling and scanning electron microscopy, and electron optics and instrumentation. The wide applicability of electron-based measurement technologies allows us to contribute to the solution of many diverse scientific and technological problems.

This year saw the expansion of the Electron Physics Group in both staff and experimental capabilities. Our new scientific staff members include J. Stroscio (from IBM and previously Cornell), M. Scheinfein (U. Arizona/Cornell), R. Cutkosky (NIST/MIT), R. French (Harry Diamond Labs), and in a shared appointment with the Surface Science Division, M. Stiles (AT&T Bell Labs/Cornell). These appointments bring us considerable additional competence in tunneling and electron microscopy, electronics, and solid state and surface theory, and we are very pleased that they joined our Group.

In the past year three major, new experiments were brought into full operation: the scanning tunneling microscope (STM), the second generation scanning electron microscope with polarization analysis (SEMPA-II), and the spin polarized photoemission facility at Brookhaven (NSLS). It is highly unusual for our experimental capabilities to increase so greatly within a one year period. The expedited completion of some of these development projects was a direct reflection of the skill and effort of the new staff members we were able to add to the group last year.

We continue our focus on interfacial phenomena with special emphasis on the use of microscopy to study microstructures, clusters, defects, growth, and dynamics on the atomic scale. Our SEMPA work involves studying the effects of size, dimensionality, shape, topography and epitaxial substrate on magnetic microstructures. The photoemission and inverse photoemission experiments focus on understanding magnetic phenomena in novel epitaxial systems through measurements of spin resolved band structure. Our STM measurements investigate the electronic structure of atoms, molecules, clusters, and microstructures on surfaces. The STM allows us to study the growth of microstructures with atomic resolution. It also permits us to verify, for example, that the novel epitaxial structures we grow have the physical structure we planned and that their observed magnetic phenomena results from our tailoring of the physical structure.

Magnetic Microstructure Research (J. Unguris, M. Scheinfein, R. Celotta, D. Pierce, and M. Kelley)

We are investigating sub-micron magnetic structures using Scanning Electron Microscopy with Polarization Analysis (SEMPA). The SEMPA technique was developed at NIST and involves the combination of an ultrahigh vacuum scanning electron microscope (SEM) with detectors that measure the spin polarization of the secondary electrons. When a magnetic sample is scanned by the SEM, the secondary electrons that are emitted retain the spin orientation that they had in the solid and are therefore directly related to the magnetization in the region probed by the incident electron beam. The result is an image of the direction and magnitude of the magnetization vector that is obtained at the same time as the usual SEM image of surface topography. In practice magnetic structures can be resolved with a resolution of about 10 nm (0.01 microns), which is the highest resolution available of any technique for looking at magnetic structures in reflection. In addition, because the escape depth of the secondaries is approximately 2 nm, SEMPA is an ideal probe of surface and thin film magnetism.

We have recently completed construction of a new SEMPA facility centered about a new SEM that is more reliable than the old one and is also a scanning Auger microprobe. The Auger microprobe provides us with a map of the chemical composition with about the same resolution and from the same area as the magnetic and topographic images. This provides us with a unique tool to study the relationships between magnetic microstructure and surface chemistry.

Current work at the new facility involves studying the structure of domain walls at the surface of iron crystals. We have found that the domain walls have a different width and rotational sense at the surface than in the bulk. We have observed these walls for surfaces prepared in different ways and at temperatures up to the Curie temperature (750 C).

In addition to basic research, we also have been collaborating with private industry by using SEMPA to help solve applied magnetics problems. An example of this is our current work with Honeywell on a new type of memory chip based upon magnetic bits with micron dimensions. We were able to image the magnetization inside of these bits with a spatial resolution previously unavailable to Honeywell and thus provide them with information useful in extending the performance of this device.

We have established joint research efforts with industry, other government laboratories, and universities. We have received a multitude of samples from major corporations interested in exploring the applicability of this technique to outstanding scientific and technological problems of concern. We expect these collaborative efforts to be scientifically fruitful, intellectually stimulating, and mutually beneficial during the next year.

Scanning Tunneling Microscopy (J. Stroscio, R. Dragoset, P. First, D. Pierce, and R. Celotta)

The scanning tunneling microscopy (STM) program in the Electron Physics Group is aimed toward understanding the physics of low dimensional structures. This focus contributes toward the microstructure emphasis in the Electron Physics Group by extending our capabilities to examine and study structures with atomic resolution. The STM operates by the principle of quantum tunneling of electrons from a sharp probe to the examined specimen, which is held within atomic distances of the probe. Our STM has recently been fine tuned and is currently operating with 3 Å lateral resolution and an extremely high perpendicular sensitivity of 0.01 Å (1 pm). The STM is operating in an ultrahigh vacuum system with thin film growth and characterization facilities.

We have begun investigating metal structures grown on GaAs substrates by molecular beam epitaxy (MBE) techniques. GaAs is thought to be the semiconductor of the future because of its very high electron mobility which is useful in ultra-high-speed semiconductor applications. Using the STM, we have discovered an extremely novel system of one-dimensional atomic structures that form with Cs atoms on GaAs(110) surfaces. This is the first observation of such structures being formed with this system.

In the STM images the Cs atoms are individually observed to line up (atom by atom) in single atomic chains along the high symmetry direction of the GaAs(110) substrate. The Cs chains are observed to be > 50 Å apart, thereby representing a truly one-dimensional system of metal atoms. Interesting scientific questions concerning the physics of such one-dimensional structures, such as are these atomic metal "wires" really metallic (as defined by a partially filled electron band), are being pursued with the STM. By exploiting the dependence of the quantum tunneling on voltage difference between the probe and sample, we are able to investigate the electronic properties of these structures, such as the development of the electronic band structure and nature of the metal-semiconductor bonding. Although these atomic "wires" are formed naturally, they demonstrate the ultimate limit of structures that may be fabricated with semiconductor technology.

A second area of investigation with the STM is concerned with the study of ultra-thin magnetic films on surfaces. This work is synergistic with our studies of magnetic microstructures using the SEMPA technology. We are presently studying epitaxially grown bcc Fe films on GaAs(110) substrates. Fe is one of the few materials which grows epitaxially on GaAs. Previous studies by NRL researchers have shown anomalous magnetic behavior in ultra-thin films. The origin of this behavior has been attributed to defects or strain in the Fe films.

Our initial measurements show that Fe does not grow in a layer by layer mode on GaAs but forms 3-dimensional clusters during an initial growth phase at 25 C. These clusters are observed to be about 50 Å in diameter. The morphology of these clusters show a preferential growth direction with grain boundaries that might explain some of the anomalous behavior in the magnetic properties. Further studies on the temperature dependence of the growth process is being investigated.

Although the physical microstructure of the magnetic thin films can be obtained with the STM on an atomic scale, the magnetic properties cannot. With the objective of probing magnetism on the atomic scale, we have been developing an STM type of system to be sensitive to surface magnetism. The experiment is a hybrid of technology developed in the Electron Physics Group, consisting of a scanning tunneling microscope with electron spin detection of electrons emitted from the tunnel junction. Earlier research by Russell Young at NIST showed the feasibility of secondary electron detection with the STM, and researchers at IBM Zurich have recently confirmed these experiments.

The "magnetic" STM and associated components are currently being fabricated and will be assembled in early FY89. The successful completion of a magnetic microscope with atomic resolution would open up a new frontier in micromagnetism.

<u>Electron - Atom Collisions Studies</u> (M. Kelley, J. McClelland, and D. Oza)

Our purpose is to study, in as complete a manner as possible, the interactions important in low energy collisions between electrons and atoms. We employ optical state preparation techniques to prepare beams of electrons and atoms in well defined quantum states and perform scattering measurements to determine the dependence of various collision cross sections on the initial state of the incident electrons and atoms. Such state-selected experiments provide substantially more information about the collision than is available from conventional measurements of differential scattering cross sections. We are particularly interested in the influence on the collision of the spin state of the incident electrons and atoms. Determination of this spin dependence provides very direct information about both exchange and the spin-orbit interaction, and provides a very stringent reliability test for current theoretical scattering calculations.

We have made spin dependent measurements for both elastic and inelastic scattering. Elastic scattering measurements were performed at an incident electron energy of 54.4 eV and at scattering angles in the range from 20° to 135° The most surprising result was that, even for sodium, a relatively light target, the spin-orbit interaction plays a significant role in the scattering. The effect on the scattering cross section is comparable in magnitude to that due to exchange. Current state-of-the-art theoretical calculations do not accurately reproduce our measurements, indicating that further theoretical work is necessary.

We have also studied inelastic scattering by way of superelastic scattering from the first excited state. Spin-polarized and oriented sodium atoms are prepared in the excited 3P state by optical pumping with circularly polarized light. By detecting only electrons that have de-excited these atoms and gained the 2.1 eV excitation energy of the atoms, we are able to study the 3S - 3P transition with very great detail. Our measurements span the energy range from 2.0 eV to 52.3 eV and the angular range from 10° to 130°. We find that spin plays a very important role at energies up to 20 eV. At the higher energies, around 50 eV, we are no longer able to see any spin dependence.

We are also attempting to provide the theoretical data for comparison with our experiments. Extensive ab initio scattering calculations are being made. These calculations include the four lowest lying atomic levels exactly and use an optical potential to account for the higher levels and the continuum. When complete, these calculations should provide the best theoretical estimates to date for the spin dependencies observed in our measurements.

Our current efforts are directed at extending the energy range in which these measurements are possible. Specifically, we wish to perform elastic scattering measurements at energies below the ionization threshold of 5.1 eV. Theoretical calculations should be quite good at the lower energies, and we wish to provide both elastic and inelastic data for comparison with theory over the range of energies where current calculations have the most difficulty, from somewhat below to several times the ionization threshold.

Inverse Photoemission Spectroscopy (M. Hart, D. Pierce, and R. Celotta)

In recent years we have applied the spin polarized electron source developed in this group to the study of ferromagnetic metal surfaces. By coupling this low energy spin polarized source with a UHV chamber equipped with a sample manipulator, an Auger spectrometer, and a LEED system a variety of unique experimental techniques have been employed to investigate the magnetic, chemical, and electronic properties of metal surfaces. Currently, we are focusing on a spin polarized inverse photoemission (SPIPES) technique to study transition metal surfaces.

Inverse photoemission complements photoemission studies by yielding energy and momentum resolved information about the unoccupied band structure at the surface. An electron incident upon the sample can undergo a radiative transition and become bound in a vacant orbital of the solid. The flux of 9.7 eV photons emitted from the sample is measured as a function of the energy, angle of incidence, and spin of the electrons. Since the energy, momentum, and spin are conserved, the final state is well defined. Because of its spin selectivity, SPIPES is applicable to a large number of areas of current interest in ferromagnetic materials.

We have recently completed a SPIPES investigation of the clean Ni(001) surface and the c(2x2) absorption systems O/Ni(001) and S/Ni(001). For clean Ni(001), we found a minority-spin character for the unoccupied 3d band, but an essentially non-magnetic character for the Ni 4sp band. These spin-dependent results confirm previous spectral assignments made for Ni(001). No spin dependence of the Ni(001) image potential surface state was found.

We are now investigating the electronic and magnetic properties of ultra-thin, epitaxial, metallic films deposited on metallic substrates with SPIPES. The first thin film system under study, cobalt overlayers evaporated in situ on Ci(111), has yielded interesting preliminary results. Changes in both the energy and spin character of the unoccupied minority and majority spin cobalt d bands have been observed with varying film thickness. These observations may lead to significant conclusions about the nature of ferromagnetic systems with reduced dimensionality.

Spin Polarized Photoemission at NSLS (D. Pierce and R. Celotta)

We have been participating in an effort at the National Synchrotron Light Source (NSLS) to study novel magnetic systems created in situ by molecular beam epitaxy (MBE). To date, the work has concentrated on the establishment of a spin-polarized, angle and energy resolved photoemission apparatus on the U-5 beamline of the UV storage ring.

This project is unique in a number of ways. First, the research team consists of 11 principle investigators from 9 institutions nationwide. These are national labs (NIST, Argonne, NRL, and NSLS), universities (Rice, Texas at Austin, Northwestern, and U. California at Irvine) and an industrial lab (AT&T Bell). This group functions both as an NSF Materials Research Group as well as an NSLS Participating Research Team. Second, the beamline is the only spin polarized facility in the United States and the only one in the world with a movable spin analyzer to permit angular studies. Third, it is one of very few beamlines in the U.S. to have an MBE capability. Finally, because of the demanding nature of the experiment, we are fortunate to have the highest flux UV beamline at NSLS. It is based on an undulator currently installed in a straight section of the ring. During the next two years this same group, acting as an Insertion Device Team, will install a new state-of-the-art undulator now under construction.

The beamline has recently been used to take spin polarized photoemission data. In the first experiment, our colleagues at NSLS have examined the angle resolved spectra of Fe(110) both in a clean state and with adsorbed sulfur. The ability to make both angle and spin resolved photoemission measurements extends greatly previous work and, even in the first experiments, calls into question previous interpretations made in the absence of spin resolved data.

We have begun measurements on the Fe on Cu(100) system. The first few layers are thought to grow epitaxially as fcc Fe, as opposed to the normal bcc form. The object of the experiment will be to observe the magnetic properties, e.g. anisotropy, Curie temperature, remanence, magnetization, etc., as a function of layer thickness and growth methodology, and to correlate them with the spin dependent electronic structure we measure. We expect this facility to greatly extend our ability to study new and interesting magnetic systems.

Electron Optics (M. Kelley and M. Scheinfein)

We have added substantially to our capabilities for the design and characterization of new electron-optical instruments. These new capabilities include sophisticated numerical algorithms used to compute electrostatic and magnetic lens fields, and improved methods of determining the optical properties of these fields. Paraxial and aberration properties can be accurately determined for electrostatic or magnetic lenses. Non-paraxial, all-order, electrostatic ray-tracing is also used for more accurate modelling of novel designs. Furthermore, a third order matrix method has been developed for use in the design and characterization of our electron optical systems.

The second generation electron spin polarimeter (SEMPA detector) and transport optics were designed, built, and interfaced to the JEOL JAMP 30 Scanning Auger Microprobe. The system, complete with scan compensation, has been fully characterized and determined to function as originally designed.

A third generation SEMPA detector and transport optics were designed to further improve the performance of the system. The technology for this new detector, which has been built and tested at NIST, has been transferred to Physical Electronics, Inc (PHI), who will develop a commercial instrument based on this design. In addition, a novel optical system for secondary electron extraction has been designed and implemented for the PHI system. This novel system is currently being applied in the PHI laboratory for their own scanning ion microscopes.

The third generation SEMPA detector has also been interfaced to a standard 180° hemispherical analyzer with input and output optics. This instrument is used to study spin-polarized photoelectron spectroscopy in a project cooperatively pursued with researchers at Brookhaven National Labs. The new optical system will eliminate spurious polarization asymmetries induced by instabilities in the positioning of the beam in the Brookhaven storage ring.

Electron Theory (D. Penn)

Our purpose is to study various aspects of electron-electron interactions in solids with application to high T_c superconductivity and surface magnetism.

We have examined the significance of satellites at binding energies of about 12 eV that are observed in photoemission experiments in the high T_c superconductors La-Sr-Cu-O and Y-Ba-Cu-O. The satellites are assumed to be caused by intra d-shell shake-up processes with a Cu $3d^8$ final state. Using the t matrix approach, we studied the effect of the electronic correlations on the one electron band structure. We found that it takes a large Coulomb interaction energy of 5 eV at the Cu site to account for the position of the satellite. This shows that the $3d^8$, two hole, bound state is a high energy excitation comparable to the 3d band width, and that electron correlations are important in the high T_c materials.

We have also studied the interaction between two test changes in a solid which can be described in terms of a total dielectric function, ϵ, that includes electronic and lattice polarization. We have shown that the eigenvalues of ϵ^{-1} are ≤ 1 for crystal stability. We have constructed such a dielectric function in the mean field approximation and shown that the correct phonon modes are determined by the low energy poles of ϵ^{-1}. Such an approach may be useful in the study of superconductivity.

We are continuing to study the process of Auger decay in the interaction of metastable helium with metal surfaces. When metastable helium atoms approach the surface of a metal, an Auger decay can take place in which a metal electron falls into an empty 1s state of helium and a second electron (the Auger electron) is ejected. Measurements of the total number of Auger electrons ejected from nickel for opposite spin-polarizations of metastable helium show a difference (normalized) that increases from 0 to 10% as the kinetic energy increases. We are formulating a theory for this asymmetry. In contrast to the standard interpretation, we expect the sp-electrons to be of crucial importance. Whereas the d-electrons carry the main moment, the sp-electrons have the largest overlap with the helium.

PHOTON PHYSICS GROUP

The Photon Physics Group investigates the interaction of electromagnetic fields on atoms and molecules in various environments in support of radiation measurements and standards programs important to NIST and the outside technical community. This work includes theoretical and experimental studies on the electronic structure of atomic and molecular systems in field free environments and in strong external fields. The Group has specialized in ionization phenomena and in nonlinear or multiphoton laser-atom interactions.

Studies are currently focused on molecular excitation dynamics, shell contraction in atoms, multiphoton transitions, atoms in high electric and magnetic fields, and the structure of highly excited atoms. Collaborative work is directed toward ultrasensitive analysis through resonant multiphoton ionization, the measurement of picosecond vuv pulses by nonlinear cross correlation techniques, and the identification of highly excited atomic states suitable for soft x-ray laser. For many of the activities, synchrotron radiation from NIST-SURF-II or Brookhaven-NSLS is used as a source of tunable vacuum ultraviolet and soft x-ray radiation.

Multiphoton Ionization Applied to Ultrasensitive Trace Analysis

(T. Lucatorto and C. Clark)

This is a collaborative effort with the Mass Spectrometry Group in the NIST Center for Analytical Chemistry having the goal of developing a resonance ionization mass spectrometric (RIMS) capability with sub part-per-billion isotopic abundance sensitivity. Present thermal ionization mass spectrometers have an ultimate isotopic abundance sensitivity of about one part in 10^7. By putting isotopic selectivity into the resonance ionization step, we hope to improve the overall sensitivity by three to five orders of magnitude.

Our RIMS studies have used special narrow bandwidth pulsed lasers to perform isotopically selective ionization. Results with the isotope pair ^{10}Be:^{9}Be show laser selectivities in excess of 3000:1, which would, in principle, increase the overall isotopic abundance sensitivity from $1:10^7$ to 3×10^{10}. However, due to the poor duty factor of the pulsed laser (roughly $1:10^5$), the sample utilization efficiency is very low, with the result that sensitivities of only $1:10^7$ are attainable with practical samples.

The problem of poor sample utilization efficiency is perhaps the single most troublesome limitation for RIMS. To attack this problem, we have begun studies on pulsed laser ablation as a method of atomization that is matched to the duty cycle of the ionization laser. Preliminary studies indicate that there are three mechanisms that limit the effectiveness of the laser pulsed ablation technique: laser plasma formation, thermal stress induced exfoliation, and molecular compound formation (e.g. oxides). In an attempt to reduce the adverse effects of these mechanisms, we have begun experiments on thin films of relatively volatile metals. Films of Zn produced by sputtering have been ablated and show advantageously low plasma formation. Present efforts are directed towards developing a suitable technique to co-sputter Zn and the analyte so that the Zn serves as a non-interfering matrix in the compositional analysis of the analyte.

Resonance Ionization Mass Spectrometry Data Service (E. Saloman)

The techniques of Resonance Ionization Spectroscopy (RIS) and Resonance Ionization Mass Spectroscopy (RIMS) have demonstrated high elemental sensitivity and the potential for almost 100% efficiency. They should become most valuable tools for analytical chemistry. For these techniques to meet their potential, they must be made available to practicing analytical chemists. Presently, much of the information needed to apply RIS and RIMS is scattered in several atomic data bases, which generally contain much more information than the chemists would need. It is the objective of this project to organize the available data and supplement it with calculations where gaps exist to provide the needed information to permit the application of RIS and RIMS to routine use in analytical chemistry.

Preliminary data sheets have been completed for ten elements this past year. Included are calculations of previously unmeasured excited state photoionization cross sections, transition rates, and autoionization rates. In the next year more data sheets will be completed. In addition the format of the data sheets will be further refined, in collaboration with the RIS-RIMS community, including the Institute for Resonance Ionization Spectroscopy at the U. Tennessee.

Soft X-Ray Emission Studies of Advanced Materials (D. Ederer)

Soft x-ray fluorescence can provide important information about the electronic states of solid state materials. Fluorescence measurements can be used to study the properties of alloys, impurities, clusters, surface layers, organics, and other fragile compounds. A novel, high sensitivity soft x-ray spectrometer especially designed for fluorescence measurements has been in operation at the NSLS for almost two years now and is the proud accomplishment of a joint NIST-U. Tennessee-Oak Ridge National Laboratory collaboration. Recent experiments have proven it to be one of the best instruments in the world for soft x-ray fluorescence measurements.

The unique capabilities of the instrument has attracted a number of collaborators including scientists at the University of Hawaii, the

University of Connecticut, the University of Uppsala, AT&T Bell Laboratories, and NIST colleagues from the Institute of Materials Science and Engineering and the Institute for Computer Science and Technology. Through collaboration with our IMSE colleagues, we have studied the electronic structure of the icosahedral phase of an aluminum manganese alloy, as well as the electronic structure of the $YBa_2Cu_3O_{7-\epsilon}$ and Bi-Sr-Ca-Cu-O superconducting ceramics. This last area of research has been funded as part of a DoC initiative on high temperature superconductors. With additional resources from this initiative, we have added a solid-state physicist (D. Mueller/Cornell) and a visiting scientist to the high Tc superconductivity project.

During the next year we will be continuing our studies of the high Tc superconductors and commence studies on implanted species of importance to the semiconductor industry. A new monochromator has been added to the instrumentation to allow for narrow band irradiation.

A few of the highlights of this program are:

a) High Tc Superconductors:

The oxygen K, soft x-ray emission spectra for the $YBa_2Cu_3O_x$ compounds with x=6, 6.5, and 7 was obtained and compared with x-ray emission spectra determined from recent band structure calculations. The K emission spectrum of O provides a measure of the p-type local partial density of states (p-LPDOS) at the oxygen sites. Good agreement is found with the calculated spectrum for x=7. As x decreases from 7 to 6.5, a chemical shift of the entire spectrum to lower energy indicates that screening is modified for all oxygen sites. The integrated intensity of the spectra is nearly unchanged by oxygen removal, indicating an increase in p-PDOS per oxygen site. These results and changes in the spectral shape suggest that itinerant electron density near the O atoms is reduced and bound electron density is increased as oxygen is removed.

We have also measured the soft x-ray K emission spectrum from oxygen in the Bi-Sr-Ca-Cu-O superconductor and found it identical with the O K emission from the 123 superconductor. The O K and the Bi valence-$N_{6,7}$ emission were in good agreement with spectra modeled after calculations based on linearized augmented plane wave method and local density band structure calculations.

b) Electronic Structure of Buried Interfaces

As semiconductor devices become smaller and smaller, and as it has become possible to synthesize new materials based on thin layered structures, the measurement of interface properties within a bulk has become extremely important to industry. This is because it is often the microstructural properties of the interface that control the behavior of the material. Interface measurements are very challenging since most diagnostic methods generate responses from the surface of the material and the bulk of the medium that completely overwhelm the response of the interface.

It is difficult to study the electronic structure of the interface between different materials basically because the interface is buried under a layer of material. Surface sensitive probes like photoelectron spectroscopy cannot be effective. X-ray fluorescence spectroscopy, although not surface sensitive, is not normally efficient enough. However, this drawback was overcome in the present experiments by making a multilayer structure consisting of 50 layers of carbon films interdigitated with silicon films. In one group of samples the thickness of the silicon film was varied from 0.3 nm to 3.0 nm, with carbon film thickness fixed at 3.0 nm. In another group of samples the silicon film thickness was fixed and the thickness of the carbon was varied. By this sample preparation technique, it was possible to enhance the signal-to-noise ratio by a factor of 50 over a single C-Si interface.

The fluorescence was excited by near threshold soft x-rays from the National Synchrotron Light Source at Brookhaven National Laboratory and detected by an ultrahigh sensitivity spectrometer. The interface signal was clearly distinguishable from the signal generated in the bulk. The silicon $L_{2,3}$ emission band from the interface resembled that of SiC and the silicon emission from the bulk resembled that of amorphous silicon.

This is a cooperative program with Lawrence Berkeley Laboratories and the University of Wisconsin.

c) Electronic Structure of Semiconductor Materials

In collaboration with AT&T Bell Labs, we studied the local valence band density of states in $Al_xGa_{1-x}As$. This material has important applications in the semiconductor industry because it has a higher conductivity and smaller, variable (with x) band gap relative to silicon.

The soft x-ray fluorescence from the valence band to the 2p aluminum core holes probes the local band structure with mostly s like symmetry. One observes a shift of several tenths of an eV in the energy position of the partial density of states localized at the aluminum site relative to the gallium in the crystal lattice. This is a new insight into semiconductor alloys that has not been incorporated into the theoretical description of these systems. Information like this has not been obtained before because techniques like photoelectron spectroscopy are not atom-specific, but rather provide a measure of the total valence band density of states integrated over all the atomic sites.

We plan to study other materials, like InP, with our Bell Labs collaborators. Also of interest are the properties of multilayer materials made with alternating $Al_xGa_{1-x}As$ and GaAs thin films to form superlattices.

d) Radiation damage in insulators

In a collaboration with the University of Hawaii, we studied electron induced radiation damage for two silicon compounds, Beryl (Be-Al-Si-O) and SiO. The Beryl radiation damage suggests a localized damage about the silicon, whereas the Al and Be retain their oxide-like structures. Silicon is reduced as a result of electron bombardment to a mixture of amorphous and crystalline Si. The radiation damage in SiO is similar to that of Beryl in that a mixture of amorphous and crystalline Si is observed. The study of radiation damage in these compounds is important because of their use as window materials in uv lasers.

Ionization Dynamics of Fundamental Atomic Systems (D. Ederer; D. Caldwell and J. Jimeniz-Mier, U. Central Florida)

A series of studies done in collaboration with the University of Central Florida has been carried out at SURF using the polarization of the synchrotron radiation beam as a probe of molecular and atomic photoionization dynamics. In helium we made the first measurements of the angular distribution of the 304 Å radiation following photoionization. The distribution reflects the alignment of the ion with the electron in a 2p orbital. The alignment is related to the ratio of the photoionization cross section to final continuum states of d symmetry to the total cross section for ionization and excitation of the electron to a 2p orbital. The measurements were in good agreement with close coupling calculations and complemented other experiments that measure the correlation among the electrons in this fundamental two electron system. The results were published in Phys. Rev. Letters.

This year measurements are being made in the energy range of a two-electron excitation resonance to determine how the correlation introduced by an additional excitation channel affects the alignment of the ion. These measurements will be completed in FY88.

Atomic Structure of Laser-Excited Atoms (T. Lucatorto and C. Clark).

Our group has a unique capability to measure the vuv photoabsorption (between 8 nm and 65 nm) of laser-excited and laser-ionized atoms. The IR-100 award-winning instrumentation includes a state-of-the-art, vuv spectrometer with a 1024 channel photoelectric detector, a 20 ns pulsed vuv source, several pulsed tunable dye lasers, and a high temperature (up to 2500°C) heat-pipe oven.

Photoabsorption studies of laser-excited and laser-ionized atoms have uncovered the dramatic effects of relatively small changes in electron screening on orbital collapse. Presently we are focusing attention on the 3p-photoabsorption spectra of the transition metals (Sc, Ti, V, Cr, Mn, Fe,.....). These spectra are all characterized by a single giant 3p → 3d resonance structure in the 50 eV energy range. Cr, however, is an exception because it has an additional, well-developed Rydberg structure lying above the giant resonance. Up to now the unique status of Cr was thought due to its being the only member with an unpaired 4s-electron in the ground state ($3p^6$ $3d^5$ $4s$ ^7S). Our recent high resolution measurements of the isoelectronic Mn^+ spectrum, which showed no well-developed Rydberg structure, show this not to be true however. The definitive Mn^+ spectrum obtained is stimulating a parallel theoretical effort to explain the exceptional behavior of Cr.

This work is a collaboration with the Atomic and Plasma Radiation Division, the University of Hamburg, and the National Institute of Higher Education (NIHE), Dublin.

Development of a Measurement Program to use the Time Structure of the Electron Beam at SURF (D. Ederer)

A new class of experiments are being planned for SURF which will utilize both lasers and synchrotron radiation. Synchrotron radiation is a source of pulsed VUV radiation that can be used to produce excitation leading to chemical reactions. By probing a sample of excited molecules undergoing a reaction with a laser locked to the storage ring radio frequency, we may obtain detailed information on the dynamics of the chemical reaction. The mode locked Nd:YAG laser with the doubler and Q-switch has arrived and we plan to install it on the SURF Storage Ring. The work will be advanced by the arrival of a guest scientist, who will work full time on this program during FY89.

Our long-term collaboration to study laser-prepared states with the Universite de Paris-Sud in Orsay, France, is winding down. A review of photoionization from excited states, co-authored by D. Ederer and F. Wuilleumier, has been published early in 1988 as a book chapter in Advances in Atomic and Molecular Physics entitled "Photoionization and Collisional Ionization of Laser Excited Atoms Using Synchrotron Radiation."

X-Ray Attenuation Cross Sections (E. Saloman)

A comparison has been carried out, in both tabular and graphical form, over the energy range 0.1-100 keV between our data base of experimental attenuation coefficients (total absorption cross sections) and cross sections obtained using two widely used sets of absorption cross section values: the semi-empirical set of recommended values produced by Henke et al., and a theoretical set of recommended values calculated by Scofield (and extended at our request down to 0.1 keV). We also evaluated whether Scofield's calculation should be subject to a renormalization from a Hartree-Slater to a Hartree-Fock atomic model and determined that the experimental data tends to argue against such renormalization.

A compilation of experimental and theoretical x-ray attenuation coefficients for this energy range (as well as a bibliography of the NIST data base), prepared in collaboration with J.H. Scofield of Lawrence Livermore National Laboratory, was published this year.

This work is a collaboration with the Ionizing Radiation Division.

Atomic Properties and Data (E. Saloman)

Relativistic multi-configuration Dirac-Fock methods have been applied to the calculation of atomic and ionic energies and transition probabilities. An initial study has been completed. It is an investigation of the energies and oscillator strengths in the ground state configuration of the sulfur isoelectronic sequence. Results have been obtained for all transitions within this configuration for the 77 ions from sulfur to uranium. They demonstrate striking effects in the f-values corresponding to atomic numbers where different configurations become important. A report on these effects was published in Physical Review A. The detailed data will be published in Atomic Data and Nuclear Data Tables.

Next year calculations will be made to determine certain transition probabilities which are very sensitive to the method used to calculate them. The significance of the change in the wavefunctions of "spectator electrons" between initial and final states will be explored.

This work is a collaboration with the Atomic and Plasma Radiation Division.

Theoretical Atomic, Molecular, and Optical Physics (C. Clark and L. Pan)

Theoretical AMO physics in the Photon Physics Group was focused on two main areas: core- and multiply-excited states of atoms in gas and condensed phases, and high-order multiphoton processes.

Our atomic structure work has been carried out in support of experimental efforts in our Division, in the Atomic and Plasma Radiation Division, and in other institutions; and with other theorists in the Surface Science Division and elsewhere. The principal achievements of this work have been:

1) Identification and classification of 3p → 5s photoabsorption features in atomic Mn, and preliminary interpretation of the 3p → 3d "giant resonance" features in Mn, Mn^+, and Cr;

2) Analysis of $4d^9 4f$ fine structure seen in electron energy loss spectroscopy of Ba in the $YBa_2Cu_3O_{7-x}$ high-T_c superconductor; determination of the valency of Ba in this compound from comparative analysis of photoabsorption data; and identification of $4d^{10}5p^6 \rightarrow 4d^9 5p^5 5d^2$ double excitation in Ba photoabsorption;

3) Interpretation of x dependence of oxygen K emission peaks in $YBa_2Cu_3O_{7-x}$ compounds in terms of fractional valence of oxygen, based on Hartree-Fock atomic structure calculations; and investigation of role of O^- and O^{2-} resonances in electron-stimulated desorption of oxygen from surfaces;

4) Identification of term dependence in the $4d^9nf$ series of I VIII and Xe IX;

5) Computation of multichannel quantum defect (MQDT) parameters of the $2p^5ns$ and $2p^5nd$ channels of Ne in good agreement with experimental determinations; and critical evaluation of effects of core polarization and the relationship of MQDT and Slater-Condon descriptions.

Work on high-order multiphoton processes has centered around the development of a general computer code for evaluating perturbation theory of atomic hydrogen in a radiation field to arbitrarily high order. This code has begun to produce results on level shifts and nonlinear susceptibilities up to 90th order, an order of magnitude higher than any previous calculations. The principal qualitative results obtained thus far are:

1) Development of a parameterization technique that separately treats background and resonant contributions, so that the behavior of level shifts and nonlinear susceptibilities can be described by a few parameters even in a spectral region containing infinitely many resonances;

2) The determination of a "critical intensity" at which the contributions from higher orders of perturbation theory exceed those of lower order. These intensities are comparable to those at which saturation of multiphoton ionization is observed in experiments;

3) Computation of cross-sections for generation of high harmonic radiation, and the evaluation of critical intensities that are in good correspondence with those inferred from the "plateau" behavior of recent experiments.

INVITED TALKS

Division 571, Radiation Physics

Celotta, R.J., "Scanning Electron Microscopy with Polarization Analysis: Studies of Magnetic Microstructure," Am. Vac. Society, Annual Meeting, Anaheim, CA, Nov. 2, 1987.

Celotta, R.J., "Polarized Electron Probes in Atomic and Surface Physics," Australian Bicentenary Congress, Sydney, Australia, January 26, 1988.

Celotta, R.J., "An Introduction to Scanning Tunneling Microscopy," STM Symposium, National Bureau of Standards, Gaithersburg, MD, May 20, 1988.

Celotta, R.J., "Improved Low-Energy Diffuse Scattering Electron-Spin Polarized Analyzer," Gordon Conference on Electron Spectroscopy, Wolfeboro, NH, July 20, 1988.

Dragoset, R.A., "Scanning Tunneling Microscopy," Physics Seminar, University of Maryland Baltimore County - Physics Department, Catonsville, MD, Feb. 10, 1988.

Furst, M.L., "SURF-II Radiometric Instrumentation Calibration Facility," SPIE Conference on X-ray Instrumentation in Astronomy, San Diego, CA, August 17, 1988.

Kelley, M.H., "Spin Dependence in Electron Atom Scattering," IXth Atomic Physics Workshop, U.S. Dept. of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Bethesda, MD, August 31, 1988.

Lucatorto, T.B., "Enhanced Isotope Abundance Sensitivity and Sample Utilization Efficiency in Pulsed RIMS," Workshop on Advanced Laser Techniques in Chemical Analysis, NIST, November 4, 1988.

McClelland, J.J., "Scattering of Spin-polarized Electrons from Optically Pumped Sodium," Physics Colloquium at Wesleyan University, Middletown, CT, October 1, 1987.

McClelland, J.J., "Scattering of Spin-polarized Electrons from Optically Pumped Sodium," Physics Colloqium at University of Kentucky, Lexington, KY, October 21, 1987.

McClelland, J.J., "Improved Low-Energy Diffuse Scattering Electron-Spin Polarized Analyzer," Gordon Conference on Electron Spectroscopy, Wolfeboro, NH, July 20, 1988.

Ott, W.R., "Far-Ultraviolet Detectors, Spectrometers, and Optics," Council for Optical Radiation Measurements Annual Meeting, National Bureau of Standards, Gaithersburg, MD, May 18, 1988.

Penn, D.R., "Analysis of Spin Polarized Inelastic Electron Scattering," Workshop on Magnetism of Surfaces, Laguna Beach, CA, October 30, 1987.

Penn, D.R., "Spin Polarization of Secondary Electrons in Metals," Rice University, Houston, TX, January 26, 1988.

Penn, D.R., "Total Dielectric Function, Algebraic Sign, Electron-Lattice Response, and Superconductivity," Chalmers University, Chalmers, Sweden, April 15, 1988.

Penn, D.R., "The Role of Inelastic Exchange Scattering in Spin Polarization Experiments," The 4th Joint MMM-Intermag Conference, Vancouver, British Columbia, Canada, July 14, 1988.

Pierce, D.T., "Experimental Studies of Surface and Thin Film Magnetism with Polarized Electrons", Physics Seminar, Arizona State University, October 26, 1987.

Pierce, D.T., "Results from Spin Polarized Electron Spectroscopy of Surface Magnetism that Puzzle Me," Surface Magnetism Workshop, Laguna Beach, CA, October 29, 1987.

Pierce. D.T., "Experimental Studies of Surface and Thin Film Magnetism with Polarized Electrons," Surface Science Seminar, Rutgers University, May 10, 1988.

Pierce, D.T., "Prospects for a Spin Sensitive STM," Research Advisory Committee Seminar, National Bureau of Standards, Gaithersburg, MD, May 20, 1988.

Pierce, D.T., "Recent Advances in Compact, Efficient Spin Polarization Analyzers," Workshop on Polarized Electron Sources and Polarimeters in Conjunction with the 8th International Symposium on High Energy Spin Physics, University of Minnesota, Minneapolis, MN, September 8, 1988.

Pierce, D.T., "Quest for Higher Spin Polarization Semiconductor Photocathodes," Workshop on Polarized Electron Sources and Polarimeters in Conjunction with the 8th International Symposium on High Energy Spin Physics, University of Minnesota, Minneapolis, MN, September 9, 1988.

Saloman, E.B., "National Bureau of Standards Data Base of Photon Absorption Cross Sections From 10 eV to 100 GeV," SPIE Conference on X-ray and Vacuum Ultraviolet Interaction Data Bases, Calculations, and Measurements, Los Angeles, CA, January 14, 1988.

Scheinfein, M.R., "Considerations for Ultimate Attainable Spatial Resolution in Microanalysis," Joint U.S./ France Workshop on Electron Beam Induced Spectroscopies at High Spatial Resolution, Aussois, France, March 14, 1988.

Scheinfein, M.R., "Scanning Electron Microscopy with Polarization Analysis (SEMPA)," Joint U.S./ France Workshop on Electron Beam Induced Spectroscopies at High Spatial Resolution, Aussois, France, March 15, 1988.

Stroscio, J.A., "Scanning Tunneling Microscopy of Semiconductor Surfaces," Fifteenth Annual Conference of the Physics and Chemistry of Semiconductor Interfaces, Asilomar, CA, February 1, 1988.

Stroscio, J.A., "Observation of Single Atom Adsorbates with the Scanning Tunneling Microscope," American Physical Society March Meeting, New Orleans, LA, March 21, 1988.

Stroscio, J.A., "STM Applied to Si and GaAs," RAC Symposium on NBS Activities in Scanning Tunneling Microscopy, Gaithersburg, MD, May 20, 1988.

Stroscio, J.A., "Scanning Tunneling Microscopy of Adsorbates on Surfaces," Middle Atlantic Regional Meeting of the American Chemical Society, Millersville University, Millersville, PA, May 25, 1988.

Stroscio, J.A., "Scanning Tunneling Spectroscopy of Single Atoms on Surfaces," Gordon Research Conference on Electron Spectroscopy, Wolfeboro, NH, July 18, 1988.

Unguris, J., "Scanning Electron Microscopy with Polarization Analysis," The Metallurgical Society Fall Meeting, Cincinnati, OH, October 12, 1987.

Unguris, J., "New Uses for Polarized Electrons," Eastern Regional Electron Spectroscopy Society Meeting, Martin Marietta, Baltimore, MD, May 10, 1988.

Unguris, J., "Scanning Electron Microscopy with Polarization Analysis - An Update," Greater Washington Area Surface Science Seminar, National Bureau of Standards, Gaithersburg, MD, May 20, 1988.

PUBLICATIONS

Division 571, Radiation Physics

Callcott, T.A., Tsang, K.L., Zhang, C.H., Ederer, D.L., and Arakawa, E.T., Soft X-ray Emission Spectra and the Bonding of Aluminum, J. de Physique, Coll. 9, Supp au n°12, Tome 48, C9-1053 (1987).

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Celotta, R.J., Unguris, J., and Pierce, D.T., Scanning Electron Microscopy with Polarization Analysis - SEMPA, Proceedings of the 45th Annual Meeting of the Electron Microscopy Society of America, 178 (1987).

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Celotta, R.J., Robins, J.L., Unguris, J., Pierce, D.T., Jonker, B.T., and Prinz, G.A., Domain Images of Ultrathin Fe Films on Ag(100) Appl. Phys. Lett. 52(22), 1918 (1988).

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Cutkosky, R.D., Frequency Dependencies of Precision Resistors, Rev. Sci. Instrum. 59(2), 381 (1988).

Cutkosky, R.D., Precision Weight Calibration with a Specialized Robot, 1988 Measurement Science Conference Proceedings, 271, January 1988.

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McClelland, J.J., Scholten, R.E., Kelley, M.H., and Celotta, R.J., Spin Sensitivity of a Channel Electron Multiplier, Rev. Sci. Instrum. 59(3), 506 (1988).

Pierce, D.T., Klebanoff, L.E., Jones, R.K., and Celotta, R.J., Spin-resolved Inverse-Photoemission Study of Ni(001) and its Chemisorption, Phys. Rev. B 36(15), 7849 (1987).

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Saloman, E.B., Effects of Configuration Mixing in M1 and E2 Transitions Between Ground-State Terms of Sulfur-Like Ions, Phys. Rev. A 38, 577 (1988).

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Unguris, J., Celotta, R.J., Pierce, D.T., and Hembree, G.G., Magnetic Microstructure Imaging Using Scanning Electron Microscopy with Polarization Analysis, Proceeding of Analytical Electron Microscopy Conference, 350 (1987).

Wen, J., Travis, J.C., Lucatorto, T.B., Johnson, B.C., and Clark, C.W., Measurement of Isotope Shifts of Two Photon Transitions in Beryllium, Phys. Rev. A. 37, 4207 (1987).

PUBLICATIONS IN PREPARATION

Division 571, Radiation Physics

Armentrout, C.J., Geddes, J.B., Lee, P., Snider, R.T., and Canfield, L.R., UV to SXR Surveys Using a Compact, Biplanar Diode Array (to be submitted, Proc. of the Seventh International Conference on High Temperature Plasma Diagnostics).

Bengtsson, L., Travis, J.C., Lucatorto, T.B., Kreider, K., and Brown, L., Laser Ablation of Thin Films as a Free Atom Source for Pulsed Rims (to be published, Proc. of the Fourth International Conf. on Resonance Ionization Spectroscopy and Its Applications, 1988).

Cooper, J.W., Clark, C.W., Cromer, C.R., Lucatorto, T.B., Sonntag, B.F., Kennedy, E.T., Costello, J.T., Junwen, C., and Tomkins, F.S., Autoionizing Resonaces in Mn, Mn+, and Cr 3p Subshell Absorption (to be submitted, Phys. Rev. Lett.).

Furst, M.L. and Madden, R.P., SURF-II Radiometric Instrumentation Calibration Facility (to be submitted to SPIE Proceedings, 982).

Korde, R., Canfield, L.R., and Wallis, B., Stable, High Quantum Efficiency Silicon Photodiodes for Vacuum-UV Applications, SPIE Proceedings 932).

McClelland, J.J., Scheinfein, M.R., and Pierce, D.T., Use of Thorium as a Target in Electron Spin Analyzers (to be submitted, Rev. Sci. Instrum.).

Pan, L., Taylor, K.T., and Clark, C.W., Computation of the A.C. Stark Effect in the Ground State of Atomic Hydrogen (to be submitted, Phys. Rev. Lett.).

Penn, D.R., Tanuma, S., and Powell, C.J., Calculations of Electron Inelastic Mean Free Paths for 31 Materials (to be published, Surface and Interface Analysis).

Penn, D.R., Chang, K.J., and Cohen, M.L., Electronic Correlations and Satellites in Superconducting Oxides (to be published, Phys. Rev. B).

Penn, D.R. and Apell, P., Free Electron Like Stoner Excitations in Fe (to be published, Phys. Rev. B).

Saloman, E.B., A Resonance Ionization Spectroscopy/Resonance Ionization Mass Spectrometer Data Service (to be published, Proc. of the Fourth International Conference on Resonance Ionization Spectroscopy and Its Applications, 1988).

Saloman, E.B., Energy Levels and Transition Probabilities in the Ground State Configuration of Sulfur-Like Ions (to be published, Atomic Data and Nuclear Data Tables).

Scheinfein, M.R., Pierce, D.T., Unguris, J., McClelland, J.J., and Celotta, R.J., Improved Low-Energy Diffuse Scattering Electron-Spin Polarization Analyzer (to be submitted, Rev. Sci. Instr.).

Scheinfein, M.R., Unguris, J., Pierce, D.T., and Celotta, R.J., Scanning Electron Microscopy with Polarization Analysis (SEMPA): High Spatial Magnetic Imaging Status Report (tc be published, Proc. of Aussois Workshop on Electron Beam Induced Spectroscopies at High Spatial Resolution, March, 1988).

Wassdahl, N., Rubensson, J.E., Bray, G., Rindstedt, J., Martensson, N., Nordgren, J., Nyholm, R., and Cramm, S., Cu L and O K Emission Spectra of the $YBa_2Cu_2O_{7-x}$ Superconductor Excited by Monochromatized Synchrotron Radiation (to be submitted, Physics Letters).

JOURNAL EDITORSHIPS

Division 571, Radiation Physics

R.J. Celotta, Series Editor, Methods of Experimental Physics.

C.W. Clark, Topical Editor for Atomic Spectroscopy, Journal of the Optical Society of America B.

D.T. Pierce, Editorial Board, Journal of Electron Spectroscopy.

SPONSORED SEMINARS AND COLLOQUIA

Division 571, Radiation Physics

Abraham, Daniel T., University of California at Irvine, "Spin Dependent Elastic and Elastic Scattering from Magnetic Surfaces," March 14, 1988.

Apell, Peter, Chalmers University of Technology, Sweden, "De-Excitation of Multiply Charged Ions," February 19, 1988.

Bartschat, Klaus, Universitat Münster, West Germany, "Excitation and Ionization of Atoms by Electron and Photon Impact," February 29, 1988.

Bashkansky, Mark, Columbia University, "Review of Recent ATI Experimental Results," December 11, 1987.

Bentley, Murry, Johns Hopkins University, "Fully Variational Hartree-Fock Calculations of Quasi-Bound Atomic States," June 8, 1988.

Bruhwiler, Paul, University of Virginia, "Charged Density Waves in Alkali Metals," April 1, 1988.

Cadez, Iztok, Institute of Physics, Belgrade, "Vibrational Excitation of Hydrogen via Recombinative Desorption of Atomic Hydrogen Gas on a Metal Surface," December 3, 1987.

Clark, R.N., University of Washington, "Chaotic Behavior of a Simple System," December 29, 1987.

Delos, John, College of William and Mary, "Atoms in Strong Fields: Quantum Manifestitations of Classical Order and Classical Chaos," June 3, 1988.

Dreyfuss, Russell, IBM T.J. Watson Research Labs., Yorktown Heights, "Laser Probing of Laser Ablation," November 17, 1987.

Dutcher, John, Simon Fraser University, "Brillouin Light Scattering Studies of Magnetic Surface Anisotropy," June 3, 1988.

Fairbank, William, Colorado State University, "Photon Burst Mass Spectrometry," November 4, 1987.

Falcone, Roger, University of California (Berkeley), "New Short Pulse X-Ray Sources From Laser Heated Solids," July 6, 1988.

Garton, W.R.S., Imperial College, "Atoms in High External Fields," January 12, 1988.

Garton, W.R.S., Imperial College, "External Field Effects in Atomic Spectra," November 17, 1987.

Glab, Wallace, Argonne National Laboratory, "Highly Excited States of Molecular Hydrogen in a Strong Electric Field," June 27, 1988.

Greene, Chris, Louisiana State University, "Two-electron Excitations in Atomic Ca," March 30, 1988.

Lefebvre-Brion, H., Universite de Paris-Sud, "Autoionization and Photodissociation in Diatomic Molecules: Application to O_2 and HCI Molecules," August 4, 1988.

Liebsch, Angskar, Institute Theoretical Physics, KFA-Julich, West Germany, "Linear and Nonlinear Response at Metal Surfaces," May 23, 1988.

Liu, Ya-Wen, Beijing University, "Progress at the Beijing Storage Ring Facility," April 29, 1988.

Izerda, Yves, Naval Research Laboratory, "Stoner Excitations in Magnetic Thin Films," April 26, 1988.

Livins, Peter, University of Virginia, "Shake-up in Soft X-ray Emission," April 5, 1988.

Malafsky, Geoffrey, Penn State University, "Primary Ion Energy Effects in the Sputtering of Single Crystal Metals," July 7, 1988.

Menendez, Manuel, University of Georgia, "Fast Atomic Collisions: A Pathway to the Three Body Coulomb Problem," July 11, 1988.

Mundschau, Michael, Technischen Universitat Clausthal, "Low-Energy Electron Microscopy," January 19, 1988.

Nayfeh, M.N., University of Illinois, "Fragmentation and Ionization of Diatomic Molecules in Intense Laser Fields," May 6, 1988.

Perera, Rupert, Lawrence Berkeley Laboratory, "Soft X-rays in Multilayers, Present and Future," March 31, 1988.

Pogatshnik, Gerry, Oak Ridge National Laboratory, "In Search of Oxide Color Center Lasers," May 6, 1988.

Silvera, Isaac, Harvard University, "Spin Polarized Hydrogen: Prospects for Base Condensation with Lyman-α Laser Cooling," October 13, 1988.

Scimica, Thomas, University of Hawaii, "Variable Angle X-ray Emission Spectroscopy: Applications to Transition Metals," April 29, 1988.

Starace, Anthony, University of Nebraska, "Electron Correlation Effects in Nonresonant Multiphoton Ionization Processes," October 15, 1987.

Thompson, Jeffrey, Oak Ridge National Laboratory, "Observation of the Ca Ion by Photoelectron Spectroscopy," June 9, 1988.

Wasson, David A., California Institute of Technology, "Many-Electron Response to Strong Laser Pulses," December 22, 1987.

Weigold, Erich, Flinders University, "Wave Function Mapping in Atoms and Molecules," July 26, 1988.

Wuilleumier, Francois, LURE, "Recent Developments in Laser-Synchrotron Expeirments," April 14, 1988.

TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Division 571, Radiation Physics

Robert J. Celotta

Member, General Committee, International Conference on the Physics of Electronic and Atomic Collisions.

Member, NML EEO Committee, 1986-88.

Charles W. Clark

Member, National Research Council Committee on Line Spectra of the Elements - Atomic Spectroscopy.

Co-director, NATO Advanced Study Institute "Atoms in Strong Fields."

Member, Ad Hoc Committee on Page Charge Analysis, Optical Society of America.

Thomas B. Lucatorto

Co-chairman, 1989 International Conference on the Physics of Electron and Atomic Collisions.

Member, Program Committee, 4th International Symposium on Resonance Ionization Spectroscopy and its Applications, 1988.

Co-chairman, Local Organizing Committee, 4th International Symposium on Resonance Ionization Spectroscopy and its Applications, 1988.

Robert P. Madden

Member, Optical Society of America Nominating Committee.

Member, Calibration and Stability Working Group of the Ozone Trends Panel.

Coordinator, International Radiometric Intercomparison of Solar Irradiance Experiments.

Member, International Committee for the International Conference on Vacuum Ultraviolet Radiation Physics.

Member, Council of U.S. Synchrotron Radiation Laboratory Directors.

Member, International Committee of the International Conference on X-ray and VUV Synchrotron Radiation Instrumentation.

Member, Synchrotron Radiation Facility Working Group (Department of Energy).

Member, NBS-NML Classification Committee for the NBS Personnel Demonstration Project.

Stanley R. Mielczarek

Member, NBS Property Review Board

William R. Ott

Member, International Working Group for Middle Atmospheric Program on Solar Spectral Irradiance Measurements, 1981-1988.

Member, Local Organizing Committee for the 4th International Symposium on Resonance Ionization Spectroscopy and Its Applications, 1987-88.

Chairman, NBS-CRR Calibrations Advisory Committee, 1985-88.

Member, NBS-NML Classification Committee for the NBS Personnel Demonstration Project, 1987-88.

Daniel T. Pierce

Member, Editorial board, Journal of Electron Spectroscopy.

Chairman, 1988 Gordon Conference on Electron Spectroscopy.

Chairman, Executive Committee, Surface Science Division of American Vacuum Society, 1988.

Program Chairman, 1987 American Vacuum Society (Surface Science Division) Meeting in Anaheim.

MAJOR CONSULTING AND ADVISORY SERVICES

Division 571, Radiation Physics

L.R. Canfield consulted with Raj Korde of United Detector Technology on applications of silicon photodiode detectors in the far ultraviolet.

L.R. Canfield consulted with Obert Wood and William Silvfast of AT&T Bell Laboratories and David Nilson of the Lawrence Livermore National Laboratory on aluminum thin film filters for x-ray laser applications.

L.R. Canfield consulted with Charles Armentrout and Joseph Geddes of KMS Fusion on narrow band detectors and filters for the far uv and soft x-ray regions.

L.R. Canfield consulted with Fred Hererro and Walter Hoegy of the Goddard Space Flight Center on the photoemission of materials on board a Venus orbiter spacecraft.

L.R. Canfield advised production personnel at Science Applications Corporation and Ball Aerospace Systems on photoemissive detectors for the vacuum ultraviolet.

L.R. Canfield advised A.L. Lane of the Jet Propulsion Lab on problems associated with detectors for space applications.

L.R. Canfield advised Howard Ogawa of Southern California University and Gary Rottman of the University of Colorado on the use of a narrow-band detector for solar flux measurements in a rocket flight.

C.W. Clark advised a group at Princeton Plasma Physics Laboratory on atomic physics problems associated with x-ray laser development.

R.J. Celotta and D.T. Pierce consulted on the production and detection of polarized electrons with researchers from Brookhaven, AT&T Bell Labs, Bell Communications Corporation, University of Texas, MIT, Argonne National Laboratory, Perkin Elmer Corporation, and the Naval Research Laboratory.

D.L. Ederer consulted with Denise Caldwell of the University of Central Florida on angular distribution of fluorescence radiation in helium.

D.L. Ederer consulted with Richard Freeman of AT&T Bell Labs on pump-probe experiments involving lasers and synchrotron radiation.

R.P. Madden consulted for NASA by serving on the "Spacecraft Instrument Calibration and Stability" Working Group of the "Ozone Trends Panel" contributing to the report to Congress entitled "Present State of Knowledge of the Upper Atmosphere 1988: An Assessment Report" as required under the Clean Air Act Amendments of 1977, Public Law 95-95.

R.P. Madden, at the request of the Director of the Earth Science and Applications Division of the Office of Space Science and Applications, NASA, is coordinating an international round-robin intercomparison of solar irradiance monitoring space experiments.

R.P. Madden is on a Naval Research Laboratory advisory panel reviewing national programs in lithography research.

W.R. Ott consulted with scientists from Lockheed Corporation and several DoD organizations on measurement needs for remote sensing applications with ultraviolet and soft x-ray radiation.

M.R. Scheinfein and M.H. Kelley consulted with NSLS staff at Brookhaven National Laboratory on spin-polarized angle-resolved photoelectron spectroscopy.

J. Unguris, M.R. Scheinfein, and M.H. Kelley consulted with the Physical Electronics Division of Perkin Elmer Corporation on commercialization of a SEMPA microscope.

TRIPS SPONSORED BY OTHERS

Division 571, Radiation Physics

R.J. Celotta presented a talk at the Australian Bicentenary Congress, Sydney, Australia, January 26, 1988.

C.W. Clark gave a Quantum Electronics Seminar at the State University of New York, Stony Brook, NY, October 30, 1987.

D.L. Ederer presented a talk at the University of Notre Dame, South Bend, IN, October 15, 1987.

D.L. Ederer gave a lecture at the Naval Postgraduate School, Monterey, CA, January 8, 1988.

D.L. Ederer presented at talk at the University of California, Riverside, CA, January 12, 1988.

D.L. Ederer presented a talk at the University of Southern California, Los Angeles, CA, January 13, 1988.

D.L. Ederer presented at talk at Argonne National Laboratory, Argonne, IL, June 17, 1988.

J.J. McClelland gave a Physics Colloquium at Wesleyan University, Middletown, CT, October 1, 1987.

J.J. McClelland gave a Physics Colloqium at University of Kentucky, Lexington, KY, October 21, 1987.

D.R. Penn gave a Physics Colloquium at Rice University, Houston, TX, January 26, 1988.

D.R. Penn presented a colloquium at Chalmers University, Chalmers, Sweden, April 15, 1988.

D.R. Penn gave an invited talk at The 4th Joint MMM-Intermag Conference, Vancouver, British Columbia, Canada, July 14, 1988.

D.T. Pierce gave a Physics Seminar at Arizona State University, October 26, 1987.

D.T. Pierce gave an invited talk at the Surface Magnetism Workshop, Laguna Beach, CA, October 29, 1987.

D.T. Pierce gave a Surface Science Seminar at Rutgers University, May 10, 1988.

M.R. Scheinfein gave a talk at the Joint U.S./ France Workshop on Electron Beam Induced Spectroscopies at High Spatial Resolution, Aussois, France, March 15, 1988.

M.R. Scheinfein gave a talk at the Joint U.S./ France Workshop on Electron Beam Induced Spectroscopies at High Spatial Resolution, Aussois, France, March 15, 1988.

J.A. Stroscio gave an invited talk at the 15th Annual Conference of the Physics and Chemistry of Semiconductor Interfaces, Asilomar, CA, February 1, 1988.

SPONSORED WORKSHOPS

Division 571, Radiation Physics

R.J. Celotta organized and chaired the Research Advisory Committee Symposium on NBS Activities in Scanning Tunneling Microscopy, NBS, Gaithersburg, MD, May 20, 1988.

M.H. Kelley organized the Atomic Physics Program Contractor's Workshop with U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Hyatt-Regency Hotel, Bethesda, MD August 31 - September 1, 1988.

T.B. Lucatorto organized, jointly with University of Tennessee, the 4th International Conference on Resonance Ionization Ionization Spectroscopy and Its Applications, NBS, April 11-15, 1988.

R.P. Madden organized a symposium on Major VUV Radiometric Facilities for the SPIE meeting on X-Ray Instruments, Multilayers and Sources, San Diego, CA, August 14, 1988.

D.T. Pierce organized and chaired the Gordon Research Conference on Electron Spectroscopy, Wolfboro, NH, July 18-22, 1988.

CALIBRATION SERVICES PERFORMED

Division 571, Radiation Physics

Type of Service	Customer Type*	SP 250 Item No.	Number Calibration or Tests
Far UV radiometric transfer standard detectors (photodiode calibrations)	1,4-8	N.A.	39
Spectrometer calibrations using SURF as an absolute source	5-7	N.A.	12
Totals			51

* Column 2: 1, calibration labs; 2, hospitals; 3, nuclear energy establishments; 4, industry; 5, US government labs; 6, DoD labs; 7, universities; 8, foreign governments.

TECHNICAL ACTIVITIES

Division 572, Atomic and Plasma Radiation Division

The Atomic and Plasma Radiation Division carries out a broad range of experimental and theoretical research on atomic structure and atomic radiation in plasmas. The division determines a large variety of atomic radiation and collision data, encompassing wavelengths of spectral lines; atomic energy levels; ionization potentials; atomic transition probabilities; plasma line broadening parameters; ionization and excitation cross sections and rate coefficients and dielectronic rate coefficients. Two data centers located in the division critically evaluate and compile atomic energy levels, wavelengths, and transition probabilities.

Since in most cases atomic radiation originates from plasmas, we are also engaged in research on the effects of the plasma environment on atomic radiation, such as studies of spectral line broadening and line shifts. We explore these effects in order to gain an understanding of atomic processes in plasmas as well as to utilize them for the development of new measurement techniques. Furthermore, well-defined atomic radiation sources are also developed as VUV radiometric standards and wavelength standards.

Our activities, which support many areas of science and technology, are undergoing significant changes in direction, since appreciable changes have occurred in the external forces that drive our priorities. There is, for example, much increased demand for the detailed understanding of atomic processes in cool plasmas, both for modelling purposes and diagnostics. These needs have arisen mainly from materials processing by plasmas, such as the widely used plasma etching of semiconductors, as well as surface cleaning by plasmas, and materials deposition by plasma sputtering techniques. For commercial applications, the understanding of all these processes on the atomistic level is the key to optimizing the operating conditions and to achieving competitive advantages. Likewise, process monitoring and modelling in plasma chemistry and spectrochemistry can be achieved on a fundamental level only with reliable atomic radiation and collision data. For these technologies heavy neutral elements, including rare earths, are of principal interest.

Very different demands arise from VUV and X-ray laser physics. in this research area, transition energies and lifetimes (or radiative decay rates) of highly stripped ions are essential for the selection and testing of potential laser systems. VUV and X-ray laser research has not only assumed importance for defense applications, but also for biological and bio-medical studies (e.g. the "water window"). We are very active both in generating atomic data, and in the development of lasing schemes.

Also, the nation's research program on magnetic fusion energy is steadily progressing, and the atomic data we produce for highly stripped heavy ions are needed there for modelling the cross-field ion transport, for estimating the effects of impurities on the plasma energy balance, and for plasma diagnostics, such as the measurement of ion temperatures. Beyond this, there is also the fundamental scientific need for an experimentally well-tested, fully relativistic atomic structure theory that accurately describes the properties of highly ionized as well as heavy atoms, including QED effects.

Finally, our vacuum ultraviolet radiometry work with plasma sources is now providing miniaturized calibrated radiation source packages to allow radiometric calibrations on board spacecraft. These are used, for example, on the space shuttle for accurate monitoring of the solar ultraviolet radiation, and are part of the Space Telescope instrumentation.

The division consists of three technical groups: Atomic Spectroscopy, Atomic Radiation Data, and Plasma Radiation. It currently has 17 professional physicists, among them 16 Ph.D.s. During 1988 the division had 17 guest scientists, from China (2), Israel (3), India (1), Sweden (3), Canada (1) and U.S.A. (7).

Some of our significant accomplishments during the past year are:

- We have proposed and are involved in experiments, with NRL and KMS Fusion groups, on two new X-ray and XUV laser schemes: lasing at 26 Å in I^{24+} ions and at 600 Å in Mo^{6+} ions. Patent applications and manuscripts are underway.

- We have demonstrated population inversion and gain in a C IV line in the theta pinch recombining plasma. Experiments in collaboration with Bell Labs with a reflective cavity give a gain of 12 for the 253 nm UV transition in C IX.

- We have published, or have in press, several major critical data compilations:

    - Spectral data tables for all or most ions of Fe, Ni, Cu and Mo.
    - Transition probability tables for all atoms and ions of the iron group elements Sc through Ni - to be published in two volumes of 500 pages each.

- We have devised a very sensitive and clean experimental test of possible violations, or confirmation, of the Pauli Exclusion Principle (PEP) by looking for a helium transition whose very existence would be a consequence of PEP violations. A preliminary experiment is in preparation.

- A procedure to accurately represent electron-impact excitation cross sections of ions in compact formulas has been developed and applied to relativistic distorted-wave Born cross sections of Be-like and Na-like ions. This is an ideal method to accurately condense the inherently massive volume of data required in modeling applications such as short-wavelength laser design and fusion plasma diagnosis.

- Advanced versions of computer codes to calculate nonrelativistic and relativistic wave functions and transition probabilities have been developed and are being tested for a wide range of atoms and ions. In addition, methods to calculate QED corrections for many-electron atoms are being developed. Theoretical energy levels from these codes are sufficiently accurate to complement high-precision spectroscopic measurements.

These and other activities are discussed in the following sections, where the principal work of the three technical groups during the past year is described.

I. Atomic Spectroscopy Group

(a) Highly Ionized Atoms

The energy levels and wavelengths for spectra of highly ionized atoms are of basic interest for testing theoretical descriptions of atomic properties, which are affected by large relativistic and quantum-field (QED) contributions. They are also necessary data for the modeling and diagnostics of high-temperature plasmas occurring in x-ray laser research, nuclear fireballs, solar flares, tokamaks and other fusion-research machines, etc. We have excited very highly charged ions in several sources: the highest temperatures were obtained in plasmas produced by the OMEGA laser at Rochester, and we have also used plasmas obtained with lasers at Los Alamos and NIST, plasmas generated in the TEXT tokamak at the University of Texas, and sliding-spark and vacuum-spark plasmas at NIST.

We completed analyses of the spectra of Al-like ions (Cu^{16+} through Mo^{29+}) and K-like ions (Cu^{10+} through Mo^{23+}) obtained with the TEXT tokamak. The energy levels of these ions were compared with Dirac-Fock calculations to test the theory and to use the smooth variation of the deviations from experiment for interpolations along the isoelectronic sequences. One result of the comparisons was that inclusion of previously uncalculated QED corrections for the M-shell electrons substantially improved agreement between theoretical and experimental values for the $3s^2 3p\ ^2P$ ground-term doublet splitting of the Al-like ions. The experimental wavelengths from these measurements are sufficiently accurate to be used as standards in fusion-plasma and x-ray laser plasma research. Similar work on ions of the Mg and Cl isoelectronic sequences is in progress (J. Sugar, V. Kaufman, Y.-K. Kim).

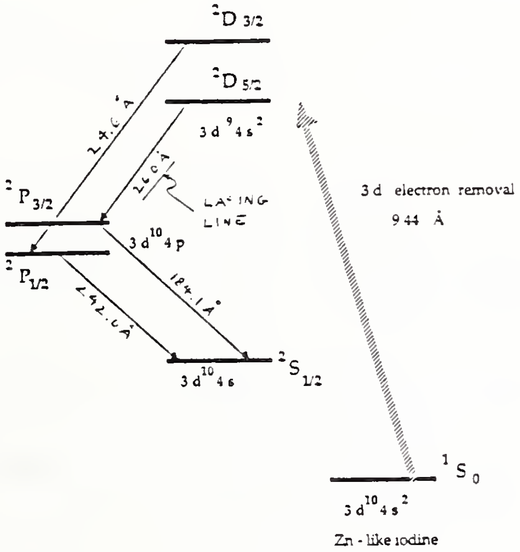
We finished work on prominent transitions in the Fe-like ions Ru^{18+} to Gd^{38+}. The spectra were obtained from laser-produced plasmas at NBS, Los Alamos, and Rochester. The energy levels for this sequence were also compared with calculations of the Dirac-Fock relativistic type and the differences were used to accurately predict missing levels and levels for ions not observed. Wavelengths for forbidden (magnetic-dipole) transitions between levels of the $3p^6 3d^8$ ground configuration, which are important for tokamak plasma diagnostics, were derived from the experimental levels. We have papers in press on the spectra and energy levels of gallium-like ions Rb^{6+} to Mo^{11+} and germanium-like ions Rb^{5+} to Mo^{10+} (J. Reader and collaborators from Lund University, Sweden, and the Naval Research Laboratory).

During the coming year we plan visits to both the TEXT tokamak and the Rochester OMEGA laser facility to excite higher-temperature spectra of heavy elements. One of the experiments planned for the Rochester visit is to extend our previous work on Na-like spectra to the rare-earths region of the periodic table (50 to 60 electrons stripped from the atoms). The one-electron spectra of this sequence are of special theoretical interest, and accurate measurements of the high-ionization stages are also needed for both x-ray laser and magnetic-fusion research.

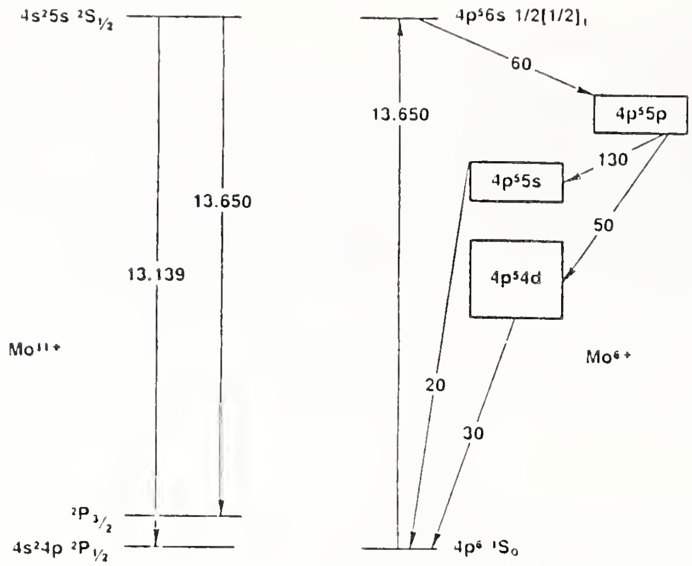
(b) Atomic-ion x-ray lasers

J. Sugar, collaborating with P.D. Morley (KMS Fusion), has predicted that inner-shell photoionization can produce lasing at wavelengths below 50 Å in plasmas generated from laser-exploded foils. Sugar worked out the case for copper-like iodine (I^{24+}) which should lase on the $3d^9 4s^2 \rightarrow 3d^{10} 4p$ doublet calculated at 24.565 and 26.026 Å (see figure). Experiments to test the idea are underway at KMS fusion, and a joint paper is in press.

Scheme for 26 Å laser in Cu - like iodine (I^{24+})



J. Reader's work on the spectra of molybdenum ions revealed a coincidence between a Mo^{6+} line and a Mo^{11+} line at 136.50 Å. Reader and U. Feldman (Naval Research Lab) have proposed a scheme for Mo^{6+} lasing at 600 Å based on using the 136.5-Å Mo^{11+} line to photopump the upper level of the coincidence transition in Mo^{6+} (see figure). Experiments to test the idea are underway. Reader has discovered that a previous analysis of the Mo^{6+} spectrum done in another laboratory is totally erroneous. He is now analyzing this spectrum to identify the candidate lasing transitions and has found all levels of 5 principal configurations.



(c) Laser Spectroscopy and High-Accuracy Determinations of Atomic Energy-Level Structures

A basic objective of our laser spectroscopy program is to test experimentally the most accurate theoretical calculations for selected atoms. The development of theoretical methods that treat electron-correlation, relativistic, and QED energy contributions accurately and consistently is one of the fundamental goals of atomic physics. Helium is of special importance because the electron-correlation contributions can be calculated to almost arbitrary accuracy in a non-relativistic approximation, and the inclusion of two-electron relativistic and QED effects is simpler than for atoms having more electrons. Our measurements, calculations, and critical analyses of the energy-level data for helium contribute to a broad effort towards increased understanding of this system.

ATOMIC BEAM SOURCE. An atomic beam apparatus designed for high precision laser spectroscopy of rare gases in metastable states has been constructed and tested. A flux of metastable helium atoms of about 10^{14}/sec/sr has been obtained, corresponding to about 2 x 10^9 metastable atoms per second at a collimation sufficient to reduce the residual Doppler width to 10 MHz (0.0003 cm^{-1}) in the visible region. We are currently readying our first laser observations of the beam source, a measurement of the 2 ^1S - 3 ^1P transition. We plan a series of measurements of the 2 ^1S - n ^1P transitions including highly excited Rydberg states. Accurate wave number determinations for this series should allow determination of the 2 ^1S ionization energy within an error of a few parts in 10^9. This will permit new tests of the most accurate theoretical calculations in helium including two-electron QED effects (C. Cromer and C. Sansonetti).

MEASUREMENTS IN HELIUM DISCHARGES. Additional precise measurements of transitions not accessible with the metastable-beam apparatus are required to establish the energies of a number of low-lying helium levels. We are currently observing some of these transitions using Doppler-free laser methods in a low-pressure helium discharge. We have obtained spectra of the $2\ ^3P - 4\ ^3S$, $2\ ^1P - 4\ ^1D$, and $2\ ^1P - 4\ ^1S$ transitions and are now attempting to make precise measurements of their wave numbers. As an outgrowth of our laser measurements in helium, we have also recorded emission spectra of low-pressure rf discharges in helium by Fourier spectroscopy. These spectra have not yet been fully analyzed, but they should provide precise measurements for some important transitions not easily observed by laser methods. Most significant of these are the $2\ ^3S - 2\ ^3P$ and $2\ ^1S - 2\ ^1P$ transitions which lie at 1.08 and 2.05 microns. These discharge measurements combined with the results of our metastable beam work and previous laser measurements will provide more accurate absolute ionization energies for virtually all low-lying levels of helium (C. Sansonetti).

MEASUREMENTS WITH FABRY-PEROT WAVEMETER. In all of our laser observations, high accuracy measurements of the dye laser wavelength are required to realize the full potential of the experiments. We have continued to upgrade the Fabry-Perot wavemeter developed in our lab to meet this requirement. Improvements in the optical system and laser beam switch have increased the reliability of the instrument, reduced the laser power required to about 0.5 mW, increased the measurement rate from about 0.7 to 2 Hz, and reduced digitization errors in the computer acquisition of the interference patterns. The instrument has been tested in the green spectral region and has now been used successfully from 4700 to 7000 Å. Throughout this region absolute accuracies of better than 3 MHz (10^{-4} cm^{-1}) are routinely obtained (C. Sansonetti).

(d) Platinum Ultraviolet Reference Wavelengths

The spectrum of a platinum hollow-cathode discharge will be used for on-board wavelength calibration of the High-Resolution Spectrograph (HRS) for the Hubble Space Telescope. Since the absolute wavelength accuracy of this instrument will be the limiting factor in a number of important planned observations, during the past several years we measured the Pt spectrum from 1032 to 4100 Å with our 10.7-m normal-incidence vacuum spectrograph. Some 3000 lines of Pt I and Pt II have been determined with an average uncertainty of ±0.002 Å. These measurements have been incorporated into the calibration codes for the HRS and are also now used in the reduction of data obtained with the still active (10 years old) IUE satellite. We have in press a paper giving accurate energy levels and wavelengths for the Pt II lines (J. Reader, N. Acquista, C.J. Sansonetti; and R. Engleman, Jr. from Los Alamos). These measurements and our other Pt measurements will also be used extensively for calibrations in high-resolution laboratory UV and VUV spectroscopy.

During the past year we made new scans of the Pt spectrum using photon-counting techniques for detection. Computer reduction of these scans will give accurate intensities for the lines. We plan to produce an extensive atlas of the entire spectrum which will be highly useful for HRS calibrations and for laboratory spectroscopy. A complete paper giving all of our Pt wavelengths is also planned. (J. Reader, N. Acquista, C.J. Sansonetti, and J. Sansonetti).

(e) Atomic Energy Levels Data Center

This center critically evaluates and compiles data on energy levels and spectral lines of atoms and atomic ions. We have just completed a compilation of the energy levels for all 29 copper spectra (Cu I - Cu XXIX) (J. Sugar and A. Musgrove). We also made substantial progress on a similar compilation of energy levels for the sulfur spectra (W.C. Martin, R. Zalubas, and A. Musgrove).

We are including critically evaluated wavelengths as part of a computerized data base on atomic spectra to be built up jointly by the Atomic Energy Levels and Atomic Transition Probabilities Data Centers. We have compiled the wavelengths and energy-level classifications for the 21 scandium spectra and have completed most of a similar compilation for the silicon spectra (V. Kaufman and J. Sugar). Our compilations of wavelengths and energy-levels classifications for all lines of Mo^{5+} through Mo^{41+} and Ni^{5+} through Ni^{27+} were published recently. Similar compilations for the spectra of all Fe and Cu ions stripped of 5 or more electrons have recently been completed or are near completion. (J. Sugar, W.L. Wiese, and Japanese collaborators).

The fourth supplement to our Bibliography on Atomic Spectra, covering the literature from 1984 through 1987, is in press (A. Musgrove and R. Zalubas). A report on laboratory research on atomic spectra of interest for astrophysics was prepared and published in the Trans. IAU (W.C. Martin). We answer many individual requests for information on atomic spectroscopic data and supply lists of references of interest for fusion-plasma research for the bibliographies issued semiannually by the International Atomic Energy Agency.

II. Atomic Radiation Data Group

The work of this group is entirely theoretical and consists of two major areas: (1) theoretical studies of atomic structure and collision processes, and (2) critical evaluation and compilation of atomic transition probability and spectral line shape data. The first activity involves the development of advanced theoretical methods and their implementation to calculate atomic data. The main areas of activity have been dielectronic recombination, relativistic quantum mechanics, electron correlation, and radiative and collisional transition rates. The critical evaluation and compilation of transition probability and spectral line shape data takes place in the Data Center on Atomic Transition Probabilities, which also maintains an up-to-date bibliography of the literature in these fields.

(a) Theoretical Studies

(1) A set of computer codes for relativistic atomic structure and collision data has been developed, updated, and implemented on the CYBER 205 at NIST. This work was carried out in collaboration with J. P. Desclaux (French Atomic Energy Commission, Grenoble, France) and P. Indelicato (Division 526 and Université de Paris). New capabilities are (i) Multiconfiguration Dirac-Fock (MCDF) wavefunction code in which the Breit interaction is now calculated in the Coulomb gauge to be consistent with QED procedures for higher order relativistic corrections; (ii) Transition probability code in which MCDF wavefunctions derived from the above code are used to calculate magnetic and electric multipole transition probabilities; (iii) Relativistic distorted-wave Born cross section code in which cross sections for both excitation and ionization of ions with arbitrary target configuration can be calculated; and (iv) Angular momentum algebra code which carries out all angular momentum algebra needed for the above codes.

All codes are based on fully relativistic theory, include correlation, and can be applied to neutral as well as highly charged atoms, hydrogen through transuranium elements. Using these codes, a variety of atomic data were calculated ranging from energy levels to ionization cross sections. As a result, two articles have been published, four articles have been accepted for publication, and a few more are being prepared for publication. (M. A. Ali, Y.-K. Kim, W.-J. Qian and E. B. Saloman, Div. 532)

(2) A systematic study of relativistic distorted-wave Born cross sections for the $2s^2\ {}^1S_0$ - $2s2p\ {}^{1,3}P_1$ excitation of Be-like ions by electron impact has been carried out. We found that the triplet excitation, which is electric dipole (E1) and spin forbidden, gradually becomes E1 allowed due to intermediate coupling, while configuration mixing in the ground state ($2s^2 + 2p^2$) remains important throughout the periodic table, changing triplet excitation cross sections by as much as 30%. These cross sections are fitted with only four or five coefficients for each transition for incident energies from the threshold to 10 keV. The fitted coefficients, in turn, are expressed in terms of simple power

series in atomic number. In order to obtain reliable Z dependence, data for a total of about 15 atoms in the periodic table are needed. About 80 coefficients thus determined reproduce cross sections for both the triplet and singlet excitations from thresholds to 10 keV for all Be-like ions in the periodic table. These coefficients provide a compact yet accurate way to store and reproduce desired cross sections in various modeling codes. (Y.-K. Kim and W.-J. Qian)

(3) In one-electron atoms at high Z, one of the largest uncertainties in the energy levels has been the effect of higher-order vacuum polarization corrections. These are corrections that are third or higher order in the external potential that go beyond the Uehling approximation. To calculate this correction for bound electrons in high-Z atoms, a coordinate space formulation of the problem that takes into account the finite size of the nucleus has been developed in collaboration with G. Soff of GSI, West Germany. Work being done on this topic consists of a systematic application of the method to calculate energy level corrections for various states over a wide range of nuclear charge.

In high-Z two-electron atoms, the dominant uncertainty in the theoretical prediction for the energy levels is due to uncalculated higher-order relativistic corrections in the Feynman diagram with two photons exchanged between the bound electrons. The nonrelativistic limit and first relativistic corrections for this diagram are known, but at high Z, higher-order relativistic corrections are important, and a complete numerical calculation is needed. In a collaboration with S. A. Blundell, W. R. Johnson, and J. Sapirstein of the University of Notre Dame, such a calculation is being carried out for the ground state of helium-like ions. We plan to extend this calculation to excited states where a comparison with experiment can be made.

One of us initiated and participated as a coordinator for a program on "Relativistic, Quantum Electrodynamic and Weak Interaction Effects in Atoms" that was held at the Institute for Theoretical Physics at Santa Barbara (January-June, 1988). Over 30 experts on atomic theory and quantum electrodynamics for many countries participated in the program. (Y.-K. Kim also participated in this workshop, April-May, 1988). One of the goals was to bring quantum electrodynamics to bear on the practical problem of calculating the structure of atoms and ions having more than one electron, especially atoms and ions with high nuclear charge, where relativistic and QED effects are significant. Much of the effort was devoted to developing a consistent formulation of a many-body QED theory. Another goal of the program was to improve the theoretical calculations of parity-violating amplitudes. Other problems such as spectra of Rydberg atoms, positronium, and positron production in heavy-ion collisions, which involve basic theory were also investigated. A book containing lectures given in the program is being edited in collaboration with W. R. Johnson of the University of Notre Dame and J. Sucher of the University of Maryland. (P. J. Mohr)

(4) Our computation of the dielectronic recombination rates of the ions isoelectronic to the elements of the second row of the periodic

table has been completed. A simple model has been used to analyze the reduction of the effective rate of dielectronic recombination by the thermal equilibrium of some of the bound, highly-excited final states produced by the recombination with the plasma electrons in low to moderate density plasmas. The computer codes have been upgraded to include configuration interaction and intermediate coupling in the atomic model. We participated in the IAEA Experts Meeting on Electron-Ion Collision Processes for the Ions of Oxygen and Carbon in Fusion Plasmas and the IAEA Meeting on Atomic Data for Fusion Plasmas. (L. J. Roszman)

(5) A method has been developed to calculate matrix elements of the electric dipole operator between Russell Saunders (L-S coupled) states, for which radial functions have been found via a Multiconfiguration Hartree-Fock (MCHF) procedure where all orbitals are left free to vary. In the past, most of the core had to be frozen in order to calculate the required angular factors under the assumption that the core orbitals were orthonormal. The capability to allow completely relaxed calculations for both the upper and lower states separately lets one account for the same degree of correlation in each state, thereby taking full advantage of the MCHF method. As a first case, we have taken the transitions $1s^2 2s^2 2p^2 3p\ {}^4D,\ {}^4P,\ {}^4S \rightarrow 1s^2 2s^2 2p^2 3s\ {}^4P$ in neutral nitrogen. Because the last term appears with a mixing coefficient of about 0.35 in the calculation of the $1s^2 2s2p^4\ {}^4P$ term of nitrogen, we have also calculated oscillator strengths for allowed transitions to that state, which will make it possible to calculate lifetimes from data taken in an experiment done by Zhu and Wiese of the division. (M. A. Suskin and A. W. Weiss)

(6) Computer codes have been written for calculating dipole transition probabilities, utilizing correlated wavefunctions from the Superposition of Configurations (SOC) programs. These codes are completely general in the sense that no assumptions are made concerning the orthonomality of the orbital sets of the two terms of the transition. Applications are currently being made to alkali and alkaline-earth elements (and isoelectronic ions), Li, Na and Be (also Be+, Mg+, B+ and C^2+). Wavefunctions are being computed including core correlation and core-valence intershell correlation, as well as the usual valence correlation corrections. (A. W. Weiss)

(7) The development of a computer code to generate spectral line profiles for multi-electron ions in plasmas continues. Spectral line profiles generated from this code have been used in the analysis of laser-produced plasma experiments at the University of Rochester Laboratory for Laser Energetics and the Princeton Plasma Physics Laboratory. A joint effort is in progress with V. L. Jacobs (Naval Research Laboratory) and C. F. Hooper, Jr. (University of Florida) on the calculation of plasma-broadened line profiles of helium-like and lithium-like satellites of hydrogenic and helium-like argon resonance lines, including non-LTE populations and broadening due to autoionization, radiative decay, electron collisions, and the plasma ion microfield. Another collaboration is underway with T. D. Hahn and W. L. Wiese to determine the ion

broadening parameters of neutral carbon, nitrogen, and argon spectral lines obtained in a wall-stabilized arc. (L. A. Woltz)

During the past year, we hosted a number of atomic theorists, some for an extended period of time, some as regular weekly visitors.

M. A. Ali (Howard University) spends one day a week here during the academic year working with Y.-K. Kim on relativistic atomic structure calculations. He spent the entire summer of 1988 working with Kim.

W.-J. Qian (Liaoning University, Shenyang, China) has completed a one-year visit with us, collaborating with Kim on the study of relativistic distorted-wave Born cross sections of Be-like and Na-like ions.

L. A. Woltz (University of Florida) has been with us for the past year collaborating with W. L. Wiese on the problems in the theory of spectral line broadening.

(b) Data Center on Atomic Transition Probabilities

During 1988, a major accomplishment of the data center was the completion, after 8 years of critical evaluation work, of two volumes, "Atomic Transition Probabilities--Scandium through Manganese," and "Atomic Transition Probabilities--Iron through Nickel." These will appear as hard-bound supplements to the Journal of Physical and Chemical Reference Data, about 500 pages each, with a total of about 18,000 transitions. During the last year, data for V II, Mn I, Fe II, Ni I, and Ni II were evaluated and compiled, which are included in the above-mentioned publication, and much proofreading was done.

The literature on f-values is continually monitored, and an up-to-date bibliography is maintained. Also, every six months, references are provided for inclusion in the "International Bulletin on Atomic and Molecular Data for Fusion," published by the International Atomic Energy Agency. We prepared a mini-bibliography on all astrophysically important literature references to be published in "Reports on Astronomy" by the International Astronomical Union. (J. R. Fuhr and W. L. Wiese)

The programming is complete to house the "Bibliography on Atomic Transition Probabilities" within dBase III. The task of entering all past citations remains, but once done, literature searches extending from the present back to 1914 will be possible. Among the key fields are author, title, species, isoelectronic sequence, and year of publication. The bibliography can be indexed on up to seven fields at a time, and the results given in printed form or as ASCII files on disc. (M. A. Suskin)

III. Plasma Radiation Group

The plasma measurements program provides essential data and measurement techniques for the analysis of plasmas, mainly for temperature and density determinations, for VUV source radiometry, and for VUV lasing schemes. The determination of collisional rate coefficients is of critical importance in plasma modeling, especially for VUV laser schemes and fusion-type plasmas. Determination of atomic transition probabilities and plasma line broadening parameters have provided many of the data needed for measurements of plasma densities and temperatures of low temperature plasmas widely used for technological applications, such as in semiconductor and materials processing, spectrochemistry and plasma chemistry. Radiometric measurements of high intensity VUV and X-ray sources have led to advances in source development for x-ray lithography. Our studies of population inversion in the theta pinch have led to a better understanding of recombination mechanisms for possible VUV laser schemes. Pulsed plasma source studies have produced promising new VUV radiometric sources. Our portable radiometric standards have been used for many spacecraft calibrations and are in increasing demand for that purpose.

(a) Experimental Test of the Pauli Exclusion Principle (PEP)

New developments in quantum field theory indicate that the Pauli principle is not necessarily absolutely rigorous, but that small violations may be allowed. This very exciting and important result calls for rigorous experimental testing of the exclusion principle. This fundamental principle is responsible for the stability of atoms and nuclei, for example, neutron stars. PEP follows from the indistinguishability of identical particles. However, some atomic states which satisfy indistinguishability are still forbidden by PEP.

We have been designing, and are embarking on, a series of experiments designed to search for such states. The simplest and most accurately calculable of such states are in helium. For each normal state of helium one can describe a state whose wavefunction exhibits a PEP-forbidden symmetry. These PEP-forbidden states have slightly different energies than the normal states, and they may be very precisely calculated.

We plan first to perform a relatively simple measurement with moderate (i.e., about 1 part in 10^{10}) sensitivity to PEP violation. Subsequently, we plan to perform a much more involved and powerful experiment which involves enrichment of any PEP-violating ground states. Implications of an observed PEP-violation would be comparable to those associated with parity violation, first observed at NBS. (D. E. Kelleher)

(b) Collisional Rate Coefficients with the 50 kJ Theta Pinch

1. In the Li-like carbon atoms, population inversions have been achieved between excited levels on a microsecond timescale for the first time on a theta pinch. This is accomplished in a plasma generated from various acetylene/hydrogen gas mixtures. Three-body recombination was

conceived to be the mechanism for these population inversions. However, theoretical modeling using the measured electron temperature and electron density profiles could not explain the observations. Charge transfer from neutral hydrogen to He-like carbon at the plasma boundary is being investigated as the mechanism for recombination.

Also, using a confocal mirror cavity, a gain factor of 12 was measured on the 2530 Å line of C IV in experiments conducted in collaboration with a group from Bell Laboratories. Experiments are continuing to further improve the gain.

2. One of the most successful soft X-ray lasers developed recently is based on 3p to 3s transitions in Ne-like atoms present in very dense laser-produced plasmas. However, several observed phenomena have defied explanation to date, in spite of using sophisticated computer models. For example, considerable gain has been observed for transitions from J=2 sublevels and significantly lower gain has been observed for transitions from the J=0 sublevel, contrary to expectations. A problem with modeling has been that there is no experimental verification in plasmas for the rates used in the computer codes. Of central importance are absolute measurements of population densities and collisional/radiative transition rates, supported by electron density and electron temperature measurements, to calibrate the computer codes. Experiments are underway to make such basic and quantitative measurements on Ne-like argon and Ne-like silicon using the NBS theta pinch.

Also, under a recent grant from NATO, collaborative experiments between the Institute of Experimental Plasma Physics at the University of Bochum, West Germany and NBS have just started to measure the excitation rate of Ne-like argon and Li-like neon as another part of an effort for theoretical code calibration. (R. Datla, R. C. Elton, J. R. Roberts)

(c) <u>Tokamak Spectroscopy</u>

In order to develop diagnostics for the measurements of absolute densities of high Z impurities in tokamak plasmas, experiments on Si-like Ni, Cu, Zn, Ge and Se are conducted by us on the TEXT tokamak, a national tokamak facility, operated by DOE at the University of Texas, Austin. New forbidden lines have been identified and their intensities measured absolutely. The absolute density of each ion can be measured if the upper and lower levels in these transitions are statistically populated. Analysis of the data is continuing to develop a criterion for statistical population along the isoelectronic sequence as a function of electron density and forbidden transition probability. (R. Datla, J. Roberts)

(d) <u>Vacuum Ultraviolet Radiometry with Plasmas</u>

Quite a bit of work has been done during this past fiscal year on the characterization of the Pt-Ne sealed hollow cathode lamp. Procedures were developed and a goniometer was designed and constructed for use in characterizing and calibrating these lamps. The following particulars were determined for a sample lamp: warmup time, stability, emission as a function of current, repeatability with ignition, spatial characteristics, impurity lines, signal as a function of pitch and yaw, and emission lifetime. A paper presenting these results is in preparation.

The data which we previously obtained in the calibration of the hollow cathode lamps for the throughput test of the Hubble Space Telescope were analyzed. A portion of the data was used in the paper "Accurate Energy Levels for Singly Ionized Platinum (Pt II)," which is soon to be published in J. Opt. Soc. Am. B. The complete body of data will be used in an atlas of lines emitted by these lamps which is in preparation.

A project was initiated to develop a body of atomic branching ratios for use in vacuum ultraviolet radiance calibrations. Analysis of existing material has already resulted in collections of branching ratios for the hydrogen, helium, lithium, and beryllium isoelectronic sequences. It is planned that the results for these sequences will be published in the near future and that these data will also be available on computer disks. Work will continue on developing branching ratios for additional isoelectronic sequences.

We are continuing to consult with scientists from NRL and NASA-Goddard on the Solar Ultraviolet Spectral Irradiance Monitor (SUSIM) and the Shuttle Solar Backscatter Ultraviolet (SSBUV) experiment. Other notable activities during this year were our participation in the CORM annual meeting held at NBS on May 18 and 19 and the publication of a condensed version of our calibration document which appeared in the NBS Journal of Research.

Efforts were continued to upgrade the accuracy and reliability of our calibrations. Work during the past year included the installation of some automated positioning equipment and computer integration for better data acquisition and analysis. A linearity test was performed to insure accurate data for measurements covering a large range in signal levels. Eight deuterium lamps were calibrated as secondary standards for our group and for the Radiometric Physics Division. In addition nine calibrations of various types were performed for customers during the year. (J. M. Bridges, J. Z. Klose)

(e) The transition probabilities of 29 prominent lines of neutral nitrogen were measured in emission with a wall-stabilized high-current arc and carefully analyzed. Our data are on average about 15-20% above those of two earlier emission studies. The intensity contributions of the extended line wings, which were not considered in the earlier experiments, fully account for this difference. On the other hand, our results--which are normalized against lifetime data--are still 8% lower than the latest theoretical data. Deviations of similar magnitude and in the same direction have also been observed in some other cases and seem to point to a basic systematic discrepancy between advanced experiments and theory (Q. Zhu, W. L. Wiese)

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Wiese, W. L., Atomic Transition Probabilities, in Reports on Astronomy, Vol. XX A (Reidel Publ. Co., Dordrecht, Holland), 1988.

Wiese, W. L., The Atomic Transition Probabilities of Argon--a continuing challenge to plasma spectroscopy, J. Quant. Spectrosc. Radiat. Transf. [in press].

PUBLICATIONS IN PREPARATION

Division 572, Atomic and Plasma Radiation

Brewer, L. R., Buchinger, F., Ligare, M., and Kelleher, D. E., Resonance-enhanced multiphoton ionization of atomic hydrogen (in preparation).

Cromer, C. L. and He, M., Double-Resonance Optogalvanic Spectroscopy of Ne in a New Ultra-Low Pressure Discharge (in preparation).

Cooper, J. W., Clark, C. W., Cromer, C. L., Lucatorto, T. B., Sonntag, B. F., Kennedy, E. T., Costello, J. T., Junwen, C., and Tomkins, F. S., Autoionizing Resonances in Mn, Mn+ and Cr 3p Subshell Absorption (submitted to Phys. Rev. Lett.).

Hahn, T., and Wiese, W. L., Transition probability ratios between 4s-5p and 4s-4p lines of neutral argon (to be submitted to Phys. Rev. A).

Kelleher, D. E., An Overview of the Ion Dynamic Effect in Line Broadening, and a Generalization of the Unified Theory, to be published by Springer Verlag.

Klose, J. Z. and Wiese, W. L., Branching Ratio Technique as Applied to Vacuum UV Radiance Calibration: Extensions and an Expanded Data Set (in preparation).

Klose, J. Z., Brightness Comparison of Several Platinum Hollow Cathode Lamps (in preparation).

Litzen, U., and Reader, J., $4s^2 4p^2$ - $4s4p^3$ transition array and energy levels of the germanium-like ions Rb VI - Mo XI (in preparation).

Mohr, Peter J., Quantum Electrodynamics Calculations, in Spectrum of Atomic Hydrogen: Advances, ed. by G. W. Series (submitted to World Scientific, Singapore).

Mohr, Peter J., and Soff, G., Vacuum Polarization in a Strong External Field, (submitted to Phys. Rev. A).

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Mohr, Peter J., Blundell, S. A., Johnson, W. R., and Sapirstein, J., Evaluation of Two-Photon Exchange Graphs for the Helium Isoelectronic Sequence (in preparation).

Mohr, Peter J., Quantum Electrodynamics of High-Z Few-Electron Atoms, in Atomic Physics of Highly-Ionized Atoms, ed. by R. Marrus (Plenum, New York), in preparation.

Mohr, Peter J. and Soff, G., Influence of Higher-Order Vacuum Polarization Corrections in Hydrogen-Like Uranium (in preparation).

Oza, Dipak H., Exchange Asymmetry in Elastic Scattering of Electrons by Sodium Atoms, submitted to Phys. Rev. A.

Qian, W.-J., Kim, Y.-K., and Desclaux, J.-P., Relativistic distorted-wave cross sections for electron impact excitations of beryllium-like ions, submitted to Phys. Rev. A.

Reader, J., Acquista, N., Sansonetti, C. J., and Sansonetti, J., Wavelengths of Platinum Hollow-Cathode Discharge (in preparation).

Roszman, L. J., Dielectronic recombination rates for O^{2+} and O^{5+} including some density effects (in preparation).

Roszman, L. J., The influence of metastable states and plasma density upon dielectronic recombination in low to moderate density plasmas (submitted to Phys. Rev. A).

Roszman, L. J., Revised dielectronic-recombination rate coefficients for the fluorine isoelectronic sequence (in preparation).

Sansonetti, C. J., Fabry-Perot Wavemeter for Rapid Precise Laser Wavelength Measurements, (in preparation).

Sansonetti, C. J., Precise Laser Wavelength Measurements: What Can We Learn from Classical Spectroscopy? (in preparation).

Shirai, T., Nakai, Y., Ozawa, K., Ishii, K., Sugar, J., and Mori, K., Spectral Data for Copper Ions, Cu VI - Cu XXIX (in preparation.)

Shirai, T., Funatake, Y., Mori, K., Sugar, J., Wiese, W. L., and Nakai, Y., Spectral Data and Grotrian Diagrams for Highly Ionized Iron, Fe VIII-Fe XXVI (in preparation).

Shirai, T., Mori, K., Sugar, J., Wiese, W. L., and Nakai, Y., Spectral Data and Grotrian Diagrams for Highly Ionized Chromium, Cr VI-Cr XXIV (in preparation).

Sugar, J., Kaufman, V., and Indelicato, P., Analysis of Magnesiumlike Spectra from Cu XVIII to Mo XXXI, (in preparation).

Sugar J., and Musgrove, A., Energy Levels of Copper, Cu I through Cu XXIX, J. Phys. Chem. Ref. Data (in preparation).

Veza, D., and Sansonetti, C. J., Ionization of Lithium Vapor by CW Quasiresonant Laser Light, (in preparation).

Wiese, W. L., Brault, J. W., Danzmann, K., Helbig, V., and Kock, M., A Unified Set of Atomic Transition Probabilities for Neutral Argon, submitted to Phys. Rev. A.

Wiese, W. L. and Robey, A. (Editors), Spectroscopic Data Tables for Ti, Cr, and Ni, Vol. 7 of Atomic-Data-for-Fusion Series, to be published by Oak Ridge National Laboratory.

Wiese, W. L., The Spectroscopic Data Base for Carbon and Oxygen, (to be submitted to Phys. Scripta).

Wiese, W. L., and Fuhr, J. R., The accuracy of atomic transition probabilities (to be submitted to Lecture Notes of Physics, Springer Verlag).

Woltz, L. A., and Hooper, C. F., Calculation of spectral line profiles of multi-electron emitters in plasmas (submitted to Phys. Rev. A).

Zhu, Q., Bridges, J. M., Hahn, T., and Wiese, W. L., Oscillator Strength Measurements for Prominent Spectral Lines of Atomic Nitrogen (to be submitted to Phys. Rev. A).

INVITED TALKS

Division 572, Atomic and Plasma Radiation

Datla, Raju U., "Recombination Into C IV in a θ-Pinch Plasma," University of Maryland Colloquium, Baltimore, MD, February 2, 1988.

Kelleher, D. E., "The Paron Calutron: An Experimental Test of the Pauli Exclusion Principle," JILA Colloquium, Boulder, CO, January 12, 1988.

Kelleher, D. E., "Field Effects on Autoionizing Resonances," International Line Shapes Conference, Torun, Poland, July 28, 1988.

Kim, Yong-Ki, "Relativistic Effects in Electron-Ion Collisions, Lawrence Livermore National Laboratory, December 14, 1987.

Kim, Yong-Ki, "Relativistic Distorted-Wave Cross Sections for Electron-Ion Collisions," Lawrence Livermore National Laboratory, June 21, 1987.

Klose, Jules Z., "Radiance of a Pt/Cr-Ne Hollow Cathode Spectral Line Source," Council for Optical Radiation Measurements, NBS, Gaithersburg, MD, May 18, 1988.

Martin, William C., Atomic Spectroscopic Data of Astrophysical Interest," Scientific Session of Commission 14, General Assembly of International Astronomical Union, Baltimore, MD, August 4, 1988.

Mohr, Peter J., "Structure of High-Z One- and Two-Electron Atoms," Atomic Physics Seminar, University of Notre Dame, South Bend, IN, October 15, 1987.

Mohr, Peter J., "Quantum Electrodynamics Tests in High-Z Atoms," Physics Dept. Colloquium, University of South Carolina, Columbia, SC, November 19, 1987.

Mohr, Peter J., "Quantum Electrodynamics Tests in High-Z Atoms," Atomic Physics Seminar, University of Southern California, February 24, 1988.

Mohr, Peter J., "Quantum Electrodynamics of Highly-Ionized Atoms," NATO Advanced Study Institute: Atomic Physics of Highly-Ionized Atoms, Cargese, Corsica, June, 1988.

Mohr, Peter J., "Quantum Electrodynamics of High-Z Few-Electron Atoms," V Division Seminar, Lawrence Livermore National Laboratory, August 23, 1988.

Reader, Joseph, "Spectra of Highly-Ionized Atoms," Symposium on Innovative Science and Technology, Los Angeles, CA, January 14, 1988.

Sugar, Jack, "Spectroscopy at NBS Related to Fusion Energy Research," University of Arizona, Tucson, AZ, November, 1987.

Sugar, Jack, "The Tokamak as a Spectroscopic Light Source," Japan Atomic Energy Research Institute, Tokai-mura, Japan, March, 1988.

Wiese, W. L., "Spectroscopic Data Compilations at NBS," Meeting of the International Network of Atomic Data Centers, Oak Ridge, TN, November 9, 1987.

Wiese, W. L., "The Spectroscopic Data Base for Carbon and Oxygen," Specialists Meeting, International Atomic Energy Agency, Vienna, Austria, May 10, 1988.

Wiese, W. L., "Accuracy of Atomic Transition Probabilities," Symposium on the Accuracy of Stellar Abundance Determinations, 20th General Assembly of the International Astronomical Union, Baltimore, MD, August 4, 1988.

Wiese, W. L., "Towards More Reliable Atomic Transition Probabilities," Physics Colloquium, University of Zagreb, Yugoslavia, September 22, 1988.

Wiese, W. L., "A Unified Set of Atomic Transition Probabilities for Argon," Institute of Physics, Belgrade, Yugoslavia, September 27, 1988.

TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Division 572, Atomic and Plasma Radiation

Daniel E. Kelleher

Member, International Organizing Committee of the Conference on Spectral Line Shapes.

Yong-Ki Kim

Member of Program Committee, APS Topical Conference on High Temperature Plasmas.

William C. Martin

Chairman, Working Group on Atomic Spectra, International Astronomical Union.

Member, IAEA Network of Atomic Data Centers for Fusion.

Member, Optical Society of America, W. F. Meggers Award Committee

Peter J. Mohr

Member, NAS/NRC Committee on Line Spectra of the Elements - Atomic Spectroscopy.

Member of Program Committee, Division of Atomic, Molecular, and Optical Physics, American Physical Society.

Member of International Advisory Committee, conference series on Physics and Highly-Ionized Atoms.

James R. Roberts

Member of TEXT Users Organization.

Jack Sugar

Chairman, OSA Fellows and Honorary Members Committee.

Mark Suskin

Member, NAS/NRC Committee on Line Spectra of the Elements - Atomic Spectroscopy.

Wolfgang L. Wiese

Member of Organizing Committee, International Astronomical Union, Commission on Fundamental Spectroscopic Data.

Chairman, Working Group on Atomic Transition Probabilities, International Astronomical Union.

Vice President, Commission on Fundamental Spectroscopic Data, International Astronomical Union.

Member, IAEA network of Atomic Data Centers for Fusion.

SPONSORED SEMINARS AND COLLOQUIA

Division 572, Atomic & Plasma Radiation

Ian P. Grant, Oxford University, Oxford England, "QED for Atoms and Molecules Using Basis Sets," October 13, 1987.

J. Bayfield, University of Pittsburgh, "Excited Hydrogen Atoms in Strong Microwave Fields: Search for Chaos in Quantum Mechanics," October 14, 1987.

Hans Schlueter, Ruhr University, Bochum, West Germany, "Spectroscopic Studies on RF Field-Strengths in Plasmas," October 27, 1987.

Julian Coutts, JILA, University of Colorado, Boulder, CO, "Collision-Induced Absorption in Calcium--Rare Gas Collision Complexes," November 6, 1987.

Elisabeth Källne, JET Joint Undertaking, Oxford, England, "X-Ray Spectroscopy at the Large Tokamaks," November 9, 1987.

Lawrence Woltz, University of Florida, Gainesville, FL, "Spectral Line Profiles of Multi-Electron Emitters in Plasmas," December 1, 1987.

W. L. Wiese, NIST, Atomic & Plasma Radiation Division, "The Transition Probabilities of Argon--A Challenge for Spectroscopy," December 15, 1987.

Ray Elton, Naval Research Laboratory, Washington, DC, "Soft X-Ray Lasing at NRL in Neon-Like Plasmas," January 5, 1988.

Sveneric Johansson, University of Lund, Lund, Sweden, "The Unpredictable Stars: On Anticorrelation Between Laboratory and Stellar Spectra," January 12, 1988.

Verne Jacobs, Naval Research Laboratory, Washington, DC, "Autoionization Phenomena in High-Temperature Plasma Processes," February 2, 1988.

Victor Kaufman, NIST, Atomic & Plasma Radiation Division, "Analyses of Tokamak and Other Spectra Using the Methods of Isoelectronic Sequences," February 16, 1988.

John Gillaspy, Harvard University, Cambridge, MA, "Quest for Bose-Einstein Condensation in Spin-Polarized Hydrogen," March 1, 1988.

Ulf Litzén, University of Lund, Lund, Sweden, "Spatially Resolved Laser-Produced Spectra of Highly Ionized Transition Metal Elements," March 8, 1988.

Manfred Kock, University of Hannover, Hannover, West Germany, "Plasma

Spectroscopy at the University of Hannover--Hollow Cathode Lamps, Branching Ratios, and Photoionization Cross Sections," March 18, 1988.

Ingvar Lindgren, Chalmers University of Technology, Goteborg, Sweden, "Towards a Relativistic Many-Body Procedure for Atomic Systems, March 25, 1988.

C. C. J. Roothaan, University of Chicago, Chicago, IL, "General Scheme for Fractional Parentage in Atoms," April 21, 1988.

Steven Rolston, Lyman Laboratory, Harvard University, Cambridge, MA, "Antiprotons and Antihydrogen," May 19, 1988.

John Hoffnagle, IBM Almaden Research Center, San Jose, CA, "Chaotic Motion of Ions in a Pauli Trap," May 31, 1988.

M. Klapisch, Hebrew University, Jerusalem, Israel, "Atomic Processes in Hot Plasmas-Model Computations with HUJI Code, August 15, 1988.

Robert Hilborn, Amherst College, Amherst, MA, "Spectroscopic Tests of the Symmetrization Postulate for Bosons," September 8, 1988.

JOURNAL EDITORSHIPS

Division 572, Atomic and Plasma Radiation

W. C. Martin, Co-Feature Editor for Journal of the Optical Society of America B, Special Issue for October 1988, "Atomic Spectroscopy in the Twentieth Century."

J. Reader, Editor, Line Spectra of the Elements, Handbook of Chemistry and Physics, CRC Press.

W. L. Wiese, Associate Editor, Journal of Quantitative Spectroscopy and Radiative Transfer.

W. L. Wiese, Editor, Atomic Transition Probabilities, Handbook of Chemistry and Physics, CRC Press.

MAJOR CONSULTING AND ADVISORY SERVICES

Division 572, Atomic and Plasma Radiation

1. The Data Centers on Atomic Energy Levels and Transition Probabilities routinely fill requests for atomic data or literature information submitted by scientists in a wide range of research areas. The requests average about 30 per month. Periodically, special reports are prepared for particular user groups. Thus, W. C. Martin and W. L. Wiese have written updates on atomic data of interest for the astrophysical community for the Transactions of the International Union (IAU), covering the three year period September 1984 through August 1987, and give review reports at the General Assemblies of the International Astronomical Union. J. R. Fuhr and A. Robey submit literature reference lists every six months to the International Atomic Energy Agency (IAEA) for inclusion in the IAEA semiannual Bulletin of "Atomic Data for Fusion."

2. J. M. Bridges consulted with NASA-Goddard scientists on tests and calibrations to be performed for the Shuttle Solar Backscatter Ultraviolet experiment.

3. Y.-K. Kim serves as a consultant to the A Division of the Lawrence Livermore Laboratory on x-ray laser development.

4. J. Z. Klose and J. M. Bridges consulted with NRL scientists on calibration work to be performed for the Solar Ultraviolet Spectral Irradiance Monitor.

5. J. Z. Klose continues to consult with scientists at the Space Telescope Science Institute on calibration work for the Hubble Space Telescope.

6. W. C. Martin and J. Reader consult and advise NASA scientists and other astronomers on standard wavelengths for calibration of the High-Resolution Spectrograph for the Space Telescope.

7. Peter J. Mohr served as coordinator for the program on Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms, January - June, 1988 at the Institute for Theoretical Physics, University of California, Santa Barbara.

8. J. Reader continues to consult with members of the x-ray laser program at Lawrence Livermore National Laboratory about the spectra of highly ionized atoms in laser-produced plasmas and the wavelength calibration of such spectra.

9. J. R. Roberts continues to serve as a member of the TEXT Users Organization (TUO). TEXT stands for Texas Experimental Tokamak and is a national plasma users facility.

10. J. R. Roberts continues to consult with members of Bell Labs on population inversion experiments in C^{+3} on the NBS theta pinch.

11. J. R. Roberts and R. U. Datla consulted with staff of the Naval Research Laboratory on population inversion experiments in Ar VIII and IX and recombination mechanisms in UV lasers.

12. L. J. Roszman continues to advise and consult with the Impurity Transport Modeling Group of the Princeton Plasma Physics Laboratory on electron-ion collision processes and other atomic data as well as the modeling of low density plasmas.

13. J. Sugar and W. L. Wiese consulted and advised the Japan Atomic Energy Research Institute (JAERI) on the compilation of spectral lines.

14. J. Sugar consulted with KMS Fusion scientists on the development of x-ray lasers.

TRIPS SPONSORED BY OTHERS

Division 572, Atomic and Plasma Radiation

Yong-Ki Kim visited the Centre d'Etudes Nucéaires de Grenoble, France, to collaborate with J. P. Desclaux on relativistic atomic collision codes, October-November, 1987, paid by a research grant from NATO.

Yong-Ki Kim participated in the Workshop on QED and Relativistic Effects in Atoms, Santa Barbara, CA, April-May, 1988.

Yong-Ki Kim was invited to attend the Workshop on Relativistic Effects in Atomic Collisions, Lawrence Livermore National Laboratory, Berkeley, CA, June 20, 1988.

Peter J. Mohr was invited to the University of Notre Dame, South Bend, IN for an Atomic Physics Seminar, October 15, 1987.

Peter J. Mohr was invited to the University of South Carolina, Columbia, SC for a Physics Department Colloquium, November 19, 1987.

Peter J. Mohr was invited to Santa Barbara, CA to serve as coordinator for the program on Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms, January-June, 1988.

Peter J. Mohr was invited to the University of Southern California, February 24, 1988 to participate in an Atomic Physics Seminar.

Peter J. Mohr was invited to Cargese, Corsica to participate in the NATO Advanced Study Institute: Atomic Physics of Highly-Ionized Atoms, June, 1988.

Peter J. Mohr was invited to Paris, France to participate in the Eleventh International Conference on Atomic Physics (ICAP XI), July 4-8, 1988.

Peter J. Mohr was invited to Lawrence Livermore National Laboratory, Berkeley, CA, to give an invited talk August 23, 1988.

Larry J. Roszman was invited to Lawrence Livermore National Laboratory, Berkeley, CA to attend a workshop on Electron-Ion Collision Theory and Computations, June 20-22, 1988.

Jack Sugar was invited to and gave a lecture at the University of Arizona in November, 1987.

Jack Sugar visited Japan Atomic Energy Research Institute (JAERI) in Tokai-mura, Japan under the U.S.-Japan fusion cooperation program to work with Japanese collaborators on atomic data compilations in March, 1988.

W. L. Wiese will travel to Yugoslavia and Poland September-October, 1988. He will visit the Universities of Zagreb, Belgrade and Krakow to discuss ongoing collaborative projects under cooperative NBS S & T programs and give seminar talks. All expenses paid by U.S.-Yugoslav Joint Board and Marie Curie/Sklodowska Foundation.

CALIBRATION SERVICES PERFORMED

Division 572, Atomic and Plasma Radiation

Type of Service	Customer	SP 250	No. of Tests	Income
Radiometer	IBM	40040S	1	$ 2.1k
Radiometer	Perkin Elmer	40040S	1	2.6k
Argon Mini-Arc	Goddard Space Flight Center	Contract	4	10.4k
Argon Mini-Arc	ETH, Zurich	40040S	1	2.3k
Deuterium Lamp	Sandia Corp.	40030S	1	1.5k
Deuterium Lamp	Univ. of Colorado	40030S	1	1.5k

SURFACE SCIENCE DIVISION

SUMMARY OF ACTIVITIES
Fiscal Years 1987 and 1988

1. Introduction

A. Background

Over the last decade, there has been a dramatic growth of surface science and its applications. This growth and its significance have been documented in detail in two major reports, the Pimentel report to the National Academy of Sciences on "Opportunities in Chemistry" (National Academy Press, Washington, D.C. 1985) and the Brinkman report to the National Academy of Sciences on "Physics Through the 1990's" (National Academy Press, Washington, D.C., 1986). Both reports describe in some detail the pervasive role of surfaces, interfaces, and thin films in frontier scientific research and in major technological applications. The scientific opportunities range from studies of the dynamical processes involved when atoms and molecules interact with surfaces to heterogeneous catalysis, physical and chemical properties of clusters, fabrication and characterization of novel thin-film and superlattice materials, and surface critical phenomena, among many other topics.

A principal goal of investigations in these areas is to obtain knowledge at a fundamental atomic and molecular level of surface and interface properties and processes. The technological applications include microelectronics, information processing, communications, fabrication of novel materials, materials processing, catalysis, corrosion, coatings, adhesion, wear, and biomaterials as well as areas of national concern such as energy generation, transportation, environmental pollution, space technology, and national security. A strong driving force in both the scientific and technological sectors is the need for improved U.S. economic competitiveness; in a 1987 analysis, the Department of Commerce has identified surfaces and thin films as having major significance for the development of new technologies.

Many measurement techniques are used to characterize surface properties (such as composition, atomic structure, electronic structure, defects, and topography) and surface processes (such as reactions, diffusion, segregation, and exposure to beams of ions, neutrals, photons, and electrons). A choice of one or more techniques is made typically on the basis of the property to be measured, the specimen material, and the specific needs (e.g., spatial resolution, chemical information, sensitivity, degree of difficulty, and cost). Many of the techniques are continually being refined and extended, as are the concepts on which they are based. The concepts and techniques that have proven successful for surface characterization are also being applied to the characterization of interfaces and thin films. In many such applications, surface material is removed by ion sputtering or other means to expose an interface or other region of interest. While very useful, artifacts can generally be introduced by the removal process and there is now a growing need for non-destructive or in situ methods of interface and thin-film characterization, particularly with the sensitivity, elemental specificity, and spatial resolution of current surface-characterization methods.

The most common type of surface measurement is the determination of surface composition. Most surface analyses now are qualitative but there is a growing demand for quantitative analyses with improved accuracy. At the present time, there are few standard procedures and limited reference data and reference materials. A variety of techniques is employed for the determination of surface atomic structures, surface electronic structure, and for investigations of surface processes such as reactions, diffusion, segregation, etc. Theories of the measurement process need to be developed for the newer techniques. For all techniques, there is a need for relevant procedures, tests to establish measurement reliability, and applicable reference data. In most cases, the measurement science needs to be developed since knowledge of the key concepts and parameters is often extremely limited. Some concepts and data are synthesized and developed from those of disciplines such as atomic and molecular physics, chemistry, and materials science.

B. Goal, Objectives and Division Programs

The goal of the Surface Science Division is to improve the quality of existing surface-characterization measurements and to extend the present capability. Specific objectives of the Division are:

(1) Perform experimental and theoretical research in surface science to provide a scientific base for surface-measurement methodology;

(2) Develop measurement methods and provide properties data for the physical and chemical characterization of surfaces and surface processes to meet identified needs of industry, government, and other groups;

(3) Develop reference procedures, reference data, and reference materials in cooperation with national and international standards organizations; and

(4) Develop expertise in selected new areas of surface science in order that NIST can provide measurement services where needs are anticipated in the near future.

The Division addresses these objectives by means of three principal program activities for which there are technical reports in the following three sections. Information on the Surface Standards Program (objective (3)) is given in section 2, the Surface Measurements Program (objectives (1) and (2)) is described in section 3, and a report on the Surface Competence Program (objective (4)) is presented in section 4.

The Division's programs are supported financially in part by other NIST offices and by other Federal agencies. These arrangements enable the Division to meet NIST objectives and standards needs and also to contribute its expertise and facilities to important national programs. During FY87 and FY88, support was received from the following offices and agencies:

Office of Standard Reference Data

- o Surface Science: Sputtering Yield Data

Office of Standard Reference Materials

- o Fabrication, Characterization, and Certification of Additional Lots of SRM 2135
- o Characterization and Certification of Cr/Cr_2O_3 Thin Film Depth Profile Material (SRM 2136)

Department of Energy

- o Structure and Reactivity of Chemisorbed Species and Reaction Intermediates
- o Laser Studies of Chemical Dynamics at the Gas-Solid Interface (joint with Molecular Spectroscopy Division)

Air Force Office of Scientific Research

- o Picosecond Laser Studies of Vibrational Energy Transfer in Molecules on Surfaces
  (joint with Molecular Spectroscopy Division)

Office of Naval Research

Surface Characterization of High-T_c Superconductors and Other Oxides using Synchrotron Radiation

U.S.-Spain Joint Committee for Scientific and Technological Cooperation

- o Structure and Reactivity in Catalysis by Metals and Oxides

C. Highlights

The Division staff have been productive over the past two years, as can be judged from the following narrative reports, the lists of publications and talks, and the involvement with standards and professional groups. There have also been successful collaborations with scientists in many other institutions and with guest scientists in our own laboratories.

We mention here some highlights of the past two years; further details are given in the indicated sections of this report.

- The discovery of the new high-T_c superconducting materials has generated intense activity at NIST as at many other laboratories. Division staff have contributed in two areas. Photoelectron spectroscopy with synchrotron radiation has been used to investigate the electronic structure and chemisorption properties of these materials (section 3.A). Field-ion microscopy has been successfully employed to characterize their microstructure; the images have an unusual striped pattern, not seen in any other type of material (section 4.A.3)

- New calculations have been made of electron inelastic mean free paths for 200-2000 eV electrons in 31 materials from which a general predictive formula has been derived (section 2.A.2(a))

- New high-accuracy measurements have been made of core-level binding energies and Auger-electron kinetic energies in copper, silver and gold for the calibration of the energy scales of x-ray photolectron and Auger-electron spectrometers (section 2.A.3)

- We have developed an <u>in situ</u> method for measuring changes in surface roughness due to ion bombardment (section 2.B.2)

- We have developed a new complex-defect model to describe radiation-enhanced diffusion due to ion bombardment (section 2.B.3)

- A new set of cooperative projects to develop standards for surface analysis on an international basis has been developed under the Versailles Project on Advanced Materials and Standards (VAMAS) and coordinated with parallel activities of ASTM Committee E-42 on Surface Analysis and of groups of the International Union of Pure and Applied Chemistry (Sections 2.C.2 and 2.C.3)

- Successful conferences on quantitative surface analysis have been held in 1986 and 1987, each attended by about 100 scientists (section 2.C.4)

- Division staff have authored 22 review articles during the past two years (section 2.D)

- We have developed improved instrumentation for photoemission and other experiments using synchrotron radiation (section 3.B)

- New grazing-angle x-ray diffraction experiments have been conducted and have shown the existence of surface-trapped diffraction waves. In addition, the registration of halogen atoms on a germanium single crystal has been established using x-ray standing waves excited under grazing-incidence conditions (section 3.D)

- We have invented a monochromator crystal for synchrotron radiation experiments that incorporates a detector for the x-rays in order to facilitate monochromator alignment. We expect a patent to be issued for this device (section 3.E)
- We have investigated fundamental mechanisms for several surface reactions important in semiconductor processing (Section 3.F)
- We have found unusual chemical properties of thin films of platinum deposited on single-crystal tungsten surfaces (section 3.H)
- We have demonstrated the first negative-ion ESDIAD (electron-stimulated desorption ion angular distributions) experiment. Results to date indicate that negative-ion ESDIAD is a useful complement to positive-ion ESDIAD (section 3.J)
- We have measured the laser-induced desorption of NO from Pt(111) and found non-thermal distributions for some of the desorbing molecules. These molecules appear to have been excited by optically excited hot electrons in the substrate (section 3.K.1)
- We have made direct measurements of the decay of vibrationally excited populations ranging from metal-cluster carbonyls to CO adsorbed on small metal particles (section 3.K.2)
- Studies have been made of the role of chaos in surface dynamics and its effects on lineshapes of vibrational spectroscopies for adsorbed molecules (section 3.L.1)
- We have investigated how selectivity can be controlled in several types of molecule-surface interactions (section 3.L.2)
- We have fabricated novel thin-film sandwich and superlattice structures which have been shown to have novel magnetic properties (section 4.A.2)
- We have constructed and tested a new instrument to measure the kinetic energy distributions of sputtered atoms and ions and their states of excitation (section 4.B.1)

2. SURFACE STANDARDS PROGRAM

The term "surface standards" is intended to cover a broad range of activities that are directed to improving the quality of surface-characterization measurements through: (1) development of needed reference data and standard reference materials; (2) leadership in standards-committee activities, the development of reference procedures, and other actions to improve the accuracy and reliability of surface-analysis measurements; and (3) publication of review articles and books that enable scientists to make surface-characterization measurements of the needed quality.

Standards are needed for the many measurement techniques used for surface characterization. The most critical needs, however, exist for standards in surface analysis, by far the most commonly made measurement. Reference data, reference materials, and reference procedures are particularly needed for reliable and efficient measurements by Auger-electron spectroscopy and x-ray photoelectron spectroscopy and in the use of these and other techniques to acquire composition-versus-depth information as a specimen is ion bombarded.

Requirements in these areas are assessed through surveys of user groups (the ASTM Committee E-42 on Surface Analysis and the VAMAS Working Party on Surface Chemical Analysis) and through focussed discussions at workshops and conferences.* Three articles describing recent progress in the provision of standards and current needs are listed in section 2.D.

The Division's efforts to provide needed reference data and reference materials are summarized in sections 2.A and 2.B., respectively. The Division also contributes to coordinated international efforts to develop reference data and reference materials in surface analysis (section 2.C). Reference procedures are developed in conjunction with three active standards groups, as described in section 2.C. Division staff authored a large number of review articles which summarize recent advances and guide scientists in making reliable measurements by particular surface techniques; these articles are listed in section 2.D.

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*For example: Workshop on Quantitative Surface Analysis, NIST, October 24, 1986; NPL-VAMAS Workshop on Quantitative Surface Analysis, National Physical Laboratory, London, November 17, 1986; Second Topical Conference on Quantitative Surface Analysis, Monterey, CA, October 30-31, 1987; and evening workshops on specific topics sponsored by the ASTM Committee E-42 on Surface Analysis and the Applied Surface Science Division of the American Vacuum Society (AVS) at the fall AVS National Symposium and the spring AVS Applied Surface Analysis Symposium.

A. Reference Data

1. Sputtering Yield Data Compilation

(J. Fine and G. P. Chambers*)

Sputtering techniques for depth-profile analysis are presently being used in conjunction with a number of surface analytical methods to analyze compositional changes of materials at surfaces and at interfaces. Many of these techniques have now progressed to the point of being able to provide quantitative sputter-depth-profile information yet the necessary sputtering yield data is not readily available in easy-to-use, evaluated form.

We are preparing a compilation of evaluated sputtering-yield data for those parameters that will have specific use in surface analysis and depth profiling. This work is supported by the NIST Office of Standard Reference Data. Our compilation will be in tabular form for those ion species (Ne, Ar, Kr, Xe, O_2, N_2, Cs) and energies (0.5 to 20 keV) and angles of incidence used in surface characterization. The compilation will contain sputtering yields for elemental targets only.

The HP-1000 Data System in the Center for Chemical Technology is being used for the data compilation. Dr. D. Neumann and members of his group have provided guidance as well as technical assistance with the software development.

Extensive use has been made of on-line abstract searching capability in order to bring our reference files up to date. Abstract searching has been completed and checked for completeness by making selected author searches. Sputtering yield papers have been identified and compiled, and data has been abstracted and entered into our data base. Certain experimental parameters needed for evaluating the reliability of the sputtering yield data have also been entered into our data base.

Sputtering yield data have been evaluated using a method based on target surface reactivity, surface oxide formation, and sputter removal rates. Limits were established for determining which data were more "reliable" (consistent) than others. Based on the setting of such limits and on the total ion dose used to obtain the measurement, we have been able to show that subsets of the yield data exist which are quite reasonable in the scatter of the data and which have the "proper" dependence on ion energy. Computer fitting routines are being developed which take into account the impacting ion and target atom masses in order to produce the "proper" shape curve for those data sets which do not contain sufficient data for fitting purposes. On completion of this phase of our evaluation scheme, we will complete the data compilation and will provide both tabular as well as graphical output of what we find to be the more reliable yield data.

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*Guest Scientist or Collaborator

2. Inelastic Mean Free Paths and Attenuation Lengths of Low-Energy Electrons in Solids

(R. L. Kurtz, T. E. Madey, C. J. Powell, R. L. Stockbauer, S. Tanuma*, Q. Wang*, and J. A. Yarmoff)

Values of inelastic mean free paths (IMFPs) and attenuation lengths (ALs) of low-energy (often 50-2000 eV) electrons are required in quantitative surface analysis by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) for correction of so-called matrix effects. These parameters also define the surface sensitivity of these and other electron-spectroscopic methods of surface characterization. The AL is distinguished from the IMFP by the fact that AL values are usually derived from overlayer-film experiments on the basis of a model in which elastic electron scattering has been assumed to be insignificant. The IMFP, on the other hand, is usually obtained from theory. IMFP values will therefore be systematically greater than AL values by up to about 15-30%, the difference being greatest for high atomic numbers and low electron energies.

Accurate values of IMFPs and ALs are urgently required for a range of materials and for electron energies of practical interest in AES and XPS. AL measurements of high accuracy are generally difficult since the values are typically in the range 3 to 30 Å and specimen characterization on this scale (morphology, thickness, homogeneity, uniformity, etc.) is difficult. Calculations of IMFPs are also difficult since approximations, particularly for electron energies below about 200 eV, may not be valid. Useful formulas are needed to enable useful predictions to be made of AL or IMFP values in materials for which no measurements or calculations have been made. Reliable predictions of this type require knowledge of the dependence of AL or IMFP on electron energy and on material parameters (e.g., density, atomic or molecular weight). It is also desired to be able to convert data for IMFPs to ALs and vice versa so that IMFP calculations can be compared simply with AL experiments and that IMFP models can, when validated, be used to predict AL values for a useful range of materials and electron energies. Finally, knowledge is needed of the extent to which concepts (and data) developed for polycrystalline or amorphous materials break down in single-crystal materials.

We report below on efforts to address some of the above-mentioned needs.

(a) Calculations of Inelastic Mean Free Paths in 31 Materials

(C. J. Powell and S. Tanuma*)

We have calculated IMFPs for 200-2000 eV electrons in 27 elements (C, Mg, Al, Si, Ti, V, Cr, Fe, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Bi) and 4 compounds (LiF, SiO_2, ZnS, and Al_2O_3). These calculations are based on an algorithm recently developed by Dr. D. R. Penn (Radiation Physics Division) in which experimental optical data are used to give information on the inelastic scattering probability as a function of energy loss and in which theory is used to describe the dependence of the scattering probability on momentum transfer. This hybrid approach enabled us to take advantage of the available optical data (that can be checked for internal consistency by various sum rules) and avoids the necessity for making assumptions about the relative strengths of various valence-electron and core-electron excitations.

The calculated IMFPs λ_i were found to be well described by the Bethe equation for inelastic electron scattering in matter:

$$\lambda_i = E/[E_p^2 \beta \ell n(\gamma E)] \quad \text{Å} \tag{2.1}$$

where E is the electron energy (in eV), E_p is the free-electron plasmon energy for the material (in eV), and β and γ are two parameters. The plasmon energy is $E_p = 28.8\ (N_v \rho/A)^{1/2}$ where N_v is the number of valence electrons per atom or molecule, ρ is the bulk density (in g cm^{-3}), and A is the atomic or molecular weight. The inelastic scattering is mostly due to valence-electron excitations; for materials with shallow core levels (binding energies less than about 30 eV), these also contribute to the inelastic scattering and the plasmon energy should be calculated with the number of these core electrons and the number of valence electrons. We have found empirically that the two Bethe parameters could be simply related to other material constants:

$$\beta = -2.52\text{x}10^{-2} + 1.05/(E_p^2 + E_g^2)^{1/2} + 8.10\text{x}10^{-4} \rho \tag{2.2}$$

$$\gamma = 0.151\ \rho^{-0.49} \tag{2.3}$$

where E_g is the bandgap energy for nonconductors (in eV).

Fig. 2.1 shows an illustrative plot of our results for aluminum. The solid line shows the IMFP results calculated with the Penn algorithm and the curve labelled TPP is a plot of Eqs. (2.1)-(2.3) using parameter values for aluminum. The dashed line shows an IMFP formula due to Szajman et al, and the dot-dashed curve gives results from the widely used empirical AL formula of Seah and Dench. In the case of Al, there is good agreement between our IMFP calculations the results calculated from Eqs. (2.1)-(2.3), the Szajman et al. formula, and the AL experimental data; the Seah and Dench formula agrees with the other results for E < 500 eV but diverges at higher energies.

For the 31 materials we have investigated so far, the rms difference between the individual IMFP values for a particular material and the values calculated from Eqs.(2.1)-(2.3) for that material was about 12%. This level of consistency was considered satisfactory considering the uncertainties in the optical data and the empirical nature of Eqs. (2.1)-(2.3). Equations (2.1)-(2.3) are therefore believed to be a useful general formula for predicting IMFPs in other materials and to be a reasonable but more approximate guide to AL values. The approximations in the Penn algorithm are likely to give systematic uncertainties in the calculated IMFPs so the new general formula is believed to be particularly useful for predicting the IMFP dependence on electron energy for a given material and the material-dependence for a given energy.

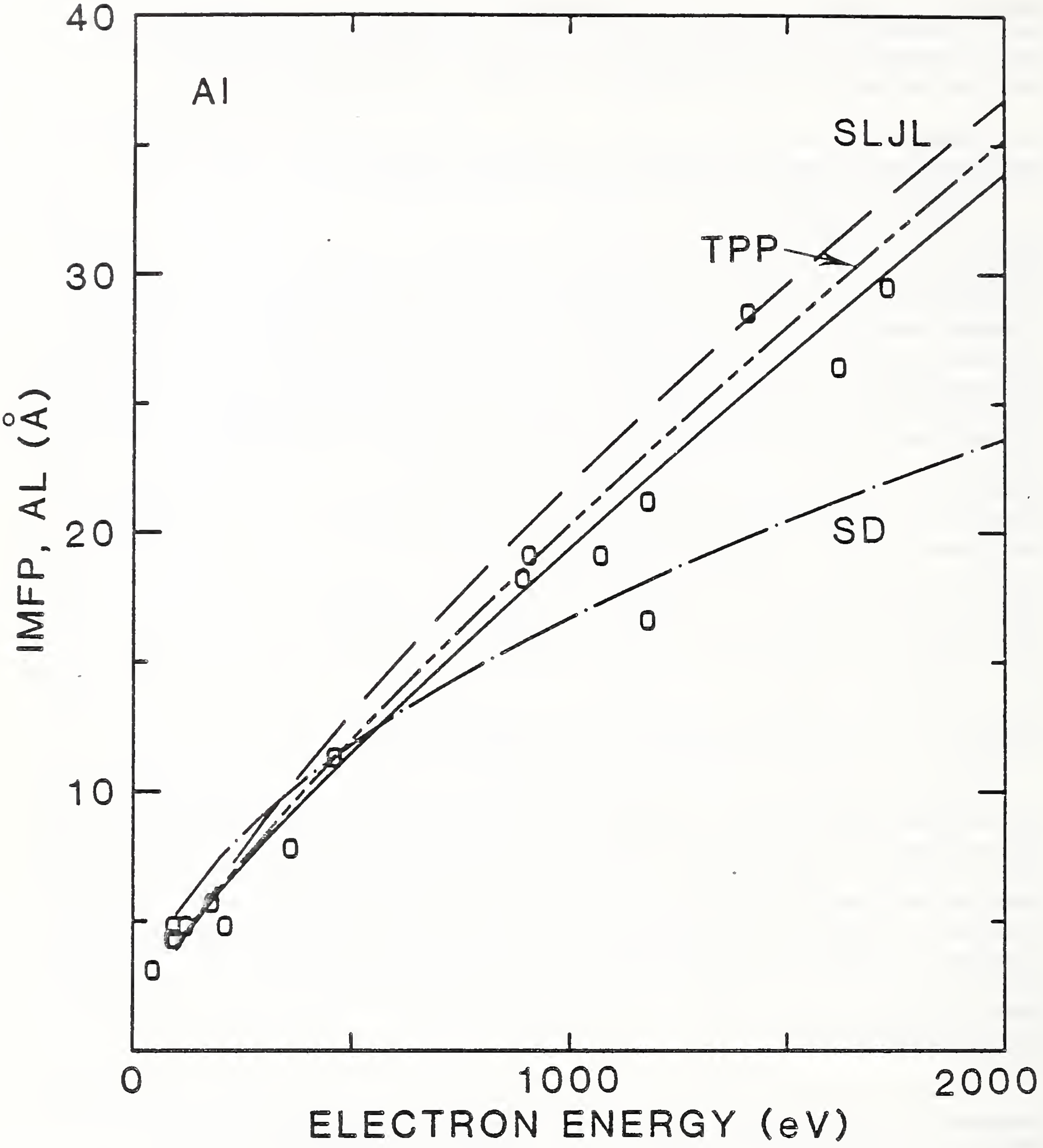

Fig. 2.1. Comparison of IMFP and AL results for aluminum. The solid line shows the calculated IMFPs and the curve labelled TPP is the general IMFP formula, Eqs. (2.1)-(2.3), using parameter values for Al. The curve labelled SLJL is an IMFP formula due to Szajman _et al_. and the curve denoted SD is the AL formula of Seah and Dench. The open circles are the AL values of Tracy.

Penn has developed a more complex algorithm with which IMFP calculations can be made for electron energies down to about 50 eV. Additional IMFP calculations with this algorithm are in progress and it is hoped to extend Eqs. (2.1)-(2.3) to correspondingly lower energies. It is also planned to extend the calculations to other materials for which the optical data are available over a substantial photon energy range (typically about 1-1000 eV).

(b) Measurements of Electron Attenuation Lengths in Condensed Molecular Solids

(R. L. Stockbauer, R. L. Kurtz, Q. Wang*, and T. E. Madey)

We have continued to improve a method developed earlier for measuring electron attenuation lengths in condensed molecular solids. In this method, electrons emitted from a substrate are attenuated by a condensed film of the sample material. Variable wavelength photoemission spectroscopy using synchrotron radiation is able to distinguish the electrons emitted by the substrate from those emitted by the overlayer. Changing the incident photon energy changes the kinetic energy of the emitted electrons allowing the measurements to be made as a function of electron kinetic energy over the range available at the synchrotron.

Since the thickness of the overlayer is critical to the measurement, three independent methods are used to determine this quantity: a measure of the number of molecules condensed on the surface, a shift of the photoemission spectral features between the first and subsequent layers, and different thermal desorption temperatures for different layers. The three methods give consistent results within experimental error.

Improvements in the experiment have been made in several areas. The first was moving the instrument to beamline 1 at SURF-II where the higher photon flux, lower second-order light, and broader energy range of the monochromator allow faster, lower-noise and lower-background measurements. With this monochromator, the energy range of the measurements was doubled to nearly 200 eV. The second improvement was to mask the energy analyzer to permit only electrons emitted normal to the surface to be detected. This eliminated the necessity for correcting the data for electrons emitted off-normal, a correction which has questionable applicability in our previous work. The third was to continually dose the sample while the photoemission data were being accumulated. This eliminated a background correction and reduced the data acquisition time by a factor of 5. Lastly, two different substrates were used in the present measurements, Cu(100) and Ni(100), to investigate effects of the substrate on overlayer growth. No significant differences were observed.

To date, measurements have been made on water, methanol, ethanol, and acetone. These condensed molecular solids were selected for measurement since there are very few measurements of attenuation lengths for organic solids. Semilog plots of the substrate intensity versus film thickness were linear over two decades which indicated layer-by-layer growth of the overlayer as opposed to three-dimensional island growth. The attenuation length as a function of electron energy appeared to follow the empirical universal curve proposed by Seah and Dench for organic molecules. They were somewhat lower than our previous results and results obtained by several other groups. A series of experiments are being planned to determine the source of the differences.

The measurements will be expanded to include atoms and molecules which are not condensable at liquid nitrogen temperature by using a new helium-cooled cold stage. Attenuation length measurements of rare gases and simple diatomic molecules (O_2, N_2, and CO, for instance) should enable assessment of IMFP calculations for these solids based on atomic excitations and ionizations. In addition, beam time has been scheduled for experiments to be performed at our Brookhaven NSLS beamline to allow the electron energy range to be extended to 600 eV.

(c) Measurements of the Attenuation Lengths of Very Low Energy Electrons in Silicon Oxide and of the Relative Si 2p Photoemission Cross-Sections at the SiO_2/Si Interface as a Function of Oxidation State and Final-State Energy

(J. A. Yarmoff and S. A. Joyce)

Core-level soft x-ray photoemission is an ideal technique for the study of interfaces owing to its ability to distinguish between the oxidation states of an atom. This technique is ideally performed with synchrotron radiation, since the tunability of the synchrotron allows for the collection of spectra with differing electron kinetic energies. As the attenuation length of electrons traveling through solids is a function of the kinetic energy, an effective depth profiling can be achieved by comparing spectra collected at different photon energies. This rather simple picture is complicated, however, by the fact that photoemission cross-sections are also functions of the photon energy, and that these functions can vary with the oxidation state of a particular atom. It is thus of importance to perform accurate measurements of both electron attenuation lengths and photoemission cross-sections as functions of electron or photon energy.

The SiO_2/Si interface is one of the most important systems for study in terms of current materials used in the fabrication of semiconductor devices. Core-level soft x-ray photoemission is an ideal technique to properly understand the structure of this system, as the interface constains three sub-oxide peaks which can be clearly resolved. In addition, films of SiO_2 can be grown of varying thickness without changing the properties of the interface.

In order to measure attenuation lengths for electrons photoemitted from these surfaces, photoelectron spectra were collected in the constant-final-state mode; that is, the energy analyzer was set to a constant kinetic energy and the photon energy was then varied. This insured that all of the electrons measured in a given spectrum have suffered the same average inelastic loss, i.e., have originated from the same average depth. Spectra were collected for kinetic energies ranging from 6 to 100 eV. The changes in intensity of each peak that are observed when varying the electron kinetic energy of detection are due to a combination of cross-section and electron scattering effects. The analyzer for these experiments accepted electrons emitted over a large solid angle so the inelastic scattering parameter meaured is an average escape depth rather than an attenuation length for a particular takeoff angle.

The average escape depth was determined by comparison of data collected from two samples with significantly different oxide thicknesses. In this case, the ratio of the silicon core-level peaks for SiO_2 and bulk Si was monitored as a function of detection energy for both samples. The difference in this ratio for the two samples is purely a result of the additional scattering occurring in the extra SiO_2 of the thicker sample. The analysis of this data produced the distribution shown in Fig. 2.2. This curve shows a local minimum at ~ 35 eV, which is most likely the result of scattering due to a bulk plasmon. The curve also contains the surprising result that at very low electron energies (< 10 eV), the

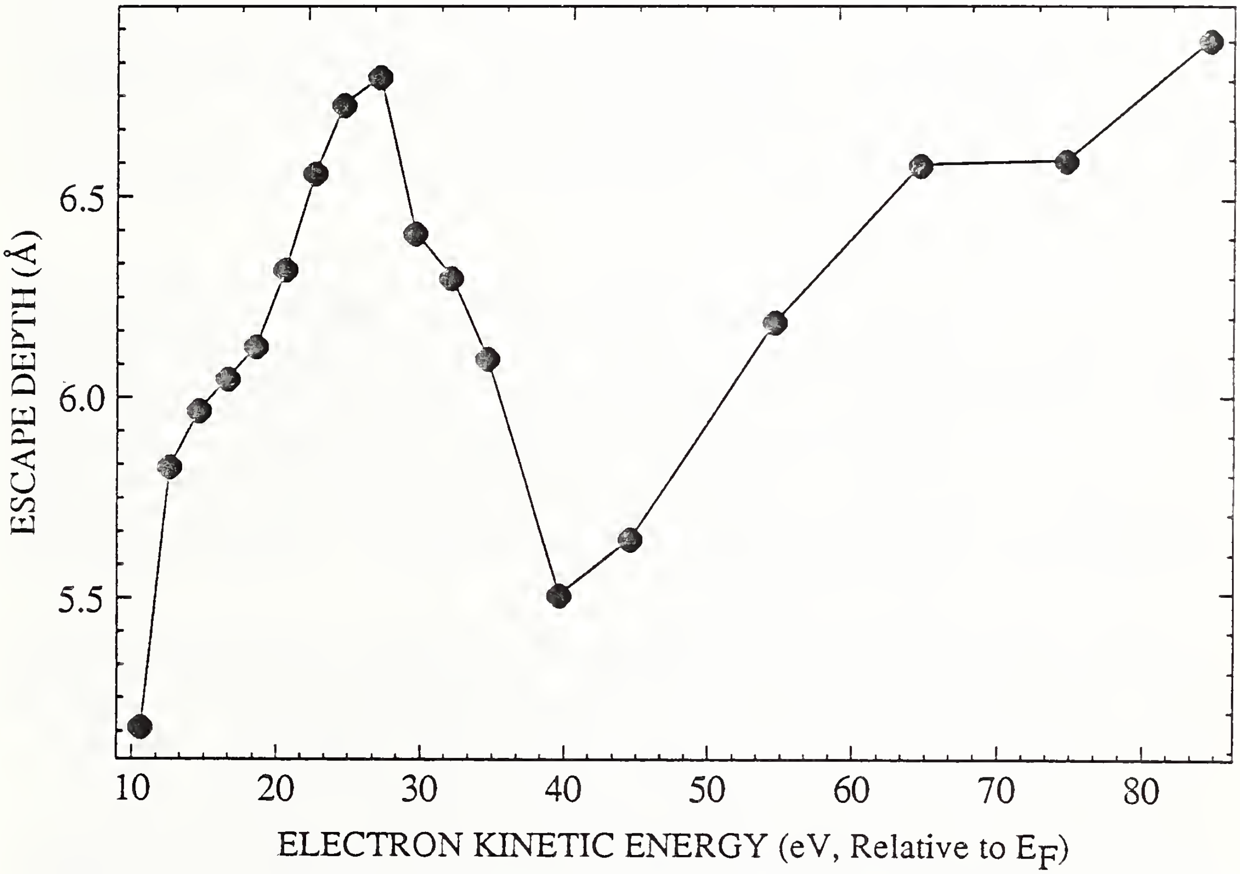

Fig. 2.2 The average escape depth determined for electrons traveling through SiO_2 as a function of electron kinetic energy.

escape length for electrons traveling through SiO_2 decreases with decreasing energy. This decrease in escape depth can be attributed to excitation of phonon modes in the SiO_2, for which there is a very large cross section. This conclusion is supported by the fact that the bulk Si photoelectron peak seen in spectra collected at very low electron energies is apparently broadened and shifted towards an apparently higher binding energy in the thicker samples. The bulk Si peak observed in the thicker samples is thus a convolution of the actual Si photoelectron peak and its loss function.

The photoemission cross-sections as a function of the electron kinetic energy were measured by preparing a sample that contained only a single monolayer of oxygen atoms. This was done by room temperature exposure of a clean Si surface to 200 Langmuirs of oxygen, which forms a surface containing all four oxidation states of Si. Since this oxide is less than a monolayer thick, a measurement of the absolute photoemission intensity from each oxidation state as a function of electron kientic energy (or final-state energy) would in essence be free of any effects of changing escape depths. This measurement showed that the photoemission cross-sections can be enhanced by as much as a factor of 2 in going from the +1 to +3 oxidation states at certain photon energies.

This work is a collaboration with Dr. F. R. McFeely of the IBM Watson Research Laboratory, and has been performed at the National Synchrotron Light Source at Brookhaven National Labortory.

(d) Universal Curves for Electron Inelastic Mean Free Paths and Attenuation Lengths

(C. J. Powell)

Since reliable knowledge of ALs and IMFPs is important for determining the surface sensitivity of various electron spectroscopies and for quantitative analyses by AES and XPS, there has been considerable interest in obtaining so-called universal curves to guide users in determining IMFP and AL values for particular materials and energies. The phrase "universal curve" came into vogue in the mid-1970s when it appeared that early AL data for different materials clustered about a common curve when the AL was plotted against electron energy. Later work, however, showed considerable scatter about the presumed universal curve.

A review article has been written that evaluates a number of proposed universal curves. Due to the difficulties in making accurate AL measurements and IMFP calculations, it is not surprising that there is a substantial scatter in data from different sources. Empirical guides, based on limited data, are convenient and useful but may be inaccurate for some conditions. A new formula, Eqs.(2.1)-(2.3) in section (a) above, is considered to be a useful guide for the IMFP dependences on material and electron energy in the range 200-2000 eV since it is based on application of a common algorithm and evaluated optical data for 31 materials. This formula is expected to be a reasonable but more approximate guide to ALs and it is hoped that it can be evaluated with AL data measured with higher accuracy than has been common in the past.

3. High-Accuracy Measurements of XPS Binding Energies and AES Kinetic Energies for Copper, Silver, and Gold

(N. E. Erickson and C. J. Powell)

The energy scales of x-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES) instruments need to be calibrated so that measurements of core-electron binding energies (BEs) by XPS or electron kinetic energies (KEs) by AES can be transferred meaningfully from one laboratory to another. The principal motivation of many practical BE and KE measurements is in the determination of the so-called chemical shifts in the energies from which chemical-state information can be obtained. Calibration of the XPS and AES energy scales enables reliable use of the available BE and KE data (if these have been acquired on calibrated instruments). The accuracy required in the calibration of the BE scales in XPS is typically 0.1 eV or better and of the KE scales in AES is typically 1 eV or better. Round robins conducted by NIST staff members about eight years ago indicated that the accuracies of BE and KE measurements then could be appreciably inferior to those required for valid chemical-state identification. In the meantime, BE data for Cu, Ag, and Au have been published by the National Physical Laboratory (NPL) and similar AES KE measurements there have recently been concluded. While we believe the NPL measurements to be of high quality, we consider that independent measurements at NIST are important to ensure maximum user confidence, particularly since there is still a discrepancy in some recently published high-accuracy measurements.

We had originally planned to calibrate the energy scale of our double-pass cylindrical-mirror analyzer (CMA) by measuring the positions of elastic peaks with electrons of known energy. By adjusting the voltage applied to the electron gun so that the elastic peak from a specimen closely overlapped the position of an AES or XPS peak from that material, it would be possible to determine the energy of electrons in the AES or XPS peak from an accurate measurement of the gun voltage and a separately measured instrumental constant (associated mainly with the selected analyzer pass energy and the work functions of cathode and analyzer). It was found, however, in a series of test measurements that the measured positions of the elastic peaks did not track accurately the voltages applied to the gun cathode. The observed deviations appear to be due to a recoil energy loss occurring with the elastic scattering process. These recoil losses depend on incident electron energy and range up to 0.2 eV for incident energies between 50 and 1250 eV with slight differences in magnitude, up to about 30 meV, for copper, silver, and gold.

The origins of the observed recoil energy losses are not clear. Published work with 20-40 keV electrons has indicated recoil losses of up to 4 eV that could be interpreted in terms of single Rutherford scattering. At the lower incident energies of present interest, the Rutherford scattering formula indicates the trends but greatly underestimates the magnitudes of the recoil losses. Other scattering mechanisms therefore have to be considered, such as those associated with phonon excitations. The observed elastic peaks probably are the envelopes of various (unresolved) phonon scattering modes for our polycrystalline foil specimens.

We have subsequently made use of accurate measurements of the voltage applied to the CMA inner cylinder corresponding to particular AES and XPS spectral features (e.g., peak maxima). XPS data were measured with a constant voltage between the outer and inner cylinders, corresponding to an analyzer pass energy of about 50 eV, and with magnesium characteristic x-rays. The binding energies of the principal peaks for Cu, Ag, and Au were measured with respect to the Fermi level of a nickel specimen, located from the position of the peak in the derivative of the spectrum in the Fermi-edge region.

Our preliminary binding energy results are shown in Table 2.1 and compared with corresponding results from NPL. Also shown are the positions of two Auger-electron peaks with reference to the binding-energy scale for magnesium characteristic x rays. The uncertainties in the NIST data represent the combined uncertainties of voltmeter calibration (5 meV) and the precision in locating the position of each peak and the Fermi level (typically between 5 and 15 meV). The NIST results agree with those of NPL within the combined uncertainties.

Table 2.1. Comparison of core-level binding energies (in eV) for the designated core levels of copper, silver, and gold as measured at NIST and NPL. The positions of two Auger-electron peaks are also shown on the binding energy scale using magnesium x rays.

Line	NIST	NPL
Au $4f_{7/2}$	84.01±0.01	84.00±0.01
Cu L_3VV	334.98±0.02	334.95±0.01
Au $4d_{5/2}$	335.19±0.02	
Ag $3d_{5/2}$	368.31±0.02	368.29±0.01
Ag M_4VV	895.75±0.03	895.76±0.02
Cu $2p_{3/2}$	932.71±0.02	932.67±0.02

We have made similar measurements of the Auger-electron peaks for copper, silver, and gold. Absolute kinetic energies were obtained by associating the magnesium characteristic x-ray energy with the observed position of the nickel Fermi edge. Our preliminary values are shown in Table 2.2. The low-energy lines of copper and gold are doublets and the two entries refer to the positions of the line components. There is again agreement between the NIST and NPL data within the combined uncertainties.

Table 2.2. Comparison of Auger-electron kinetic energies for copper, silver, and gold (in eV) as measured at NIST and NPL. The first stated uncertainty refers to the precision of measurement and the second uncertainty to the accuracy in establishing the absolute energy scale.

Line	NIST	NPL
Cu $M_{23}VV$	61.20±0.02±0.04	61.17±0.04±0.02
	63.48±0.02±0.04	63.45±0.04±0.02
Au $N_{67}VV$	70.20±0.15±0.04	70.12±0.04±0.02
	72.18±0.04±0.04	72.26±0.04±0.02
Ag M_4VV	357.85±0.03±0.04	357.87±0.01±0.02
Cu L_3VV	918.61±0.02±0.04	918.68±0.01±0.02
Au $M_5N_{67}N_{67}$	2015.71±0.04±0.04	2015.56±0.02±0.04

The new XPS binding energy and AES kinetic energy data for copper, silver, and gold appear to be satisfactory for checking and calibrating the energy scales of AES and XPS instruments.

4. Reference Data for X-Ray Photoelectron Spectroscopy and Auger-Electron Spectroscopy
(C. J. Powell and N. E. Erickson)

A project was initiated in FY82 with funding by the NIST Office of Standard Reference Data (OSRD) to prepare compilations and evaluations of core-electron binding energies and of the kinetic energies of selected Auger electrons for a wide range of elements and compounds. In particular, data are being compiled of the "chemical shifts" that can give useful information on the chemical state of a particular element. Data of this type are now scattered throughout the scientific literature but there is a need both for a convenient single source and for evaluation of the sometimes conflicting data. The reference data are being compiled by Dr. C. D. Wagner, a contractor to NIST, and the Surface Science Division is providing technical review.

The compilation and evaluation of these data have been completed. The resulting data base consists of some 13,000 entries and is to be published shortly in the Journal of Physical and Chemical Reference Data. OSRD is currently developing a data system so that the data base can be accessed from computer terminals.

5. Composition Depth Profiles and Inelastic Background Subtraction in XPS

(W. F. Egelhoff, Jr., and I. Jacob*)

It is well known in x-ray photoelectron spectroscopy (XPS) that the primary photoelectrons undergo inelastic losses as they propagate through the specimen material. These inelastic scattering events result in an inelastic tail that begins under the main XPS or elastic peak and trails to lower kinetic energies. The deeper the emitting atom is located in the specimen, the greater is the intensity of this inelastic tail relative to the elastic peak. Theoretical work by Dr. S. Tougaard of Odense University, Denmark has indicated that the relative strengths of the elastic peaks and the inelastic tails might be used as a method of non-destructively obtaining compositional depth profiles. However, there has so far been no standard reference materials available to evaluate this theoretical work.

A collaboration has been initiated with Dr. Tougaard to evaluate his proposed method. We are making angle-resolved XPS measurements of the elastic peaks and inelastic tails for epitaxial sandwich structure in which a single atomic layer of one element, e.g., Cu, is sandwiched between epitaxial layers of a different element, e.g., Fe. Marked changes occur in the relative elastic to inelastic intensities as a function of depth for the XPS peaks of the single layer. Using carefully controlled epitaxial growth, samples are being grown that provide data in a form ideally suited to evaluation of the theory and its parameters. This work is expected to lead to improved theoretical models for inelastic scattering in XPS, accurate prediction of the shape of inelastic tails, and improved background subtraction algorithms for quantitative XPS compositional measurements and depth profiling. This work is contributing to the VAMAS project described in more detail in section 2.D.2.

6. Uncertainties in Quantitative Surface Analyses by Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy

(C. J. Powell)

The two most popular techniques used to make quantitative analyses of surfaces are Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). Such analyses are frequently used to identify the surface phases present on a specimen, to determine the concentrations of elements or compounds in those phases, and to measure the variation of composition as a function of position (both parallel or normal to the surface). A surface analysis comprises a series of operations that typically includes instrument setup, specimen positioning, data acquisition, data manipulation, and data analysis. These operations involve a sequence of measurements that are combined and/or compared with other data to yield an experimental result. This result could be the detection of a particular element or compound, the distribution of a species across a surface or with depth, the comparison of a spectrum from one specimen with that of a reference (a specimen from a different batch or a published result), or a quantitative analysis. The final result of the surface analysis has an uncertainty that reflects the separate random and systematic uncertainties in the various measurements and sources of data.

In a collaboration with Dr. M. P. Seah of the UK National Physical Laboratory, a detailed analysis has been made of the individual steps in AES and XPS analyses and of the various sources of uncertainty. Although adequate repeatability (precision) is often achieved, there are many sources of systematic uncertainty that make accuracy statements very difficult. The major sources of systematic uncertainty are associated with the complexity of typical specimens, with knowledge of instrument performance, and with limitations of current methodology and data. We have identified the sources of uncertainty in these areas and the extent to which there are adequate sources of reference data, reference materials, and reference procedures to guide analysts in making measurements of the desired accuracy. Although the details of the analysis are specific to AES and XPS, many aspects are applicable to other techniques of surface analysis.

7. PIN Diode Detectors for Synchrotron X-Rays

(T. Jach)

The use of PIN silicon photodiodes as a replacement for ion chambers in x-ray synchrotron radiation experiments was pioneered at NIST. The original work included performance data on five different commercially available photodiodes at x-ray energies of 1.2-3.0 keV. The diodes offer important advantages over ion chambers and their use has spread in the synchrotron community.

We have expanded the previous work by additional characterizations of commercial photodiodes in energy response and spatial resolution. The work was performed in collaboration with Drs. J. P. Kirkland and R. A. Neiser of the Naval Research Laboratory and experiments were carried out using the X-23B beamline at the Brookhaven National Synchrotron Light Source. This beamline offered orders of magnitude improvement over the previous measurements done in the laboratory with an x-ray tube in terms of x-ray flux, energy range, and freedom from harmonic contamination. We have published data on the response of four commercial photodiodes in the energy range 3.6-11 keV, as well as response curves for sensitivity vs. illumination position for one type of diode. The work has led to a model of how these diodes, which are designed to respond to visible light, perform at x-ray energies.

The use of PIN silicon photodiodes (both commercial and our own specialized devices) has become common for x-ray detection experiments performed at synchrotron sources by several groups at NIST and elsewhere. We intend to continue characterizing and modeling appropriate types both to assist the synchrotron community and to further our own applications in experiments.

B. Reference Materials

1. Developments and Production of Standard Reference Materials for Sputter-Depth Profiling)

(J. Fine and D. Marton*)

The objective of this project is to develop standard reference materials (SRMs) that will allow convenient determinations of ion-beam sputter-removal rates in commonly used surface-analysis instrumentation. Thin-film reference materials of known thickness will be used to calibrate ion-gun current densitites for particular operating conditions. This information together with sputtering-yield data for a range of materials will establish depth scales in the measurement of depth profiles.

We have previously developed, fabricated, and certified SRM 2135, a multilayered Ni/Cr thin-film structure for calibrating sputter depths and erosion rates, for monitoring ion beam stability, and for optimizing sputtering conditions to achieve maximum depth resolution. The material consists of nine alternating metal thin-film layers, five layers of Cr and four of Ni, sputter deposited onto one side of a polished Si(100) substrate. With support from the NIST Office of Standard Reference Materials, SRM 2135 has been certified for total Ni and total Cr content, individual layer uniformity and Ni + Cr bilayer uniformity, and individual layer thickness.

SRM 2135 was issued in the fall of 1985 and by the spring of 1986, our initial stock of 80 specimens was sold. Since then, we have calibrated and put in stock two additional batches: SRM 2135a (1986) and SRM 2135b (1988). The last batch of Ni/Cr, SRM 2135b, was certified for total Ni and Cr using methods different from those we had previously used (polarography and plasma spectroscopy instead of neutron activation analysis). We were able to show that these new methods are adequate for future Ni and Cr certification.

The total sales of SRM 2135 is now more than 140. The material has been sold to many US laboraories and to institutions in other countries. In addition to its intended purposes, SRM 2135 has been used as a test material for sputtering studies, for laboratory intercomparisons, and for performance of commercial equipment.

Work is now in progress on the fabrication of a large additional stock (600-900 pieces) of SRM 2135. Because the fabrication facility used previously is no longer available, we are developing new fabrication techniques at the Comsat Laboratories in Germantown, MD. We anticipate that their planar magnetron sputter-deposition apparatus will produce satisfactory materials and that the film thickness uniformity will also be satisfactory. At present, prototype materials are being fabricated in order to evaluate interface structure and sample-to-sample film-thickness uniformity.

A new "marker-type" SRM has been under development along with improved Auger profiling techniques necessary for its characterization. This Cr/Cr_2O_3 multilayered thin-film structure consists of 6 well-defined, thin oxide marker layers (about 3 monolayers thick) separated by Cr films which are about 40 nm thick. The uniformity of the marker layer spacing is better than 3% (one standard deviation); it should be very useful both as a depth profile standard for secondary-ion mass spectrometry analysis as well as a sensitivity standard for Auger analysis. Certification is now almost complete and we anticipate that this SRM will be ready for issue in December 1988.

We are planning to develop a new SRM consisting of Cu, Ag, Au, and Si. This material is intended as a convenient means for calibrating the energy scales of Auger-electron spectrometers (AES) and x-ray photoelectron spectromers (XPS). It is being developing in response to our recent survey (section 2.B.4) and will provide a simple means of using the new high-accuracy XPS binding-energy and AES kinetic-energy data obtained at the UK National Physical Laboratory and at NIST (section 2.A.3) for Cu, Ag, and Au. Recently, it has been suggested that Si would be a useful calibration material for AES. The material should also be useful in checking analyzer intensity scales.

We plan to fabricate this SRM by sputter-depositing each element on a silicon wafer in an ultrahigh vacuum environment and at rates such that the films will have very fine grains (i.e., be nearly amorphous). Each film will be separately deposited and positioned adjacent to each other so that users can clean the surfaces easily by ion bombardment. We anticipate that the main development effort will be in producing films sufficiently fine grained that electron diffraction effects will be negligible.

2. Sputtering-Induced Surface Microroughness of Metallic Thin Films (J. Fine and D. Marton*)

Changes in surface microtopography which often occur during sputter-depth-profile analysis can significantly affect the measured depth resolution of interfaces. To better understand the importance of this roughening effect on interface analysis, we have correlated measurements of surface roughness obtained while Auger sputter-depth-profiling thin metallic multilayered systems with that of the observed Auger interface widths.

We have measured r.m.s. roughness of three test surfaces in situ using optical total-integrated-scattering (TIS) techniques. In this method, the specimen is illuminated with a collimated light beam and the off-specularly reflected light is related to the surface roughness and to the reflectivity of the investigated surface. The light scattering and Auger measurements were both carried out in an Auger-electron spectrometer used for depth profiling experiments. A light beam from a He-Ne laser source (λ = 632 nm) was directed perpendicular to the specimen surface and an ellipsoidal (or hemispherical) mirror was used to collect the off-specular light. Measurement of the off-specular light intensity was obtained with a Si detector using lock-in techniques.

We have made test measurements on three different metallic thin-film multilayer structures: SRM 2135 consisting of Ni and Cr; an Ag/Ni test structure; and the Cr/Cr_2O_3 material that is to be issued as an SRM shortly (section 2.B.2). The details of these structures are shown in Table 2.3.

Measurements of the r.m.s. surface microroughness for the three materials as a function of sputtered depth are shown in Fig. 2.3 for bombardment by argon ions of 1 and 4 keV energy. We find that the surface roughness increases with sputtered depth as well as with the energy of the impacting ions.

Table 2.3. Specimen structures used for measurement of sputtering induced surface microroughness.

Specimen	Layer type	Number of layers	Single-layer thickness [nm]
Ni/Cr	Cr	5	50
	Ni	4	63
Ag/Ni	Ni	6	50
	Ag	5	4
Cr/Cr_2O_3	Cr	8	40
	Cr_2O_3	7	1-2

The data in Fig. 2.3 were fitted to the equation:

$$R_q = b \langle z \rangle^a \tag{2.4}$$

where R_q is the r.m.s. roughness, $\langle z \rangle$ the average sputtered depth, and b a constant. The exponent a was found to be between 0.42 and 0.51 for the Ni/Cr and Ag/Ni materials, and 0.83 for the Cr/Cr_2O_3 material. For the Ni/Cr and Ag/Ni samples, a is close to the expected value of 0.5 for a random distribution of surface areas of different sputtering yields. In the case of the Cr/Cr_2O_3 sample, the depth dependence is close to linear, although it is expected that the microstructure of the Cr layers of this sample is similar to that of the Ni/Cr sample. The presence of the Cr-oxide layers may be responsible for the rapid increase of the surface roughness.

The surface roughness measurements of the Ni/Cr and Ag/Ni specimens have been correlated with depth-resolution (interface-width) measurements obtained on the same samples by Auger depth-profiling and show that the surface topography developed due to ion bombardment is a major cause of

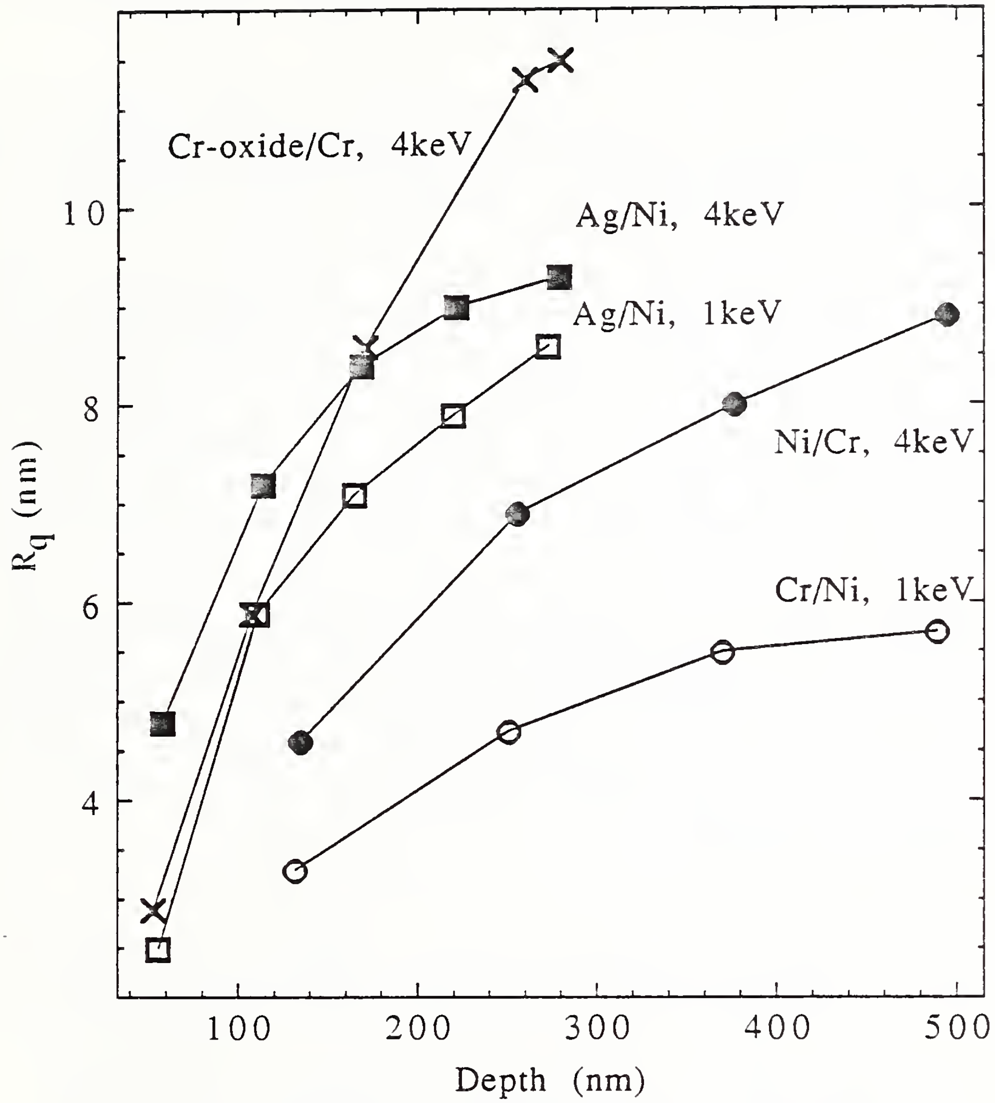

Fig. 2.3. Variation of r.m.s. surface microroughness of Ni/Cr, Ag/Ni, and Cr/Cr_2O_3 multilayer films as a function of sputtered depth under argon ion bombardment at the indicated energies.

interface broadening in sputter-depth profiling. These results are in good agreement with the predictions of a statistical model which considers differences in sputtering yields for the differently oriented crystallographic planes present in polycrystalline metallic layers. The data presented are the first direct quantitative measurement results on surface topography developed due to ion bombardment and measured without breaking the vacuum.

3. Radiation-Enhanced Diffusion During Sputter-Depth Profiling

(J. Fine, D. Marton*, and G. P. Chambers*)

Radiation-enhanced diffusion (RED) is believed to be an important factor contributing to increased interface broadening during sputter-depth profiling. We describe here two series of experiments to characterize this phenomenon in more detail, one at room temperature and the other at elevated temperatures.

In our first series of experiments, we have investigated the interface broadening in Auger-electron sputter-depth profiling measurements on Ni/Ag multilayered thin-film structures (section 2.B.2). The interface broadening observed in this system is determined by a number of factors, the main two being roughening and RED. These two factors can be separated using the assumption that roughness leads to a symmetric profile shape, while an asymmetric shape is caused by RED. This concept is confirmed by interface broadening results which increase with depth (for subsequent Ag layers) for surface roughness, but remain independent of depth for diffusion.

We have found effective diffusion rates of Ag in Ni substantially greater than the grain-boundary diffusivity at room temperature when the thin-film structures were bombarded by argon ions of 1 and 4 keV energy. The observed diffusion rates were found to depend linearly on sputtering rate and thus on ion current density; the diffusion rates were also greater for 4 keV ion bombardment than 1 keV bombardment. The linear dependences on ion current density suggest that the observed diffusion rates are dependent on defect concentration.

In our second series of experiments, we have measured depth profiles while sputtering the Ni/Ag thin-film structures at different temperatures. At about 130°C, we find an abrupt transition at which the Ag profiles become very sharp and more well defined. This new and unprecedented result has enabled us to develop a new model for RED based on a complex defect mechanism. We propose that the complex defects can be long-lived (minutes), that the defects can diffuse long distances (~ 20 nm) much greater than the range of ion mixing, and that they can dissociate at elevated temperatures and give rise to a temperature dependence in RED which depends on the difference between the defect binding energy and the solute migration energy along these defects. At temperatures between 400 and 600 K, it appears that dissociation of the complex defects occurs at a rate faster than can be compensated for by the increased mobility of the Ag atoms. Such individual defect properties have previously been observed in a number of separate experiments but have not previously been found to be consistent with one set of results.

We believe that our new way of probing RED mechanisms allows us to observe, in real time, phenomena which have not been so clearly characterized. We have then been able to develop a new complex-defect model that may provide a general description of RED due to ion bombardment. Our observations also indicate that it may, by appropriate temperature control, be possible to control transport processes in RED and to achieve improved depth resolution at interfaces during sputter-depth profiling.

4. Survey of Needs for Standard Reference Materials in Surface Analysis

(J. Fine)

We have recently completed a survey in which users of surface analysis equipment were asked to assess needs for additional standard reference materials. This survey was conducted among the membership of ASTM Committee E-42 on Surface Analysis and the national representatives and participants in the VAMAS Surface Chemical Analysis Working Party (section 2.C.2). Each person was asked to give their opinions on the desirability of a number of possible types of reference materials using a numerical scale ranging from 1 (low interest) to 5 (high interest).

The survey results are summarized in Tables 2.4 for sputter-depth profiling (SDP) and in Table 2.5 for Auger-electron spectrosocpy (AES), x-ray photoelectron spectroscopy (XPS), and secondary-ion mass spectrometry (SIMS). For SDP applications, participants suggested that a single-layer thin-film system would be suitable for the first need in Table 2.4, a single- or multi-layer thin-film system for the second need, a multi-layer or marker-type thin-film system for the third need, and a multi-layer thin-film system for the fourth need. The most commonly sought types of material systems were metal-metal interfaces (by far), metal oxide-metal interfaces, semiconductor-semiconductor interfaces, semiconductor oxide-semiconductor interfaces, and metal-semiconductor interfaces.

Table 2.4. Summary of survey responses for reference materials in sputter-depth profiling (69 responses).

	Need	Average Rating
1.	Calibration of depth scale and erosion rate	4.0
2.	Measurement of interface resolution	3.9
3.	Optimization of sputtering conditions to produce narrowest interface widths	3.8
4.	Verification of constancy of erosion rate (test for stability of ion-beam current density)	3.1

For applications in AES, XPS, and SIMS, a variety of types of materials were suggested ranging from single elements (line energies or mass scale; analyzer transmission function and energy resolution in AES and XPS; relative line intensities in SIMS), to metal alloys (relative line intensities; analyzer transmission function and mass resolution in SIMS; homogeneous multicomponent system for AES, XPS, and SIMS; and detection limits in AES and XPS), monolayer metal films on a single-crystal substrate (fractional or complete monolayer calibrations), ion implants in semiconductors (detection limits in XPS and SIMS; relative line intensities in SIMS), and mixed oxides (homogeneous multicomponent system for SIMS).

Table 2.5. Summary of survey responses for reference materials in AES, XPS, and SIMS

Need	Average Rating by Technique		
	AES	SPS	SIMS
A. Number of responses	35	33	22
B. Needs			
1. Spectrometer Calibration			
(a) Line energies (or mass scale)	3.3	3.6	3.0
(b) Relative line intensities	4.1	3.9	3.8
(c) Analyzer transmission function	2.8	3.0	3.5
(d) Energy or mass resolution	3.0	3.1	2.9
2. Calibration of Surface Composition			
(a) Fractional monolayer on a substrate	3.2	3.2	2.4
(b) Complete monolayer or bilayer	3.4	3.4	2.8
(c) Homogeneous multicomponent system	3.9	3.7	3.8
3. Detection Limits	3.2	2.8	4.2

C. Standards Committee Activities

Division staff members are active on the ASTM Committee E-42 on Surface Analysis and with two international groups, the Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards (VAMAS) and the International Union of Pure and Applied Chemistry (IUPAC). Three articles have also been published recently (section 2.D) that give overviews of the work of these organizations in developing reference procedures together with information on sources and needs of reference data and reference materials for surface analysis.

D. Review Articles and Books

1. Review Articles

Staff members in the Division author many review articles and book chapters that provide information on measurement methods, relevant reference data, reference materials, theories of the measurement process for many surface spectroscopies, and surface standards. The titles of review articles published during the past two years are listed below:

(a) "Electron and Photon Stimulated Desorption: Probes of Structure and Bonding at Surfaces", T. E. Madey, Science <u>234</u>, 316 (1986)

(b) "Field Emission Microscopy - Trends and Perspectives", A. J. Melmed, <u>Chemistry and Physics of Solid Surfaces VI</u>, (Springer-Verlag, New York), 325 (1986).

(c) "Core-Level Binding-Energy Shifts in Solids and at Surfaces", W.F. Egelhoff, Jr., Surface Sci. Reports <u>6</u>, 253 (1987)

(d) "Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces", J. W. Gadzuk, in <u>Vibrational Spectroscopy of Molecules on Surfaces</u>, J. T. Yates, Jr. and T. E. Madey, eds., Vol. 1 of <u>Methods of Surface Characterization</u> (Plenum, New York), 49 (1987).

(e) "Incoherent Neutron Inelastic Scattering: Vibrational Spectroscopy of Adsorbed Molecules on Surfaces", R. R. Cavanagh, J. J. Rush, and R. D. Kelley, in <u>Vibrational Spectroscopy of Molecules on Surfaces</u>, J. T. Yates, Jr., and T. E. Madey, eds., Vol. 1, of <u>Methods of Surface Characterization</u> (Plenum, New York), 183 (1987).

(f) "Mechanisms and Applications of Electron Stimulated Desorption in Surface Science", T. E. Madey, Vacuum (TAIP) <u>37</u>, 31 (1987).

(g) "The Interaction of Water with Solid Surfaces: Fundamental Aspects", P. A. Thiel and T. E. Madey, Surface Sci. Reports <u>7</u>, 211 (1987).

(h) "Core Level Spectroscopy: A Dynamics Perspective", J. W. Gadzuk, Physica Scripta <u>35</u>, 171 (1987).

(i) "Dynamics of Molecular Collisions with Surfaces: Excitation, Dissociation, and Diffraction", S. Holloway, M. Karikorpi, and J. W. Gadzuk, Nuclear Instruments and Methods B <u>27</u>, 37 (1987).

(j) "Neutron Scattering Studies of Hydrogen in Catalysts", T. J. Udovic and R. D. Kelley, in <u>Hydrogen Effects in Catalysis: Fundamentals and Practical Applications</u>, Z. Paal and P. G. Menon, eds. (Marcel Dekker, New York), 167 (1988).

(k) "Radiation Damage in Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy", T. E. Madey, in Analytical Electron Microscopy-1987, D. C. Joy, ed. (San Francisco Press, CA), 345 (1987).

(l) "Reference Materials, Reference Data, and Reference Procedures for Surface Analysis: National and International Standards Activities", C. J. Powell, in Electronic Materials and Processes, eds. N. H. Kordsmeier, C. A. Harper, and S. M. Lee (Society for the Advancement of Material and Process Engineering, Covina, CA), 252 (1987).

(m) "The Quest for Universal Curves to Describe the Surface Sensitivity of Electron Spectroscopies", C. J. Powell, J. Electron Spectrosc. 47, 197 (1988).

(n) "The Development of Standards for Surface Analysis", C. J. Powell, Surf. Interface Anal. 11, 103 (1988).

(o) "Synchrotron Radiation Studies of the Electronic Structures of High-T_c Superconductors", in Thin Film Processing and Characterization of High-T_c Superconductors, J. M. E. Harper, R. J. Colton, and L. C. Feldman, eds., American Vacuum Society Series 3 (American Institute of Physics, N.Y.), 222 (1988).

2. Review Articles in Publication

We list below the titles and abstracts of review articles in the course of publication.

(a) "Cross Sections for Inelastic Electron Scattering in Solids," C. J. Powell, Ultramicroscopy

(b) "Precision, Accuracy, and Uncertainty in Quantitative Surface Analyses by Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy", C. J. Powell and M. P. Seah, J. Vac. Sci. Tech.

(c) "Electron and Photon Stimulated Desorption", Benefits and Difficulties", T. E. Madey, A. L. Johnson, and S. A. Joyce, Vacuum

(d) "The Semiclassical Way to Molecular Dynamics at Surfaces", J. W. Gadzuk, Annual Reviews of Physical Chemistry

(e) "Epitaxy of Metals on Metal Substrates: The Contributions of Field Emission Microscopy", A. Ciszewski and A. J. Melmed, Appl. Surface Science

(f) "Molecular Desorption from Solid Surfaces: Laser Diagnostics and Chemical Dynamics", D. S. King and R. R. Cavanagh, Advances in Chemical Physics: Molecule-Surface Interactions

(g) "The Status of Reference Data, Reference Materials, and Reference Procedures in Surface Analysis", J. T. Grant, P. Williams, J. Fine, and C. J. Powell, Surf. Interface Anal.

3. Books

(C. J. Powell and T. E. Madey)

While there are many books and review articles on different aspects of surface science and its applications, there is a dearth of information on how to make reliable surface-characterization measurements. There is, in essence, a large information gap between review articles in which the latest scientific advances are discussed and manufacturers' handbooks in which the operation of commonly used surface-characterization equipment is described.

Arrangements have been made with a commercial publisher to produce a series of books, "Methods of Surface Characterization," which will address this need. Two Division staff members (Powell and Madey) and three other scientists (A. W. Czanderna at the Solar Energy Research Institute; D. M. Hercules and J. T. Yates, Jr., at the University of Pittsburgh) constitute an editorial board that will oversee the production. A series of four volumes is currently planned which will describe the principles, techniques, and methods considered important for surface characterization. It is intended to describe how important surface-characterization measurements are made and how to ensure that the measurements and interpretations are satisfactory (to the greatest extent possible). The approach of the series will be pedagogical or tutorial.

The first volume in the series, "Vibrational Spectroscopy of Molecules on Surfaces," was published in 1987. This volume contains descriptions of the major methods used to measure vibrational spectra of surface species. The emphasis of the volume is on the basic concepts and experimental methods rather than an extensive survey of literature in the field.

Three other volumes of the series are at an advanced stage of preparation. Two volumes will describe the techniques and methods for electron spectroscopy and ion spectroscopy, respectively, and will concentrate on techniques for which commercial instrumentation is available. The other volume will contain descriptions of techniques for specimen handling and depth profiling together with information on the common artifacts and problems associated with the bombardment of surfaces by electrons and ions.

3. SURFACE MEASUREMENTS PROGRAM

A. Photoemission Studies of the Electronic Structure and Chemisorption Properties of High-Temperature Superconducting Materials
(R. L. Kurtz, R. L. Stockbauer, and S. W. Robey)

The recent discovery of superconducting materials with critical temperatures in the range 90-120 K has generated intense interest and activity. Many scientists are trying to understand the physical properties and the mechanisms of superconductivity in the various copper oxides; others are trying to develop the materials so that they can be used successfully in devices.

We have initiated a project in which photoelectron spectroscopy is being applied to understand the electronic structure and to investigate the chemisorption properties of the new high-T_c materials. Our work has been expedited by a combination of relevant experience and of available equipment. We have previously studied metal oxide systems and know how to handle and prepare samples for measurement as well as how to interpret photoemission data. We are aware of the pitfalls one encounters in making photoemission measurements at low temperature, such as the propensity for samples at low temperature to adsorb water present in trace amounts from the background gas in the vacuum chamber. Our experience with dosing clean surfaces with controlled amounts of gas allows us to make quantitative measurements of the initial stages of degradation of these materials. We have a dedicated beamline at the NIST synchrotron light source SURF-II. This has enabled us to perform new experiments quickly and to continue the experiments for as long as necessary to answer the questions which present themselves during the experimental run, a luxury not available to most other synchrotron groups. Finally, we are one of the few groups which had a sample mount which was coolable to liquid nitrogen temperature which allowed us to make measurements above and below the critical temperature.

This project has been supported in part during FY88 by the NIST initiative on High Temperature Superconductors and in part by the Office of Naval Research.

1. Photoemission Studies of 1-2-3 Superconducting Compounds

One of the basic questions concerning the new superconductors is the nature of the electronic interactions which lead to the superconductivity. The answer to this question lies in knowing the electronic structure of the new material. Photoemission spectroscopy is a powerful technique for elucidating electronic properties and has provided data which can be compared directly with band structure calculations.

Having the facilities to obtain photoemission spectra on cold samples, we were one of the first groups to publish spectra obtained with sample temperatures above and below T_c. Contrary to earlier reports, there was no change in the spectra with temperature.

Comparison of the spectra for a series of Sr-doped La superconductors as well as with Ho and Y compounds showed that their valence band structures were nearly identical, all having a low density of states at the Fermi level and a broad valence band consisting of mixed Cu 3d and O 2p states. This low density of states at the Fermi level did not agree with band structure calculations. The discrepancy was explained by the fact that these materials are highly correlated compounds in which electron-electron interactions are strong and therefore one-electron models would not be expected to adequately describe the system.

We were the first to publish resonant photoemission spectra of the 1-2-3 compounds, i.e., spectra as a function of incident photon energy. By observing the photon energy at which valence spectral features are enhanced, we were able to associate each of the multitude of peaks with the particular elemental component of the compound. Without this added degree of sophistication, such identifications are, at best, tenuous.

From knowledge of the photon energy at which two copper satellite features resonated as well as their binding energy, it was possible to determine that the dominant valence state of Cu in the 1-2-3 compounds was 2+. This was contrary to proposals at the time based on formal charge balance that 1/3 of the copper should be in a 3+ state. The explanation is that these are covalent compounds rather than ionic and therefore the concept of formal charge balance does not apply.

One of the features in the valence band spectra has as yet not been fully characterized. This feature at 9.5 eV binding energy appears in most of the materials and resonates with the onset of O 2s core excitations near a photon energy of 20 eV. This resonant behavior is very sensitive to the amount of oxygen in the high-T_c material. Details of the nature of the electronic states involved in this transition are currently being investigated.

2. Surface Degradation Studies Using Controlled Dosing of Atmospheric Gases

In the course of the resonant photoemission experiments at low temperature, it was realized that the high-T_c materials were very susceptible to adsorption of background gases in the ultrahigh vacuum chamber. It was also well known that the 1-2-3 compounds rapidly degraded when exposed to air. Photoemission spectra were obtained from freshly scraped samples before and after exposure to measured amounts of atmospheric gases. It was found that the 1-2-3 compounds react rapidly with H_2O with a sticking probability of nearly 1 to form hydroxide compounds. This is apparently the initial step in the degradation process and is why the samples degrade so rapidly in air. The reaction with CO_2 to form carbonates is less likely but still significant and points out that storage in desiccators as has been the common practice may not be sufficient for long-term protection. CO is less reactive by several orders of magnitude as is O_2. This latter result is a bit surprising since these compounds take up and lose oxygen so readily.

This study also pointed an error in several publications that claim to observe reversible changes in the photoemission spectra of the 1-2-3 material related to the superconductivity as the samples were cycled from 90 K to room temperature. These changes are now thought to be solely due to the reversible adsorption of background gases in the analysis chamber.

We have emphasized the importance of in-situ sample preparation in our publications and in our comments on the copious number of papers we are asked to review for major journals. Many of these reported changes as the samples are temperature cycled are due to lack of in-situ sample cleaning and to background gas adsorption.

3. Studies of New High-T_c Materials

Our most recent endeavors concern measurements on the new bismuth and thallium based superconductors. While these results are preliminary and we will repeat the experiments with better characterized materials when they are available, we do find some differences from the 1-2-3 compounds. The samples appear to be more susceptible to radiation damage from both electron and photon beams. This indicates that experiments using even a relatively low electron or photon beam flux (electron-excited Auger spectroscopy, inverse photoemission, or x-ray fluorescence, for instance) are likely to induce enough surface damage to produce erroneous results during the short time needed to acquire data.

Controlled adsorption experiments on the Tl-based compound produced results similar to those from the 1-2-3 compounds. H_2O adsorption produced an hydroxide species while CO_2 and CO produced a carbonate species. However, it appears that this surface is at least an order of magnitude less reactive than the 1-2-3 compounds.

4. Thin Film Evaporation Facility

One of the most important uses of the new high-T_c materials will be as thin films in electronic devices. We expect that the evolution of such devices will be similar to that of thin-film semiconductors. Since surface science played such a crucial role in semiconductor development, we expect that it will play as important a role in the superconductor device development. The primary thrust of our efforts in the future, then, will be directed toward the characterization of the electronic structure and chemisorption properties of high-T_c superconducting thin films.

To date, the primary experimental problem of high-T_c thin films has been surface preparation. Films are usually produced in one chamber and then transported through air to a second chamber for analysis. Since the normal surface preparation techniques of ion sputtering and annealing destroy the surface stoichiometry of these multi-component systems, there is no satisfactory method of cleaning the films once they are in the analysis chamber. Our present technique used on bulk samples of scraping to obtain a clean surface cannot be applied to the films since they are not thick enough to survive this macroscopic treatment.

To overcome this problem, we plan to attach a thin-film deposition chamber to our photoemission analysis chamber so that, with a sample transfer system, the freshly made films can be delivered directly to the analysis chamber without exposure to air. This will be a valuable facility for studying the surface properties of thin films. We should emphasize that we will not undertake an extensive program on the methodology for growing high-T_c thin films but rather we will use recipes developed by others to produce the films. We will concentrate on their characterization.

Our current plans call for a chamber containing 6 evaporation sources with independent evaporant beam monitors and controllers. This number is adequate for deposition of the currently known high-T_c compounds from elemental sources and should suffice for any reasonable compounds discovered in the future. Additional side chambers will be attached for fast substrate introduction through a load-lock and for high-pressure oxygen annealing if necessary. In-situ monitoring of film growth will be accomplished with reflection high-energy electron diffraction and the critical temperature of the film will be measured with a movable four-point probe. The sample will be mounted on the helium-cooled cold head so the temperature can be lowered to 20 K for these measurements.

Procurement has been made of some vacuum hardware, pumps, beam monitors, and electronics. Design of the vacuum chamber and sample transfer system is underway. We hope to have an operational system within one year.

Initial experiments will involve the study of the electronic structure of oriented thin films using the angle-resolved photoemission capabilities of the ellipsoidal mirror analyzer. As with our studies on bulk material, this information can be compared directly with band-structure calculations. Likewise, stability of the films toward atmospheric gases will be studied using controlled gas dosing. Future experiments will include studies of the growth of metal overlayers on the superconducting films which will be important for understanding the properties of interfaces and electrical contacts.

B. Studies of Oxide Surfaces, Thin-Films, and Desorption Processes Using Synchrotron Radiation

(R. L. Stockbauer, R. L. Kurtz, S. W. Robey, R. A. Demmin, D. E. Ramaker, and T. E. Madey)

The major goals of this effort are to determine the electronic structure of surfaces, thin-films, and adsorbates using variable-wavelength photoelectron spectroscopy and to identify the electronic excitations which lead to ion desorption. Synchrotron radiation provides the incident photons for both experiments with its tunability being its greatest asset. In the photoemission experiment, the tunability allows us to probe resonances which can be used to identify peaks in the valence band as well as to increase sensitivity to minority states on the surface. In the ion yield measurements, the tunability allows us to obtain ion yield data (ion intensity as a function of photon energy) which are correlated with photoemission results to identify the excitations which initiate the ion desorption process. This work has been supported in part by the Office of Naval Research.

1. Water Adsorption on Defective and Nearly-Perfect TiO_2(110).
(R. L. Kurtz, R. L. Stockbauer, and T. E. Madey)

Our long-term interest in the electronic structure and chemistry of oxide surfaces continues with a synchrotron radiation photoemission study of the interaction H_2O with defective and nearly-perfect TiO_2(110) surfaces at temperatures between 160 and 300 K. This work was performed as part of a co-operative agreement between the United States and Spain and involves a collaboration with Dr. E. Roman and Prof. J. L. de Segovia of the Instituto Ciencia de Materiales, CSIC, Madrid. Defect sites have been implicated in the adsorption process and, by tuning the photon energy to 47 eV, we find that a resonant process gives an enhanced photoemission sensitivity to these Ti^{3+} 3d defect states. Defects are produced on TiO_2(110) by annealing to 1000 K in ultra high vacuum; subsequent exposure to 10^4 Langmuirs O_2 produces nearly perfect surfaces, as judged by the suppressed Ti 3d emission.

Both nearly perfect and defective surfaces give rise to dissociative adsorption of H_2O at 300 K but the defective surface has a saturation coverage that is nearly an order of magnitude less than that of nearly perfect TiO_2(110). The enhanced sensitivity to the Ti^{3+} defect states has allowed the observation of a surprising effect: the dissociative adsorption results in increased defect-state intensity on both the nearly perfect and the defective surfaces. This apparent charge-transfer to the substrate implies that a new mode for the dissociation process is needed. At 160 K, H_2O adsorbs molecularly on both the nearly-perfect and the defective surfaces. Subsequent annealing experiments allow estimates of the interaction energies involved in the dissociation process.

This work will continue with an investigation of ammonia adsorption on the defective and nearly-perfect TiO_2(110). In addition, other surfaces of TiO_2 will be studied along with MgO and oxidized Mg metal. This latter study is important in understanding the role of surface geometry in the ion desorption process.

2. Calculations of Surface Dynamics in the Ion Desorption Process
(R. L. Kurtz)

In a collaboration with Dr. R. E. Walkup of IBM, a computer program has been written to calculate classical trajectories of ions desorbed from a surface. The dynamics of the surface atoms in the neighborhood of the desorbing ion are calculated in addition to the motion of the ion itself. This allows for the investigation of the reaction of the neighboring atoms to forces induced by the desorbing ion. Pair-wise potentials are used to calculate the potential energy surface governing the ion and neighboring atom motion.

O^+ desorption from TiO_2 was calculated since it is the prototype system used by Knotek and Feibelman to explain positive ion desorption from ionic insulators. The calculations established the time scale for desorption, and predicted the ion kinetic energy and angular distributions which can be directly compared with our experimental results. The calculations provide qualitative insight into the effects of lattice recoil and the origin of site-dependent desorption probabilities. Better agreement between the results of the calculations and the experimental data is anticipated when the effects of complications such as steps and defects are considered.

One system we propose to calculate is O^+ from MgO. This is a very ionic material and therefore, in the Knotek-Feibelman model, should have a high O^+ desorption probability. Our experiments have shown otherwise and we suspect that since the Mg in the lattice is relatively light, it can move fast enough to absorb the recoil energy from the desorbing O^+ such that the ion never leaves the surface. The calculations on the dynamics of this system should show clearly whether or not this is the case.

3. Photoemission Study of Ba and BaO Films on W(100)
(R. L. Kurtz, R. L. Stockbauer, and T. E. Madey)

As part of a collaboration with Drs. D. R. Mueller and A. Shih of the Naval Research Laboratory and with Dr. E. Roman and Prof. J. L. de Segovia of the Instituto Ciencia de Materiales, CSIC, Madrid to study the surface chemistry of dispenser cathodes, a study was made of the interaction of O_2, CO_2, and H_2O with bulk BaO and with BaO adsorbed on W(100). Using photoemission to identify the reaction products in the adsorbed layer, it was found that H_2O reacts with bulk BaO to form $Ba(OH)_2$, while CO_2 forms a surface layer of $BaCO_3$. The water reaction is unique in that a thick $Ba(OH)_2$ layer is formed; this result indicates water is able to penetrate the hydroxide layer. Water and carbon dioxide also react with a BaO monolayer adsorbed on W(100) to produce adsorbed OH and CO_3 species bound to the tungsten substrate. The presence of a BaO monolayer appears to enhance the interaction of O_2 with the tungsten substrate.

This work has been extended to include photoemission, ion desorption, and chemisorption studies of BaO overlayers on W(110) and of Ba on Ir(100).

4. Photoemission Studies of Pt Overlayers on W(110)
(R. A. Demmin, R. L. Kurtz, R. L. Stockbauer, and T. E. Madey)

A new class of experiments was initiated to investigate the electronic states and surface chemistry of metal-on-metal systems in collaboration with Drs. D. R. Mueller and A. Shih of the Naval Research Laboratory. Such systems are important in thin-film semiconductor devices and metal catalyst systems. The first measurements were made for Pt overlayers 0-6 monolayers thick on W(110) and for CO adsorbed on these surfaces. Valence band spectra of the films and shifts in the positions of the 4σ and $5\sigma/1\pi$ peaks for adsorbed CO were related to thermal desorption results of CO on these films. The first layer of Pt yielded a valence-band photoemission spectrum that was unlike those of subsequent layers; i.e., the intensity 1-2 eV below the Fermi level was greatly reduced, similar to the electronic structure of a noble metal. Moreover, the adsorption of CO on a Pt monolayer was weaker than on W or Pt alone. However, this surface adsorbed CO more strongly than did noble metals and ultraviolet photoelectron spectra from CO adsorbed on Pt/W(110) did not show features characteristic of CO adsorbed on a noble metal.

Other results were interpreted in structural terms. Tungsten core levels shifted with the addition of Pt, consistent with the suppression of surface-shifted core levels, and did not indicate alloy formation. Work function measurements and spectra for adsorbed CO suggested that Pt adatoms in sub-monolayer coverages do not form 2-dimensional islands unless the surface is annealed. Other related studies of the surface chemistry of thin-films of Pt on W(110) are described in section 3.H.

The ability to customize valence electronic states by suitable choices of substrate and overlayer metals makes the metal-on-metals field intriguing. The multi-source evaporation chamber being constructed for the thin-film high-temperature superconductor effort will be extremely useful for preparing well-characterized films for these studies.

5. Implementation of Helium-Cooled Cold Stage
(R. L. Stockbauer, R. L. Kurtz, and S. W. Robey)

We have recently purchased a helium-cooled cold head and movable stage. We plan to use these items in electron attenuation-length experiments (see section 2.A.2(b)) to condense molecules that cannot be condensed at liquid nitrogen temperatures, for instance, the rare gases, and diatomic molecules such as N_2, O_2, and CO. This facility will also be critical in our work on thin-film high temperature superconductors. We plan to determine the critical temperature of thin-films by making resistance-versus-temperature measurements in situ. The closed-cycle helium refrigerator will allow these measurements to be made down to 20 K.

The cold stage will also be useful for photon-stimulated desorption measurements on small diatomics as well as small organic molecules such as methane. The use of simpler molecular systems for these studies should encourage more detailed calculation of the phenomena influencing the ion desorption probability.

6. Ellipsoidal Mirror Analyzer
(R. L. Stockbauer, R. L. Kurtz, and T. E. Madey)

The construction and initial testing of the ellipsoidal mirror analyzer has been completed and the instrument is in the process of being installed on beamline 1 at SURF-II. The capabilities of this instrument are outlined in section 4.B.2. We expect this instrument to play a pivotal role in most of our photoemission projects. For instance, in the thin-film high-temperature superconductor program, the analyzer will provide angle-resolved photoemission data from oriented films of the material. Comparisons of such data to band structure calculations provide a valuable test for theory and computational methods. It is becoming clear that simple, one-electron models do not adequately describe these systems since electron-electron correlations are important. More sophisticated, multi-electron cluster calculations will be needed to better describe the electronic states of these materials.

The analyzer will also be used extensively in the ion desorption program to investigate the details of desorption dynamics. Its ability to measure ion kinetic energy as a function of desorption angle will provide, for instance, a test of the reneutralization probability as a function of takeoff angle and energy. Likewise, since it is able to distinguish the masses of the desorbed ions in the angle-resolved patterns, we will be able to better correlate the two-dimensional ion patterns with the surface geometry.

7. Second Surface Science Beamline Instrumented at SURF-II
(R. L. Stockbauer, R. L. Kurtz, and S. W. Robey)

With the installation of the ellipsoidal mirror analyzer on beamline 1 at SURF, it was necessary to find a new home for the instrument which had served us so well over the past 10 years, the double-pass cylindrical-mirror analyzer. It was decided to outfit the instrument with a new computer and updated programs and reinstall it on beamline 8. The computer system and some of the electronics that replaced those that had to stay with the ellipsoidal mirror analyzer on beamline 1 were provided by the Radiation Physics Division.

With the new beamline 8 facility, we hope to be able to devote more experimental time to the electron attenuation-length and ion-desorption measurements from condensed molecular systems. This will leave the ellipsoidal mirror analyzer on beamline 1 free to investigate the high-temperature superconductors and angle-resolved photon-stimulated desorption.

8. X-ray Beamline at Brookhaven National Laboratory
(R. L. Stockbauer, R. L. Kurtz, and T. E. Madey)

Our collaboration with Drs. J. Rife, W. R. Hunter, and M. Kabler of the Naval Research Laboratory to instrument a beamline at the Brookhaven National Synchrotron Light Source has not been active over the past two years due to the extended shutdown of the x-ray ring. During this time the NRL group has extensively tested and modified the monochromator, optics, computer control to render the instrument more usable.

Our primary use of this beamline will be for those experiments needing the higher energy photons (currently up to 600 eV). For instance, the electron attenuation length measurements on condensed molecular solids will benefit greatly from the higher photon energy which will extend the electron kinetic energy range. We also anticipate investigating the effect of core-level excitations on ions desorbed from condensed molecular layers. The extended range of the monochromator will allow these studies to be done at the C, N, and O core levels of the condensed molecules and organic compounds which we have studied previously.

9. Theory of Stimulated Desorption
(D. E. Ramaker)

During the last two years, our work has addressed the important issue of secondary electrons and the role it plays in photon-stimulated desorption (PSD). This investigation has shown that, in cases for which the direct Auger-stimulated-desorption process is active, the indirect x-ray-induced electron-stimulated-desorption (ESD) contribution (i.e. that contribution arising from secondary electrons) is generally on the order of 40% or less. On the other hand, when the direct Auger-stimulated desorption process is suppressed by some mechanism, the indirect process can dominate. For chemisorbed systems, the indirect process is essentially always negligible.

During this past year, we have initiated a study of the mechanisms for ESD of negative ions from surfaces. In simple diatomic molecules, negative ions are known to be produced by dissociative desorption (i.e. resulting from a transient negative molecular ion) and by dipolar dissociation (through an excited neutral molecular species). The dominant mechanism of ESD ion angular distributions (ESDIAD) of negative ions from polyatomic molecules adsorbed on metallic surfaces is, however, much more complicated and therefore not at all clear. Furthermore, it is not even clear that the desorption angle of the negative ions directly reflects the bond angles on the surface, as was found for the positive ions. However, recent NIST experimental work (see section 3.J) has shown that the ESDIAD of F- ions from NF_3/Ru(0001) does complement the F+ ESDIAD. Currently we are designing experiments which we hope will reveal the active mechanisms, and which will determine whether negative-ion ESDIAD can lead to direct bond-angle information. Detailed comparison of the experimental results with gas-phase dissociation data and with theoretical results is contemplated.

C. Dynamical Effects Associated with Core-Level Ionization
(T. Jach)

The NIST synchrotron beamline X-24A at the Brookhaven National Synchrotron Light Source has been utilized to obtain detailed information on the radiative excitation of deep core levels in atoms and molecules. Our present experimental apparatus allows for the irradiation of a gas sample with highly monochromatic, polarized x-rays in the energy range 2- 7 keV, with analysis of the energy and polarization of the resulting x-ray fluorescence. The combination of high incident photon flux, excellent energy resolution, and polarization detection, any one of which by itself would have opened up a new region of the physics of dynamical atomic processes, has produced a considerable body of experimental data that we are starting to understand. The results are producing a gratifying response in the theoretical community. An understanding of the experimental and theoretical problems involved in the gas-phase results has been invaluable in anticipation of similar studies we plan to perform on atoms and molecules on surfaces. Several areas of progress are listed here. This work has been conducted in collaboration with Drs. D. W. Lindle and P. L. Cowan of the NIST Quantum Metrology Division.

1. Polarization Dependence of Molecular X-Ray Fluorescence

The fluorescent x-rays observed on exciting a Cl K electron in the molecule methyl chloride (CH_3Cl) exhibits an unexpected degree of polarization. The initially polarized synchrotron beam selectively excites molecules aligned for a maximum dipole moment into an antibonding state which is selected by the incident energy. Because the time scale of core relaxation is short compared to molecular motion, the x-ray fluorescence which results from radiative decay is highly polarized as well. By means of the polarization and energy analysis capability of our spectrometer, we are able to determine the exact molecular orbitals which participate in excitation and decay of this molecule as a function of incident energy. This work is performed also in collaboration with Drs. R. E. LaVilla and R. D. Deslattes of the NIST Quantum Metrology Division and with Drs. J. A. Sheehy, T. Gil, and P. W. Langhoff of Indiana University.

2. Perturbation Effects of Excitonic States in Chlorine-Containing Molecules

The x-ray absorption spectrum of Cl in $CFCl_3$ shows a strong "white line" just below the K-edge. This line corresponds to a transition in Cl from 1s to the lowest unoccupied molecular orbital, $6a_1$. By varying the incident x-ray energy, we are able to selectively excite transitions to this orbital, to higher lying orbitals, and into the ionization continuum. The $K\beta$ emission spectrum of Cl in the excited neutral molecule shifts by 1 eV when compared to the emission spectrum from the molecule with ionized Cl. Additionally, an emission line can be identified as the de-excitation of the excitonic state. The energy shift allows one to estimate the perturbation of the exciton on the core level. This work is performed also in collaboration with Dr. R. C. C. Perera of the Lawrence Berkeley Laboratory.

D. X-Ray Diffraction Applied to Surface and Interface Research

(T. Jach)

A program has been initiated to use grazing angle diffraction (GAD) from semiconductor surfaces to study the registration of atomic overlayers. Highly collimated x-rays from a synchrotron light source are diffracted through a large angle while incident on the surface of a semiconductor at a grazing angle. The interference between the incident, specularly reflected, and reflected-diffracted beams sets up an x-ray standing wave (XSW) electric field at the surface. The x-ray fluorescence from adatoms illuminated by the XSW can be used to determine their position to a high degree of accuracy (about 0.01 Å laterally). The diffraction studies are conducted using x-rays in the 6-12 keV energy range in the B-cave at the Cornell High Energy Synchrotron Source. The configuration of this source makes it very favorable for investigations using highly collimated beams in this energy range. The program has yielded results in two quite different areas of physics: the registration of adatoms on highly regular crystal surfaces, and the microscopic behavior of x-rays at realistic interfaces. This work has been conducted in collaboration with Drs. M. Bedzyk and Q. Shen at Cornell University.

1. Dynamical Diffraction of X-Rays at Grazing Angles of Incidence

The grazing angle diffraction geometry was selected because it produces XSWs which can be translated parallel to the crystal surface. The behavior of the various x-ray beams which result is complex and non-intuitive when treated by the theory of dynamical diffraction. We have carried out the first extensive experimental studies of the phase space of this diffraction at several energies from 6 to 12 keV using a highly polished single crystal of Ge as the specimen. The results indicate generally excellent agreement with the theory although there are some slight discrepancies. We have also determined which regions of phase space yield experimental conditions which most closely approximate the theory for the purpose of producing accurate XSW results. This work is performed also in collaboration with Dr. P. L. Cowan of the NIST Quantum Metrology Division.

2. Direct Observation of Surface-Trapped Diffracted Waves

The theory of GAD predicts the existence of a diffracted wave which is trapped in a layer as little as tens of angstroms thick at the surface of the crystal. We have observed this wave directly for the first time by means of GAD from a Ge crystal whose surface was specially prepared by photolithography and etching. Our interest in the behavior of this diffracted wave is twofold. First, the trapped wave excites only atoms which are either at or near the surface. Second, the trapped wave is able to escape only by means of deviations from a rigorously smooth crystal surface. Observation of the intensity of any escaping diffracted beam gives a measure of surface roughness which can be followed down to an atomic scale since there is no background signal. Our data on the escape of the trapped beam from our prepared surface indicates an unusual and unexpected relationship between the intensity of the escaping diffracted beam and its wavevector. The investigation of these results has yielded some insight into the deficiencies of theories commonly used to determine roughness of surfaces by x-ray scattering or reflection high-energy electron diffraction. Future measurements will involve etching a 1 μm grating into the surface of a Ge diffraction crystal to obtain a quantitative relationship between the periodicity and height of the roughness and its effect on surface diffraction. This work is conducted also in collaboration with Dr. D. Novotny of the NIST Semiconductor Electronics Division.

3. X-ray Standing Wave Determination of Adsorbate Positions on Germanium

The GAD technique has been applied to observe the registration of halogen atoms deposited by chemical preparation of a polished Ge single-crystal surface. In this geometry, the XSWs are modulated parallel to the crystal surface giving atomic position information parallel to the surface. In x-ray fluorescence detection of L x-ray emission from submonolayers of Cl and I on Ge, taken during GAD at energies of 6, 8, and 12 keV, we are able to determine that the halogen atoms occupy approximately the same on-top sites that they are observed to occupy in ultra-high vacuum (UHV) conditions. The "real world" measurement which was made here is, of course, impossible to make using surface science techniques which depend on ultra-high vacuum. The grazing angle XSW method is one of the few ways in which experimental data obtained in UHV can be compared to chemical processes at atmospheric pressure. The program is developing in several parallel directions. We are analyzing existing data to obtain atomic positions to as high as accuracy as the fluorescence signal permits. We are investigating the feasibility of GAD at a buried interface of a semiconductor and another semiconductor or metal film. Finally, we are constructing a vacuum chamber containing a precision goniometer for XSW studies under UHV conditions. The chamber will permit the detection of electrons emitted from atoms excited by XSW, allowing for the separation of elements which produce overlapping emission lines in our low-resolution x-ray fluorescence spectra.

E. Development of Silicon Diode X-Ray Detectors for Synchrotron Radiation Research

(T. Jach)

The explosion of scientific activity which employs radiation from synchrotron light sources has been paralled by the development of sophisticated instrumentation. Requirements exist now for x-ray detectors which cannot be satisfied by traditional detectors such as ion chambers or scintillation crystals. The wide dynamic range of x-ray intensity (10 orders of magnitude or more) to which a detector may be subjected is compounded by other complications such as the requirement to operate in ultra-high vacuum. More sophisticated detectors are being developed to meet the needs of present experiments in a collaboration with Drs. J. Geist, G. Carver, and D. Novotny of the NIST Semiconductor Electronics Division.

Our most recent development has been a monochromatizing crystal which incorporates the detection of x-ray diffraction by means of an integrated photodiode. Most x-ray monochromators use sequential diffraction from two semiconductor crystals to obtain energy resolution in the synchrotron beam. By integrating a planar photodiode detector into the surface of the second silicon crystal, we are able to observe radiation from the first crystal. On correctly aligning the second crystal to the Bragg condition, the change which occurs in the extinction depth for the radiation in the crystal is detected by the embedded photodiode. A particular application of this device is the detector in the feedback loop necessary to maintain alignment of the crystals under conditions of extended operation.

The incorporation of a detector into a crystal without distorting it as a diffracting device proved to be a challenging problem. We believe this invention will have widespread application as synchrotron beamlines and x-ray monochromators become accepted tools in applications such as x-ray lithography and medical angiography. The Department of Commerce is proceeding to apply for a patent on this device.

F. Studies of Surface Reactions Using Synchrotron Radiation

(J. A. Yarmoff and S. A. Joyce)

Investigations have been made of several different surface reactions using the techniques of photoelectron spectroscopy and photon-stimulated desorption with synchrotron radiation.

1. Mechanistic Studies of the Selective Chemical Vapor Deposition of Tungsten on Silicon and SiO_2 via WF_6

(J. A. Yarmoff)

The chemical vapor deposition (CVD) of tungsten on silicon via WF_6 is technologically important because of the ability to deposit these films selectively. That is, W will deposit onto regions of bare Si while, under the same conditions, it will not deposit onto SiO_2. This selectivity makes W CVD useful as a process for forming interconnects in an electronic device. The usefulness of the technique is limited, however, due to problems encountered when trying to make very small structures. It is thus of importance to understand the detailed chemical mechanisms operative in this process in order to utilize it, and other selective CVD processes, to a finer degree. This work is a collaboration with Dr. F. R. McFeely of the IBM Watson Research Laboratory and has been performed at the Brookhaven National Synchrotron Light Source.

The experiments are performed using a system with which films can be grown in an ultra-high vacuum (UHV) dosing chamber, and then transferred under vacuum into the spectrometer. The samples are then measured with soft x-ray core-level photoemission. The initial experiments were performed to study the mechanism for deposition on clean silicon. It was found that WF_6 completely dissociates upon interaction with Si but that at room temperature, the deposition process is self-poisoning. This is because the fluorine liberated from WF_6 ties up dangling Si bonds which are necessary to induce the dissociation. At elevated temperatures (~450°C), the reactions proceeds because silicon can be etched one monolayer at a time at these temperatures.

The recent results involve the study of the mechanisms responsible for the selectivity. It has been found that absolutely no growth will occur on a thin layer of thermal oxide at any temperature below the desorption temperature of oxygen itself. However, small defects can be introduced into the oxide layer by Ar ion bombardment. If this is done, tungsten is then deposited by exposure to WF_6. However, the tungsten is not in the zero-valent oxidation state, as it is after deposition on clean Si. Tungsten deposited on a damaged oxide is itself oxidized. Further experiments are planned in order to more completely understand the mechanisms for selectivity of CVD reactions.

2. Photon-Stimulated Desorption of Fluorine from Silicon
(J. A. Yarmoff and S. A. Joyce)

Reactions of fluorine with silicon provide a good model for fundamental chemical reactions involved in the etching of semiconductors. Because of the ionic nature of fluorine bonds, it is also an ideal system for the study of the physics of the photon-stimulated desorption (PSD) process. PSD of F+ has been performed at the National Synchrotron Light Source at Brookhaven National Laboratory. Surfaces were prepared by exposure of clean Si to XeF_2. Surfaces covered by a various mixtures of SiF, SiF_2 and SiF_3 species can be prepared with coverages ranging from approximately one monolayer to several monolayers. The latter situation results from steady-state etching of silicon. The chemical shift associated with each Si oxidation state can be readily ascertained with core-level photoemission, and is approximately 1 eV per attached fluorine atom.

When measuring the PSD yield in the vicinity of the Si 2p edge, it has been found that the position of the edge for any given oxidation state correlates with the transition from the bonding 2p atom to the conduction band minimum (CBM). For surfaces covered with monolayer amounts of fluorine, it has been shown from measurements of the angular dependence of the PSD yield that F+ desorbs from monofluoride units adsorbed on Si (111) along the normal direction from the sample, while F+ coming from trifluorides desorbs along a more grazing angle. This allows for the separation of the PSD yield curves for the two oxidation states. In addition to showing an edge 2 eV higher than the monofluoride edge, the yield curve for F+ desorbing from SiF_3 shows structure due to the existence of localized Rydberg-like final states (3s and 3p) which is absent from the monofluoride yield curves. Recent measurements have shown that the ion kinetic energies associated with transitions to these final states are higher than the ion kinetic energies for transitions directly to the CBM. Thus, the ions desorbed via transitions to these final states have followed a different PSD mechanism.

Additional studies have concentrated on the F 1s edge, at which the polarization dependence of the PSD yield was measured for samples covered solely with monofluoride units. In this case, the results showed a strong polarization dependence which was virtually identical to that obtained by measuring the absorption at the F 1s edge. This dependence showed a sharp feature just above threshold whose intensity was parallel to the F-Si bond. It turned out that a measurement of this type was very sensitive to the condition of the sample; small amounts of contamination reduced the sharpness of the polarization dependence of the absorption without affecting the PSD. Thus, a comparison of the absorption yield to the PSD yield is a very sensitive method for determining sample purity.

Further work is planned to study the effects of long exposures to monochromatic light. Preliminary results have indicated that fluorine desorption can be enhanced from particular oxidation states by tuning the photon energy to a transition from the Si 2p level associated with that oxidation states to the CBM. While this is certainly the case for ion desorption, it may not be true for the total yield of desorbed products. Thus, samples will be measured with photoemission before and after long exposures to the light.

3. Photoemission and Photon Stimulated Desorption Studies of PF_3 Adsorbed on Ru(0001)

(J. A. Yarmoff, S. A. Joyce and T. E. Madey)

Electron Stimulated Desorption Ion Angular Distributions (ESDIAD) collected for PF_3 adsorbed on Ru (0001) have shown a multitude of patterns which have been interpreted as due to F^+ coming from adsorbed PF_3, PF_2 and PF units. Initially, the surfaces were covered with undissociated PF_3 and the electron beam damage during the ESDIAD measurements resulted in the dissociation of the PF_3. This model has been tested by performing photoemission and PSD measurements at the Brookhaven National Synchrotron Light Source. The photoemission date showed clearly formation of PF_2, PF and P from a surface initially covered solely by PF_3 and subjected to beam damage. Additionally PSD measurements at the P 2p edge have been correlated with the oxidation state of the adsorbed phosphorus. It is planned to measure the PSD of F- ions since these have also been shown to possess unique ESDIAD patterns.

4. Studies of MoS_2 Surface Chemistry

(J. A. Yarmoff)

MoS_2 exists in a layered structure which gives it excellent properties as a solid lubricant. Single crystals of MoS_2 occur naturally and can be cleaved to give clean, well-ordered surfaces in ultra-high vacuum. These surfaces have the property that the traditional cleaning method of ion-bombardment followed by annealing is unsuccessful, since the ion-bombardment causes preferential loss of S. In the layered-crystal structure, S atoms cannot diffuse perpendicular to the layers in order to refill the empty lattice sites. This effect has been studied at the Brookhaven National Synchrotron Light Source in a collaboration with Dr. J. R. Lince of the Aerospace Corporation.

The effect of 1 keV Ne+ ion bombardment on the clean, ordered MoS_2 (0001) surface was studied using high-resolution photoelectron spectroscopy. For low ion fluences, S-vacancy-defect formation occurred in the MoS_2 lattice with the concurrent formation of a small amount (<10%) of dispersed Mo(0). For fluences greater than $\tilde{}1x10^{16}$ $Ne+/cm^2$, the Mo(0) was the predominant species in the surface region, while the remaining species consisted of amorphous MoS_{2-x} and a polysulfide species. Annealing the sample to temperatures up to 1000 K resulted in the formation of metallic Mo coexisting, in approximately equal amounts, with reformed MoS_2 in a surface with no long-range order. A qualitative depth distribution of the chemical species present after Ne^+ bombardment was determined by varying the photon energies employed for core-level spectroscopy. The results indicate that the preferential sputtering of sulfur over molybdenum occurred predominantly through a mechanism involving chemical-bonding effects, specifically through the preferential emission of polysulfide ions over other species in the bombarded region.

Additional work was performed on the chemical aspects of metal adsorption on MoS_2. This work has important applications in the ability to bond the lubricant to a working part. Due to the nature of the MoS_2 structure, metals in general tend to form islands with rather poor bonding to the surface. To date, both Fe and Mn adsorption have been studied. Deposition of thin films of Fe on MoS_2 basal plane surfaces resulted in only a small decomposition of the MoS_2, indicating only a limited chemical reaction. Annealing chemically reformed the MoS_2, but produced a disordered sample that included small amounts of Fe in the lattice and did not show a LEED pattern. Mn, on the other hand, had a large reaction with the MoS_2, forming MnS and Mo metal. Annealing of this did not reform the MoS_2, but did produce a sufficient order to produce a LEED pattern. Further work is planned in which metal adsorption on chemically treated substrates will be studied. Such a treatment of a substrate may lead to a more uniform coverage.

G. Impact Collision Ion Scattering Spectroscopy

(J. A. Yarmoff)

Experiments are planned to study epitaxial growth, adsorbate geometry, melting phenomena, and other geometrical aspects of surfaces using impact collision ion-scattering spectroscopy (ICISS). An instrument is currently under construction which employs a 5 keV Li ion gun and an electrostatic analyzer mounted at a 170° scattering angle. ICISS is performed by monitoring the yield of singly scattered species as a function of the angle between the ion beam and the sample. A manipulator with stepping-motor-controlled rotations is being employed for the angular control. The advantage of using ICISS compared to conventional low-energy ion scattering is that the analysis is simplified by only considering the shadowing effects of the incoming ion beam. Alkali ions are used also to simplify the data analysis by eliminating the need to consider the neutralization of the scattered ions, as is the case with noble gas ions.

H. Reaction Kinetics over Model Single-Crystal Catalysts

(R. A. Demmin, S. M. Shivaprasad* and T. E. Madey)

The overall objective of this research has been to provide a molecular understanding of heterogeneous catalytic chemistry on well-characterized single crystal surfaces. Among the areas studied are the catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen on metal surfaces, the mechanism of catalytic poisoning and promotion, and the reforming of alkanes over model supported Pt catalysts. The apparatus employed for these studies contains high pressure reactors contiguous to ultrahigh vacuum surface analysis chambers. This work is supported in part by the Office of Basic Energy Sciences, Department of Energy.

During the last two years, we have continued a new effort to characterize the properties of model thin-film catalysts prepared by evaporating monolayer films of a metal (Pt) onto single-crystal metal substrates (the close-packed W(110) surface and the atomically rough W(111) surface). Such catalysts serve as model systems for understanding the properties of mixed-metal catalysts: these materials have received considerable attention recently because they often exhibit superiority over single-metal substrates as practical catalysts. It is also known that mixed-metal systems can exhibit remarkably different chemisorption properties from those of either metal alone, and we have found striking evidence for this in our own work.

We are studying the growth, thermal stability and surface chemistry of Pt overlayers (sub-monolayer to multiple-layer coverages) on W(110) and W(111) by means of a variety of surface science methods, including Auger Electron Spectroscopy (AES), low-energy electron diffraction (LEED), thermal desorption spectroscopy (TDS) of a probe molecule, CO, and ultraviolet photoemission spectroscopy (UPS) using synchrotron radiation.

Based on our studies of Pt/W(110), we find evidence for a strong interaction between platinum and tungsten that causes platinum deposited on tungsten to bind more strongly to the substrate than to neighboring platinum atoms. As a result, heating multiple layers of platinum on W(110) causes all but the first layer to agglomerate into three-dimensional clusters on the surface of the tungsten. The first layer remains dispersed in a single atomic layer with the crystal structure of the underlying tungsten and requires a higher temperature for evaporation than does the excess platinum.

The effects of the interaction between platinum and tungsten is manifested in the surface chemistry of the platinum-covered surface in the presence of reactive gases such as carbon monoxide and oxygen. A platinum monolayer on W(110) adsorbs carbon monoxide more weakly than either bulk platinum or the tungsten substrate, but the surface begins to exhibit adsorption behavior more like platinum with the addition of a second layer of platinum. Likewise, platinum on the surface of tungsten can alter the adsorption of oxygen, causing it to bind in different locations on the surface and desorb at a lower temperature than it would from pure tungsten.

The unique nature of the platinum monolayer is reinforced by the results of valence-level photoelectron spectroscopy experiments performed at the NIST SURF-II synchrotron radiation facility. As noted in section 3.B.4, the layer of Pt yields a valence spectrum that is different form those of subsequent layers; i.e., the intensity 1-2 eV below the Fermi level is greatly reduced, suggesting the electronic structure of a noble metal. The fact that the electronic structure of this surface is unlike those of the individual tungsten and platinum surfaces provides a possible explanation for the altered surface chemistry towards carbon monoxide and oxygen.

Chemical shifts observed in the tungsten core levels upon the addition of Pt indicate the elimination of surface-shifted core levels. This is consistent with a model in which the Pt remains dispersed on the surface of W(110), and does not form a Pt/W alloy. Work function measurements and UPS spectra for adsorbed CO suggest that Pt adatoms in fractional monolayer coverages do not coalesce into islands until the surface is annealed.

The structure of the Pt films on W(110) and the influence of coadsorbed oxygen on the Pt structure have been examined using LEED. Fractional monolayer coverages of Pt grow pseudomorphically in registry with W(110), and remain pseudomorphic upon annealing to > 1500 K. As indicated above, multilayers of Pt break into three dimensional clusters upon annealing; the clusters display Pt(111) surfaces oriented in one of two distinct registries with W(110), depending upon the deposition and annealing conditions. Oxygen facilitates clustering of Pt on W(110), even for fractional monolayers of Pt.

Our studies of Pt on the atomically rough W(111) are somewhat preliminary, but exhibit interesting behavior. Annealing of a Pt monolayer results in the formation of microfacets on the W surface believed to have (211) orientation. Apparently, the surface energy of Pt-covered W(211) is lower than that of Pt-covered W(111), thus driving the faceting of the W surface. The faceting is reversible, and the surface relaxes to (111) after thermal desorption of the Pt. To the best of our knowledge, this is the first report of microfaceting in a metal-on-metal overlayer system. This observation has interesting implications for the microstructure of mixed-metal supported catalysts.

We have also initiated studies of CO oxidation over Pt-covered W(110) in an attempt to identify unusual catalytic activity of monolayer thin-film catalysts.

I. Studies of Adsorption and Reaction on Metal Catalysts Using Inelastic Neutron Scattering

(R. D. Kelley* and J. E. Nicol*)

Inelastic Incoherent Neutron Scattering (IINS) studies of adsorbates on catalyst surfaces are providing new insights into the vibrational spectroscopy of hydrogen and hydrogen-containing species absorbed at the surfaces of high-area catalysts. Neutrons are a highly penetrating form of radiation, even in a spectral energy range (< 1200 cm^{-1}) where all the samples are optically opaque.

Although IINS activities in the Surface Science Division are now being phased out, we are still continuing a novel series of IINS experiments begun previously involving the use of an isotopically pure ^{60}Ni substrate. The idea is to use pure ^{60}Ni to reduce neutron scattering by substrate phonons to a level which will make possible studies of the vibrations of surface species which do not necessarily involve hydrogen. In effect, the low IINS cross section of ^{60}Ni will "make the bulk transparent". We plan to examine low-frequency torsional modes of surface molecules (NH_3, CH_2) and to study surface diffusion of adsorbed species. A further use of the ^{60}Ni material will include an attempt to measure adsorbate ordering with high-resolution neutron diffraction. We have a sufficient quantity of ^{60}Ni metal which is being prepared as a Raney Ni catalyst for these measurements. The catalyst is being prepared in collaboration with Dr. M. Kelley of Dupont de Nemours who has developed procedures for fabricating good quality Raney Ni. This activity has been supported in part by the Office of Basic Energy Sciences, Department of Energy.

J. Studies of Molecular Structure and Reactivity on Surfaces Using ESDIAD

(S. A. Joyce, A. L. Johnson, and T. E. Madey)

A continuing challenge in surface science is to determine the structures of molecules on surfaces, particularly in the absence of long-range order. The goal of this project is to provide a direct determination of the structures of adsorbed molecules using the electron-stimulated desorption ion angular distribution (ESDIAD) method, and to correlate the results with measurements based on other surface-sensitive techniques.

The ESDIAD method was developed at NIST and is based on electronic excitation of surface molecules by a focused electron beam (20 eV to > 1000 eV). This causes desorption of atomic and molecular ions from the surface, and is the surface analog of gas-phase dissociative ionization. The ions desorb in discrete cones of emission, in directions determined by the orientation of the bonds which are ruptured by the excitation. Thus, ion desorption angles provide direct information about surface bond angles.

During the past year, we have demonstrated the first negative-ion ESDIAD experiment with results for fluorinated molecules. We have also determined bonding structures of small halogen-containing complexes on metal surfaces. This work has been supported in part by the Office of Basic Energy Sciences, Department of Energy.

1. Negative-Ion ESDIAD

The goal of the present work is to measure the electron-stimulated desorption (ESD) angular distributions of negative ions, and to attempt to answer several fundamental questions. Does negative-ion ESDIAD contain structural information about adsorbed molecular species? How do negative-ion yields and angular distributions compare to positive-ion ESDIAD? Is the information redundant to positive-ion ESDIAD, or is there new information available?

For these first studies, we have chosen three molecules (PF_3, $(CF_3)_2$-CO, NF_3) known to yield F^- ions upon electron impact in the gas phase. Adsorption is carried out on Ru(0001), a surface for which adsorption studies of these species have been reported. The essential results of these measurements are: (a) we can detect large quantities of F^- (as well as F^+) ESD ions, (b) the F^- ESDIAD patterns are different for the three molecules, as well as for different bonding modes of each molecule, and (c) the structural information contained in the F^- ESDIAD pattern is different from and complementary to the F^+ ESDIAD results.

The major technical challenge in negative-ion ESDIAD is to separate the large secondary-electron signal from the much weaker negative-ion signal (smaller by ~10^5). This is accomplished using time-of-flight techniques. The flight paths are short, ~2 cm, and the ion angular distributions are displayed on a phosphor screen after image intensification using a double microchannel plate detector. In our ultrahigh vacuum display analyzer, the electron flight time is ~30 ns and the flight time for an F^- ion is ~800 ns. Single ion detection is achieved. The typical electron bombardment energy is 200 eV, the pulsed electron beam has a width of ~800 ns, and the repetition rate is ~10^4 per second. Data accumulation times for ESDIAD are of the order of a few seconds.

Mass-resolved ESDIAD patterns (both positive and negative ions) are obtained using a data acquisition system composed of a video camera, video recorder (with time base corrector), image processor (digitizer and computer) and graphics display. The data are processed in various ways (contour plots, intensity maps, perspective plots) and can be displayed with false color.

Figure 3.1 illustrates the F^- ESDIAD observed for a saturation coverage of PF_3 on Ru(0001). The anisotropy in F^- emission observed here, when combined with low-energy electron diffraction (LEED) and thermal desorption spectroscopy (TDS) data, led us to propose the following model for adsorbed PF_3. The PF_3 is bonded via the P atom to a single Ru substrate atom. At saturation coverage, the (3 x 3)R 30° layer causes a

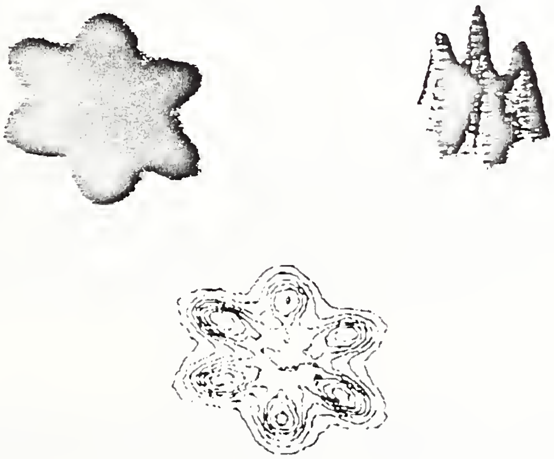

Fig. 3.1. F^- ESDIAD patterns for monolayer of PF_3 adsorbed at 110 K on Ru(0001) and annealed to 273 K. Upper left: F^- ESDIAD image as it appears on phosphor screen of ESDIAD apparatus. Upper right: Perspective plot of F^- ESDIAD, obtained using digital video image processor. Bottom: Intensity contour map of F^- ESDIAD.

hindering of rotational freedom, and the PF_3 is "locked in" to azimuthal registry with the Ru(0001) substrate (see Fig. 3.2). To reduce overlap of the van der Waals radii of neighboring F atoms, the PF_3 is also believed to tilt, as indicated in Fig. 3.2.

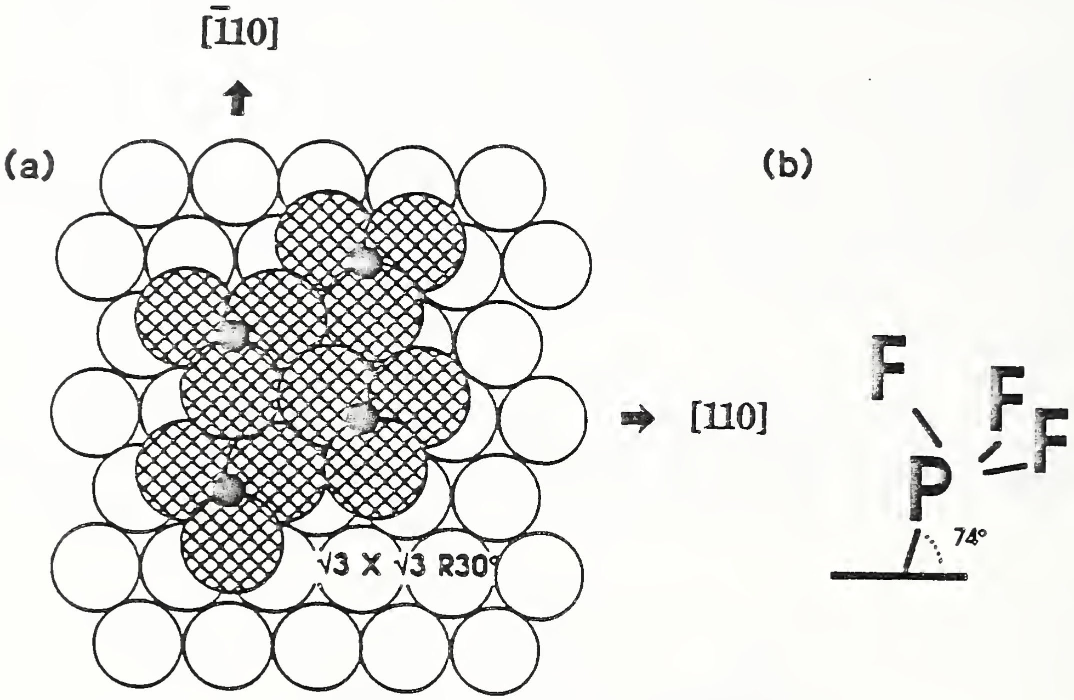

Fig. 3.2. Models of the bonding configuration of PF_3 on Ru(0001). (a) Lattice model drawn to scale, showing "interlocking" PF_3 molecules on hexagonal Ru(0001) substrate. (b) Bonding model (side view) for the proposed inclined PF_3 configuration.

The results to date indicate that negative-ion ESDIAD is a very useful complement to positive-ion ESDIAD. The F^- ESDIAD data for PF_3 on Ru(0001) provide insights into the adsorbate structure not available in F^+ ESDIAD data. Negative-ion ESDIAD is particularly effective for studies of surface bonding geometry in fluorine-containing molecules.

2. Determination of Bonding Structures of Small Halogen-Containing Molecules

Both positive-ion and negative-ion ESDIAD have been used in conjunction with LEED and TDS to study the bonding of PF_3, $(CF_3)_3CO$ and NF_3 to Ru(0001).

For fractional monolayer coverages at 80 K, PF_3 is bonded via the P atom with the F atoms pointed away from the surface. A "halo" of F^+ emission indicated azimuthal disorder over a wide temperature range (80 to > 450 K), suggesting that the molecules are freely rotating about the Ru-P axis. As coverage increases, the "crowding" causes azimuthal ordering due to hindered rotation as indicated in Figs. 3.1 and 3.2. The adsorbed species are highly electron-beam sensitive, and PF_3 dissociates to form absorbed PF_2 and PF fragments during irradiation.

Measurements for $(CF_3)_2$ Co indicate that at least one binding state of the parent molecule is bonded in azimuthal registry with the Ru(0001) substrate. The NF_3 adsorption is predominantly dissociative, with little azimuthal ordering on planar Ru(0001).

We plan to expand the negative-ion ESDIAD to other molecules likely to produce negative-ion fragments. Suitable candidates are O- from N_2O and CO on Ru(0001) and H- from H_2O and NH_3 on Ru; all of these species yield negative ions in the gas phase. We will also initiate studies of other small halogen-containing molecules, e.g., SF_6, CF_4, C_2F_6, HF, etc. We plan to use negative-ion ESDIAD to search for molecular reorientations due to interaction between adsorbed molecules (CO, N_2O, PF_3) and impurity alkali atoms (K, Na) or impurity oxygen atoms. Finally, we will carry out studies of the surface chemistry of semiconductors; in particular, we will search for negative-ion emission for small molecules (CaF_2, PF_3, HF, H_2O) adsorbed on Si(100) and Si(111).

We plan to apply digital positive-ion ESDIAD to interesting problems involving the structure and dynamics of small molecules on metal surfaces to address question of the following type. Is CO perpendicular to the surface or "inclined" at atomic steps on Pt surfaces? Does H_2O bond to Pt(111) with the H atoms pointed toward the surface or away from the surface in the presence of adsorbed K^+? What is the bonding site of HCOO on Ag(110) and Cu(110); is the "long bridge" or the "short bridge" occupied?

K. Laser Diagnostics of Surface Dynamics

(J.D. Beckerle, S.A. Buntin, R.R. Cavanagh and L.J. Richter)

Optical spectroscopies offer several powerful advantages over other techniques when investigating molecular processes at surfaces. In particular, the spectral and temporal resolution afforded by state-of-the-art laser methods is unrivaled by any other technique.

The objective of this project is to bring modern laser-based diagnostics to bear on a variety of problems in the area of molecular dynamics at surfaces. A variety of laser based methods are used to explore divers topics including: the potential for optically driven surface reactions;

the decay rates of vibrationally excited adsorbates at surfaces; and the response of surface layers to transient optical excitation. This work is conducted in close collaboration with Drs. M.P. Casassa, E.J. Heilweil, D.S. King and J.C. Stephenson of the NIST Molecular Spectroscopy Division.

1. Laser-Induced Desorption

Building on a series of experiments which had used laser-excited fluorescence to characterize the internal-state distributions of NO molecules thermally desorbed from metal surfaces, we recently began to use the same state-specific diagnostics to explore desorption induced by laser excitation of metal surfaces. This initial work was conducted on a Pt foil. Although the experiments were originally designed to utilize only the thermal heating of the surface by the incident laser, several surprising observations were made, including detection of a desorption channel whose kinetic energy exceeded the peak surface temperature by a factor of four. More remarkable, the kinetic energy in this channel increased with the rotational energy of the state, a result which suggested a desorption-laser wavelength dependence of the kinetic energy.

We have now been able to measure the laser-induced desorption of NO from Pt(111). The presence of two distinct desorption channels is confirmed, and we can now identify the slow (thermalized) channel with a weakly bound NO state (Ea ≈ 10 kcal/mole), while the channel which displays a variety of non-equilibrium characteristics is associated with NO bound to a-top sites. These latter species desorb with non-Boltzmann rotational distributions and inverted spin-orbit populations at the three desorption wavelengths employed. The kinetic energy was characterized as a function of desorption-laser wavelength and NO state; we found a clear reduction (by 30%) at 1064 nm compared to either 532 or 355 nm. In addition, while desorbed NO in the first excited vibrational level was readily detected for 532 and 355 nm excitation, the $v = 1$ channel was effectively closed. These observations have led us to the conclusion that this desorption channel is a manifestation of NO coupling to the nascent optically excited electrons of the platinum. Inverse photoemission has identified vacant NO orbitals approximately 1-2 eV above the Fermi level, consistent with the proposed mechanism. We have further conjectured that the inverted spin orbit population may be the result of the involvement of a negative-ion resonance and its subsequent reneutralization.

In future experiments we hope to extend the wavelength range covered with the desorption pulse, reduce the duration of the desorption pulse, and investigate the importance of surface roughness and impurities on the desorption dynamics. In addition, we will extend these types of measurements to laser-induced desorption from semiconductor surfaces. A new manipulator is being fabricated which will permit a low enough temperature to be achieved to permit the study of NO adsorbed on Si(111). It will be possible to excite this system with photon energies both below and above the band gap. If desorption is driven by hot electrons in the substrate, then the wavelength dependence should be even more dramatic than that observed for platinum.

We plan to investigate the desorption dynamics of hydrogen since this represents an important prototypical system for understanding the fundamental steps in a range of surface processes, ranging from semiconductor etching, energy storage, and atom-atom recombination. We are presently developing a laser system to be used for state-specific characterization of H_2 near the LiF cut-off. Calibration and characterization of the detection efficiency is planned for the coming year.

This work is supported in part by the Department of Energy.

2. Time-Resolved Measurements of Vibrational Energy Transfer

The decay of vibrationally excited state populations at surfaces has received considerable theoretical attention, but experimental efforts in this area have been restricted to indirect measurements (lineshape measurements and collisionally induced energy transfer). Direct, time-resolved measurements of the relevant decay rates provide the central theme for this project. We have focused on the vibrational depopulation time of CO bound to metal atoms in a range of systems.

Metal carbonyls consisting of a single metal atom with six CO ligands have been measured in dilute solution. The CO ($v = 1$) lifetime is approximately 500 ps, but can range up to 1000 ps depending on solvent.

Metal carbonyls containing a single metal atom and only one carbonyl ligand are found to relax much faster than the fully carbonylated systems. The relaxation rate is found to be dependent on the vibrational modes of the other ligands bound to the metal.

Dilute solutions of metal-cluster carbonyls ($M_x(CO)_y$; $x = 2$, 4, or 6) in $CHCl_3$ have been measured to determine if the observed T_1 times show any dependence on the size of the metal cluster. While these experiments did not reveal any size dependence, several intriguing results emerged:

- Bi-exponential decays were observed for the first time. The source of these signals will require further experiments to clarify their origin, but preliminary experiments indicate that there may be rapid energy transfer between two CO stretching modes ($T_1 \approx 40$ ps) followed by a slower relaxation of the vibrational excited state ($T_1 \approx 350$ ps).

- In addition to the transient bleaching normally observed in these pump-probe experiments, conditions were found where the pump pulse leads to transient absorption. This effect has been characterized as a function of laser wavelength and power, and can be adequately accounted for in terms of contributions from CO in $v = 2$ (and higher) vibrational levels.

- The metal cluster compounds have been supported on SiO_2 and the changes in the T_1 times have been compared to the relaxation rates observed in $CHCl_3$ solutions. The T_1 times were found to be reduced by a factor of four in the presence of the SiO_2. This change in T_1 has been attributed to the participation of SiO_2 in the relaxation process. At this time, it has not been possible to identify which of several relaxation mechanisms are involved.

In an effort to probe larger metal particles, metal clusters (of ill-defined particle size and shape) have been prepared by reduction of SiO_2-supported metal salts. Transmission electron microscopy measurements indicate that mean particle diameters of about 35 Å are obtained. The infrared spectra of adsorbed CO are comparable to those in the published literature. We have observed a non-exponential decay using 2 ps infrared pulses. It is readily apparent that the CO bound to these particles have a significantly different response to vibrational excitation than any of the other supported-cluster compounds studied. Work is underway to characterize the nature of this prompt response. In addition to examining the role of laser wavelength, intensity, CO isotope, and sample preparation conditions on the observed transient, theoretical modeling is in progress to provide a measure of the nature of the low-lying electronic levels associated with metal particle of this size.

This work is supported in part by the Air Force Office of Scientific Research.

3. Single-Reflection Infrared Pump-Probe Experiment

The advantage of measuring vibrational-relaxation rates for adsorbates on well-characterized single-crystal surfaces is readily apparent. We have therefore constructed an ultra-high vacuum system in which to conduct single-reflection infrared pump-probe measurements. The system is equipped with Auger-electron spectroscopy, low-energy electron diffraction, ion-sputtering facilities, mass spectrometer, and optical ports for infrared measurements. The system is presently being used for single-reflection Fourier-transform infrared experiments in order to confirm the lineshape and line position for the samples generated in our laboratory. It is planned that this facility will be coupled to the 2 ps laser source during the coming year.

L. Theory of Dynamical Molecular Processes at Surfaces

(J. W. Gadzuk)

This project is part of a continuing effort directed to understanding both the static and dynamic behavior of atoms, molecules, solids, surfaces, radiation and their mutual interactions. This understanding comes from consideration of the microscopic atomic-scale properties of individual entities as well as from larger-scale statistical properties of ensembles. Based upon our studies, phenomenological model theories and numerical simulations are constructed which relate to the chemical physics and statistical-mechanical behavior and to the intrinsic properties of relevant physico-chemical systems. In addition, a significant effort is invested in the study of the role of an actual measurement process in determining observed quantities in different surface spectroscopies. Ways in which measurement-process-specific quantities such as line shapes, satellite structures, etc. provide additional information on system dynamics are of considerable interest.

1. Chaos, Non-Linear Dynamics, and Vibrational Spectroscopy

We have initiated an in-depth study using numerical simulations and modeling of non-linear systems. In spite of progress in many other fields, the impact of the recent advances in non-linear dynamics/chaos on surface physics research has been minimal. Possible areas in the chemical physics of surfaces which could benefit from ideas out of the chaos world are being explored. Of particular emphasis are the implications of quasi-periodic versus irregular (chaotic) nuclear dynamics on: (1) vibrational spectroscopy and lineshapes of adsorbed molecules; (2) state specific vs. statistical molecular dynamics and chemical reactivity of both adsorbed molecules and molecular beams; (3) relationships between spectroscopy and scattering; and (4) iterative maps as a mathematical model for long-time surface processes.

The following specific example, drawn from our recent studies, highlights some connections between "chaology", vibrational spectroscopy, and surface dynamics. As is widely realized, many molecular systems can be characterized by a two-degrees-of-freedom model in which one degree of freedom is the subsystem of interest and the other is "everything else". With this in mind, let us suppose that vibrational spectroscopy is to be performed on an adsorbed molecule in which the potential energy function of the intra-molecular stretch vibration is a harmonically coupled to the molecule-surface bond and can be modeled in terms of a paradigm of non-linear dynamics, the Toda system and a closely related derivative, the Henon-Heiles model. The Hamiltonian for the Toda system is

$$H_{Toda} = 1/2\ (p_x{}^2 + P_y{}^2) + \frac{1}{24}\ \{\exp\ (2y + 2\sqrt{3}\ x) + \exp\ (2y - 2\sqrt{3}\ x) + \exp\ (-4y)\} - 1/8 \qquad (3.1)$$

where y is the intra-molecular stretch coordinate and x is the adsorption bond coordinate.

The potential curves implied by Eq. (3.1) and shown in Fig. 3.3(a) vary smoothly outward from the origin in both x and y, displaying a threefold symmetry. If Eq. (3.1) is expanded to cubic terms in x and y, we obtain the Henon-Heiles Hamiltonian

$$H_{HH} = 1/2(p_x{}^2 + p_y{}^2) + 1/2\ (x^2 + y^2 + 2\ x^2y - 2/3\ y^3) \qquad (3.2)$$

whose potential energy surface (PES) is shown in Fig. 3.3(b). This PES is quite similar to the Toda PES. From a dynamics point of view, these related systems are interesting because motion governed by H_{Toda} is quasi-periodic for all energies whereas complete quasi-periodic dynamics with H_{HH} occurs only for $\epsilon_{tot} < 0.1$. The onset of chaos begins at this point and increases as ϵ_{tot} is raised.

The strategy of the present study is to consider the adsorption resonance as either a Toda or a Henon-Heiles PES. Since Toda dynamics are regular whereas Henon-Heiles dynamics undergo a transition to chaos, we demonstrate the relevance (or lack of it) of chaotic behavior to surface vibrational spectroscopy and "reaction dynamics."

Using the spectral analysis technique developed by Marcus and coworkers, the vibrational lineshape associated with excitation of a mode characterized by a displacement coordinate q(t), is given by the power spectrum of q(t):

$$I(\omega) = \left(\frac{1}{2\pi}\right) \lim_{T\to\infty} \left(\frac{1}{2T}\right) \left\langle \left| \int_{0}^{2T} q(t) e^{i\omega t} \, dt \right| \right\rangle , \tag{3.3}$$

where q(t) is the trajectory followed by the coordinate subject to prescribed initial conditions characterizing the excitation/adsorption processes. The time evolution is obtained numerically from Hamilton's equations using either Eq. (3.1) or (3.2). Here we make an equivalence between dipole excitation of the intra-molecular stretch and initial displacement of the y coordinate (with a small non-zero x-displacement).

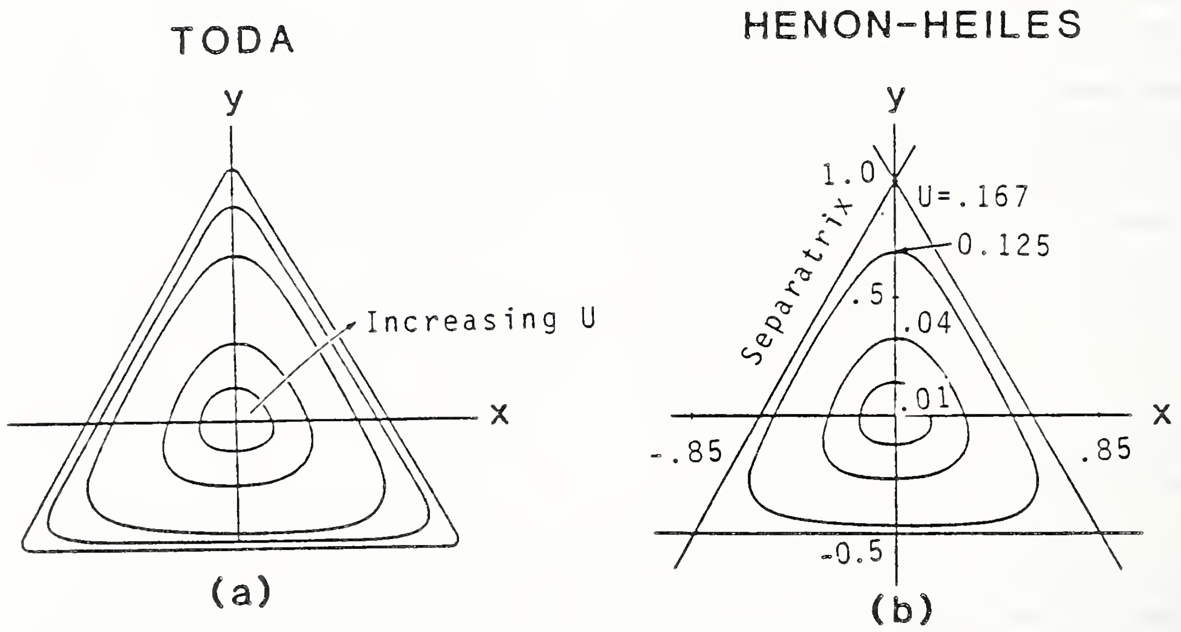

Fig. 3.3 (a) Potential well for the Toda Hamiltonian showing lines of constant potential U. (b) Potential well for the Henon-Heiles Hamiltonian showing lines of constant potential U, for closed equipotentials (U ≤ 1/6) only.

Trajectories for the Toda and Henon-Heiles potentials have been calculated and fast-Fourier transformed. The resulting lineshapes obtained from Eq. (3.3) are shown in Fig. 3.4 (a)-(d) for both potentials with the initial y displacement treated parametrically. The Toda lineshape, Fig. 3.4 (a), remains sharp for all initial conditions (and thus total energy).

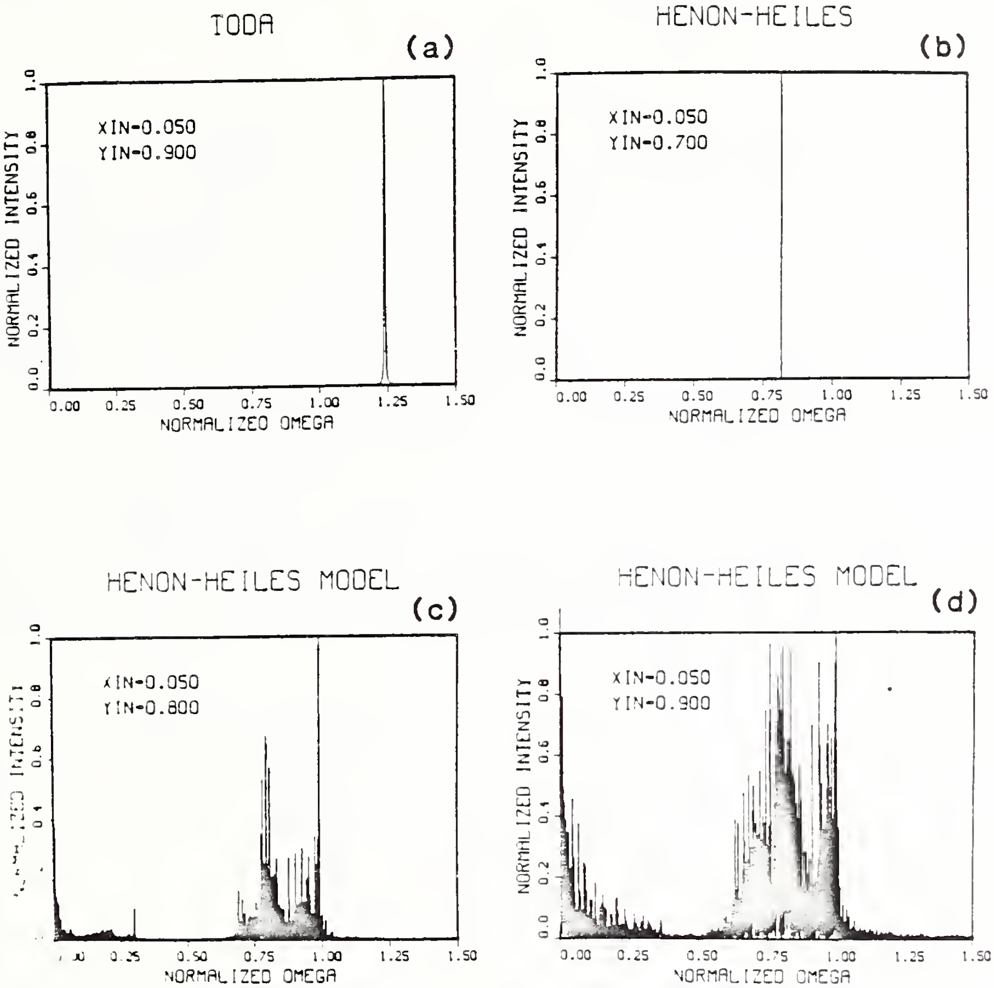

Fig. 3.4 Vibrational lineshapes for (a) Toda and (b-d) Henon-Heiles systems. The Toda lineshape (a) remains sharp for all initial displacements whereas the originally sharp (b) Henon-Heiles lineshape spreads out (c-d) for initial displacements corresponding to energies above the chaotic threshold.

This result is a characteristic of the quasi-periodic motion on the Toda PES. In contrast, the Henon-Heiles lineshape shows an evolution as the initial displacement and hence total energy increases. For small displacements in which $\epsilon_{tot} < 0.1$, the lineshape is sharp as shown in Fig. 3.4 (b).

For larger displacements in which ϵ_{tot} exceeds the chaotic threshold, the lineshape broadens and spreads throughout the spectral range, as seen in Figs. 3.4 (c) and (d). It is thus reasonable that vibrational spectroscopy exploit these characteristic signatures of quasi-periodic vs. chaotic dynamics in order to provide additional information to the scattering or reaction dynamicist on the nature of the intermediate precursor state. This is one of our ultimate goals.

2. Selectivity in Surface Dynamics

Selective control of the rate and outcome of chemical events, based on molecular-level manipulations, is a major goal in chemical physics. Laser-assisted chemistry is one area which has offered such hope. Although "surface-assisted chemistry" is certainly capable of statistically controlling rates and outcomes, it is only recently that bond selectivity has been considered within the context of surface dynamics. The physical basis for many proposed scenarios in selectivity can be summarized as follows. At some time $t = 0$, the molecular system is placed in an initially prepared, non-stationary state (say by electronic excitation) and is then allowed to time-evolve. At a later time $t = \tau_R$, the time-evolution of the initially excited state is interrupted. By choosing the time delay τ_R appropriately (depending upon system specifics), it is possible to achieve non-statistical control of the distribution of final quantum states and/or products. Amongst the different realizations of τ_R-dependent selectivity considered, currently within the context of analytically soluble models, we include: (i) the zero-energy sticking problem (ZESP); (ii) vibrational population inversions in molecule-surface scattering; and (iii) resonant electron-stimulated desorption.

Due to the relevance of the ZESP to the proposed milliKelvin trapped Na atom-surface experiments at NIST, we present here some recent advances based on the scenario stated in the above paragraph. Given an atom or molecule-surface scattering situation involving temporary non-stationary-state formation, the probability that the surrounding environment or internal degrees of freedom remain unexcited is

$$P_o(\tau_R) = |\sum_{\tilde{m}} |\langle 0|\tilde{m}\rangle|^2 e^{-i\epsilon_{\tilde{m}}\tau_R/\hbar}|^2 \tag{3.4}$$

where $P_o(\tau_R)$ is given in terms of $|\langle 0|\tilde{m}\rangle|^2$, the "generalized Franck-Condon factors" between the ground state and $|\tilde{m}\rangle$, the ambient eigenstates associated with the temporary non-stationary state. With regards to the ZESP, the basic premise is that in the limit of a zero-kinetic-energy incident beam, any inelasticity in the molecule-target collision is sufficient to cause the molecule to stick to the target surface. Thus, within the present picture, the zero-energy sticking probability is

$$S \approx \lim_{\epsilon_p \to 0} \{1 - P_o(\tau_R(\epsilon_p))\} \tag{3.5}$$

which demonstrates that "selectivity" in sticking can, in principle, be controlled by varying τ_R.

Within this context, the ZESP has been investigated for two analytically tractable cases. In the first case, the surrounding dissipative medium is taken to be the electron-hole pair excitations of the substrate. The exact no-loss intensity in a scattering event is then

$$P_o(\tau_R) = [1 + (\omega_c\tau_R)^2]^{-\alpha} \qquad (3.6)$$

where $\epsilon_c \equiv \hbar\omega_c$ is a cutoff energy of order the conduction bandwidth, and $\alpha \approx (\delta/\pi)^2 < 0.25$ where δ is the dominant Fermi-level electron phase shift associated with the localized potential of the incident atom or molecule. In Fig. 3.5(a), Po = 1 - S, given by Eg. (3.6), is drawn as a function of $\omega_c\tau_R$, and α is varied parametrically within a range likely to apply for real-surface scattering situations. With a not-unreasonable value of $\alpha \approx 0.1$ for strongly interacting chemisorbed systems and $\epsilon_c = 10$ eV, the value of τ_R for 50% elastic scattering ($P_o(\tau_R) = 0.5$) is $\tau_R \approx 2 \times 10^{-15}$ sec. For such systems, significant depletion in the no-loss line is to be expected.

The second example involves "vibrationally assisted sticking" due to the resulting intramolecular vibrational excitation in a diatomic molecule-surface collision involving charge transfer and thus temporary negative molecular-ion formation. In this case, the exact no-loss intensity has been shown to be:

$$P_o(\tau_R) = \exp[-2\beta_o(1-\cos\omega\tau_R)] \qquad (3.7)$$

where

$$\beta_o = \Delta\epsilon_r/\hbar\omega$$

and $\Delta\epsilon_r = \frac{1}{2}\kappa q_o^2$ is the relaxation energy or Franck-Condon shift associated with the harmonic potentials ($\omega = \sqrt{\kappa/\mu}$) displaced with respect to each other by q_o in the $A_2 \leftrightarrow A_2^-$ transitions. As with electron-hole pairs, the ZESP is $S = 1 - P_o$ with P_o given by Eq. (3.7).

In analogy with Fig. 3.5(a), $P_o(\tau_R)$ given by Eq. (3.7) is shown in Fig. 3.5(b) as a function of $\omega\tau_R$ taking β_o parametrically. (Note: $\beta_o \approx$ 1-3 for A_2/A_2^- displaced oscillators of C, N, O diatomics.) Unlike P_o due to the continuum of electron-hole pairs (Eq. (3.6)) which is a monotonically decreasing function of intermediate state lifetime, P_o from a localized oscillator, Eq. (3.7) is periodic. If τ_R is such that $\omega\tau_R$ is an odd (even) integral multiple of π, maximum (minimum) oscillator excitation occurs. Thus the commensurability between the oscillator frequency and the time delay between curve crossings is a crucial factor in controlled selectivity and the vibrationally assisted ZESP.

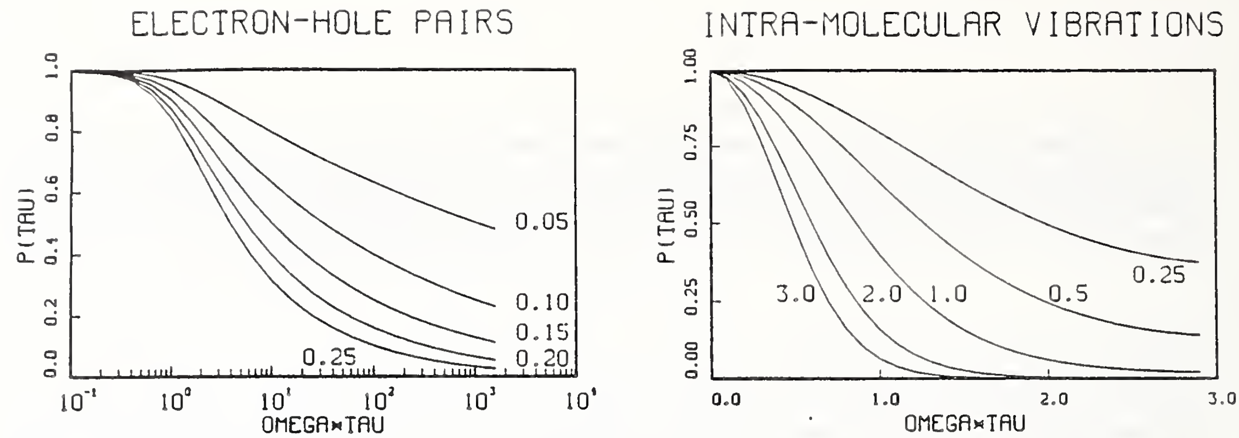

Fig. 3.5 (a) P_o vs. $\omega_c\tau_R$, from Eq. (3.6) with α varied parametrically (left) and (b) P_o vs. $\omega\tau_R$, from Eq. (3.7) with β_o varied parametrically (right).

3. Semi-classical Surface Dynamics

There exists a wide range of system-independent and seemingly different molecular-level phenomena which show an aesthetically pleasing unity when considered as problems in time-dependent quantum mechanics. This belief has served as a main guiding principle in much of our work in the chemical physics of surfaces. For instance, one might ask, what do photoemission lineshapes and/or satellites, stimulated desorption energy distributions, vibrational overtone losses in electron energy-loss spectroscopy, and internal-state excitation in molecular beam scattering have in common? A new and worthwhile perspective on the physics and chemistry of such surface processes has been attained through inquiries focused on common aspects of nuclear dynamics experienced in these surface spectroscopic and molecular processes. The results have been presented in an invited review article for Annual Reviews of Physical Chemistry.

We plan to continue work in the area of surface reaction dynamics with near-term emphasis on the determination of self-consistent reaction trajectories, realistic electron-hole pair coupling constants, determination of energy-redistribution patterns amongst translational, vibrational, rotational, and electronic degrees of freedom of "reactant" molecules and electron and phonon modes of surfaces. Analyses are made for controllable dynamic and reactive conditions with synthesis of the various components of the elementary reaction theories into theories of experimentally realizable processes. Special emphasis will be placed on the phenomenon of dissociative surface processes and on the role of non-linear dynamics.

In addition, analysis will be made, whenever possible, of novel experimental results. Current interest includes laser-assisted surface processes and state-to-state analysis, high-resolution surface vibrational spectroscopy, picosecond pump-probe studies of molecular vibrational relaxation times in the presence of small metal clusters showing quantum-size effects, and other experimental probes of non-adiabatic effects.

4. SURFACE COMPETENCE PROGRAM

The Surface Competence Program is a part of the NIST "Competence Program." The NIST program was introduced to provide long-term support of the establishment and maintenance of areas of excellence in science and technology contributing to the NIST mission and the projected needs of the NIST clientele.

The Surface Competence Program was established in 1984 with two principal components, "Novel Two-Dimensional Materials" and "State Characterization of Energetic Species Ejected from Surfaces". The initiation of this program represents a new focus on these topics. The principal objectives of each program component are described in the following two main sections together with reports of individual projects.

A. Novel Two-Dimensional Materials

In recent years an increasing awareness has developed of the important modifications in physical properties which occur in materials as they approach the ultra-thin two-dimensional limit. Some examples of unusual behavior discovered in such systems include the enchanced catalytic properties of a gold surface with two monolayers of platinum compared to bulk platinum, superconductivity of a silver monolayer on germanium, the quantum Hall effect, the enhanced magnetism in alternating monolayers of iron and cobalt, the electrical properties of metal-semiconductor junctions (Schottky barriers), and multiple quantum-well systems for optical logic devices. These examples suggest a whole new range of scientifically and technically important chemical and physical properties waiting to be explored in the two-dimensional regime. Concepts and methods developed in surface and interface science have been particularly valuable in many areas of application, and it is believed that these concepts and methods can be further developed and extended to two-dimensional systems with component thicknesses from one to one hundred atomic layers.

There exist major gaps in current understanding of the fundamental principles which govern the chemical and physical properties of layered structures in the two-dimensional limit. In this component of the program, it is planned to synthesize and determine the fundamental chemical and physical properties of ultrathin layered materials with layers so thin (a few atoms thickness) that they exhibit two-dimensional behavior. Knowledge of the factors influencing the growth and properties of ultrathin layered systems is expected to allow optimization of desired chemical and physical characteristics and will thus benefit a number of scientific fields ranging from catalysis to novel semiconductor devices.

We are performing work in two main project areas. First, we are planning to develop the techniques needed to synthesize, by alternating monolayer deposition, a new class of materials: non-equilibrium ordered alloys. The structural properties of these materials as grown and during thermal processing will be investigated by x-ray and electron diffraction. The chemical reactivity, catalytic activities, and magnetic properties of these materials will also be investigated. Second, we plan to determine the microstructure and microcomposition of candidate layered structures by atom-probe and field-ion microscopy methods with emphasis on the interface region. These techniques provide composition and structure data with near-atomic spatial resolutin. An emphasis in this area during the past year has been an investigtion of the new high-temperature superconducting materials. In a third area, now concluded, we have investigated theoretically the properties of two types of novel thin-film materials.

1. Determination of Surface Structure by X-Ray Photoelectron and Auger-Electron Diffraction

(W. F. Egelhoff, Jr., D. A. Steigerwald, K. Ong*, and I. Jacob*)

There are a number of techniques for determining the atomic structures of ordered and disordered surfaces, each having distinct advantages and limitations. During the past few years, we have been developing another structural technique, termed the "searchlight effect," which can be conveniently used in conjunction with two common techniques for measurement of surface composition, x-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES). It has been found in prior NIST work that XPS and AES intensities are strongly enhanced along nearest-neighbor and next-nearest-neighbor axes of a crystal. The angle-resolved spectra thus provide intensity peaks that point out what are in effect the "bond directions" in the near-surface region. The searchlight effect is a powerful probe of short-range order in the top few monolayers of a crystalline surface.

We have been continuing to develop additional understanding of the important diffraction mechanisms that give rise to the searchlight effect. In addition, we have been exploiting the technique for surface structural analysis.

We have made progress in investigations of the diffraction processes through semiclassical calculations of diffracted intensities. Semiclassical results are especially instructive for visualizing the single and multiple scattering processes involved in diffraction and can provide insights often missing in the obscurities of partial-wave expansion (full quantum) treatments. This work has led to an improved understanding of how the first few scattering events tend to form the enhanced intensity of the searchlight effect and subsequent scattering events defocus the searchlight beams so that the technique is useful as a probe of near-surface short-range order. The searchlight effect has been demonstrated to give direct insights into the thin-film microsctructure that would be difficult to obtain by other techniques.

Figures 4.1 and 4.2 show examples of experiments in which the calculations have assisted interpretations of the results. The data of Fig. 4.1 are angular profiles of the Ni CVV Auger peak from a Ni(100) specimen covered with 12 monolayers (ML) of cobalt. The cobalt film is thick enough to defocus the searchlight beams from the underlying nickel crystal. On heating the structure, however, the nickel intensity increases and the angular profiles show structure which indicate that Ni atoms are diffusing through the cobalt film and forming a random alloy. At temperatures above 900 K, the Ni atoms occupy the top 2 or 3 ML of the surface and the searchlight beams are well developed.

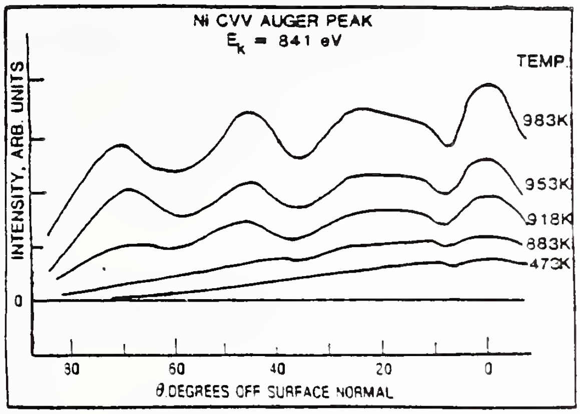

Fig. 4.1. The angular dependence of the Ni CVV Auger peak for increasing annealing temperatures for a 12 ML epitaxial film of Co on Ni(100).

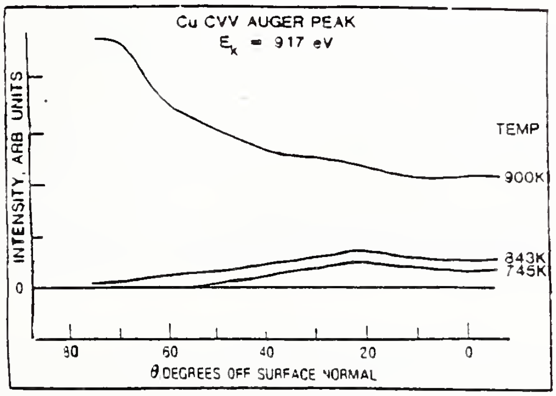

Fig. 4.2 The angular dependence of the Cu CVV Auger peak for increasing annealing temoeratures for an epitaxial sandwich structure of 17 ML Ni on 3 ML Cu on Ni(100).

Figure 4.2 shows similar data for another thin-film structure. Angular profiles are plotted for the Cu CVV Auger peak ansing from a 3 ML Cu layer on Ni(100) which has been covered by 17 ML layer of Ni to form an epitaxial sandwich. No searchlight beams are observed on heating the sandwich and it can be concluded that no near-surface alloy is formed. Instead, 1 ML of Cu segregates to the surface (a second monolayer is required to produce a searchlight beam) and the remaining Cu diffuses deeper into the Ni. A random alloy does not form upon heating in this case even when it is expected.

The searchlight effect has been applied to a variety of other surface structural problems. We have made a study of the short-range order (i.e., bonding site) around a submonolayer coverage of Ni atoms that have thermally diffused into a GaAs(110) surface to pin the Schottky barrier. We have observed and analyzed some unusual crystal structures that occur in epitaxial growth of Au film and Au-Ag sandwich structures on Ni(100). The searchlight effect has also played a key role in a major new activity begun during the past two years, the study of magnetic elements in novel crystal structures produced by epitaxy; this work is described in the following section.

We plan to continue ways of improving the power of the searchlight effect further. A new XPS system has been designed that will enable more complete and efficient measurements of the searchlight effect and other diffraction phenomena than are possible with the present eighteen-year-old XPS instrument. The new system will have a gonimometer-mounted analyzer that will be used to measure the angular distributions of photoelectrons, Auger electrons, and scattered ions. This facility will be used to characterize the structural, magnetic, and electronic properites of a variety of thin-film materials.

2. Magnetic Thin Films, Sandwiches, and Superlattices
(W. F. Egelhoff, Jr., D. A. Steigerwald, and I. Jacob*)

Surface magnetism and the magnetism of ultrathin films is an area of surface science that has experienced very rapid growth in the past 3 to 5 years. This growth is motivated, in part, by the recognition that, in the near future, the advanced thin-film media used for magnetic recording will need to be of smaller dimensions then at present. Such thin films can be usefully studied by the powerful techniques of surface science. The importance of such studies is due to the size and economic significance of the magnetic recording industry and to the fact that magnetic properties are notoriously structure sensitive.

During the past two years, we have initiated a project in which the XPS searchlight effect (described in the previous section) is used as a surface-structural diagnostic of different thin-film structures we have fabricated. Specifically, we use the searchlight effect to learn how to grow magnetic thin films with improved structural integrity and in novel or unusual crystal structures. We also use other techniques such as reflection high-energy electron diffraction (RHEED), low-energy electron diffraction (LEED), XPS intensities, and XPS core-level shifts. Rapid progress has been made with this array of techniques.

The first magnetic thin-film system we have investigated consisted of Fe layers on Cu(100). The literature on this system is both voluminous and awash with controversy, with no careful structural studies having been conducted. We found that contrary to the universal assumption that Fe grows in a layer-by-layer mode, in fact such a mode is extremely difficult to achieve. Segregation of Cu and agglomeration of Fe are pronounced effects under the conditions of growth used in earlier work. Clearly, structural imperfections of diverse sorts were a major factor in the controversy.

In our work, we have developed growth methods, based on low-temperature epitaxy and subsequent gentle annealing, that produce Fe films of high quality. We have then fabricated sandwich and superlattice structures by growing Cu epitaxially on the Fe.

A typical superlattice structure is illustrated in Fig. 4.3. We have found that the Fe films grow in the face-centered cubic structure on Cu(100) rather than with the body-centered-cubic structure of bulk Fe. The superlattice structure of Fig. 4.3 consists of a set of 3 ML thick single crystals of fcc-Fe sandwiched between Cu(100) surfaces. With such a novel crystal structure, it was thought that novel magnetic properties might occur.

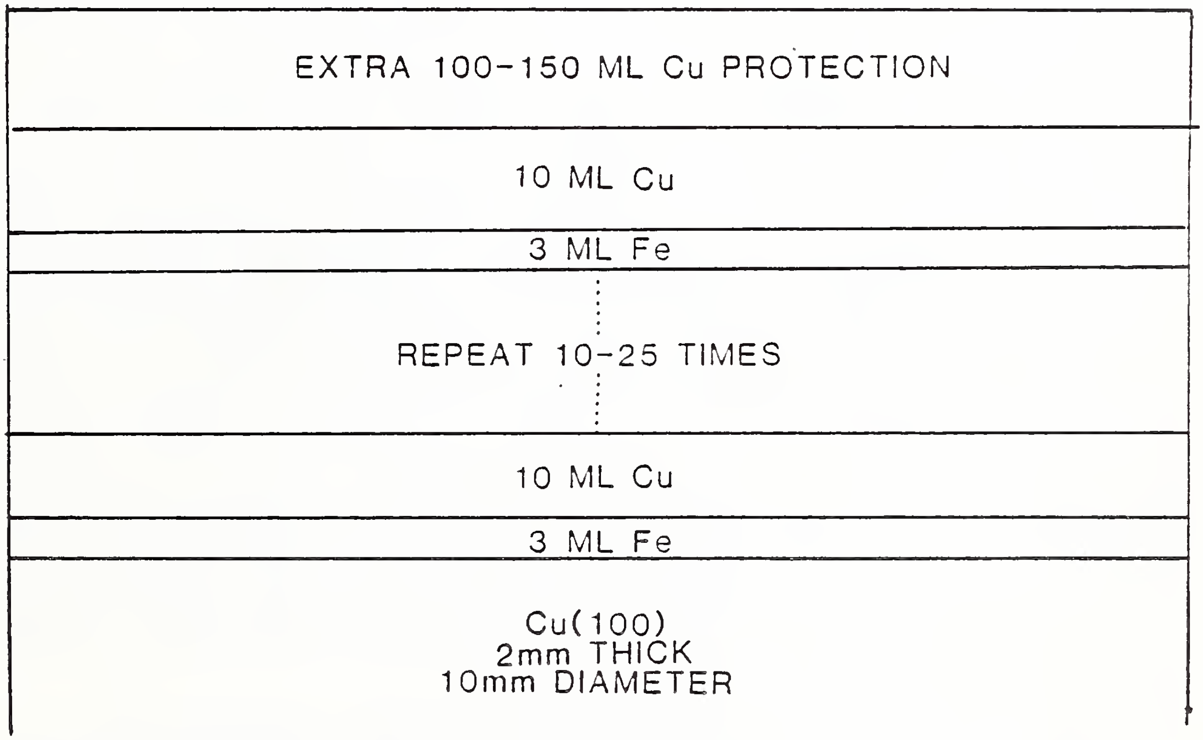

Fig. 4.3 A typical superlattice structure consisting of Cu and face-centered-cubic Fe.

In collaboration with Prof. B. Heinrich's group at Simon Fraser University in Canada, we have made Brillouin light scattering measurements and ferromagnetic resonance measurements on several sandwich and superlattice structures. We have found that our careful preparation of the Fe films has produced a major improvement in the magnetic properties of fcc-Fe films as compared to earlier work. Our films are ferromagnetic at room temperature and exhibit a strong perpendicular anisotropy holding the magnetic moment normal to the film. This anisotropy is uncommon, valuable, and a much-sought-after property for high-density magnetic recording. We have found that Fe film thicknesses of 3 ML produce the best magnetic properties.

Other groups have expressed an interest in collaborations to measure the properties of the novel and exotic crystal structures we are presently synthesizing. The group of Dr. R. F. Willis at Cambridge University in England is presently using neutron spin-flip methods to measure the absolute magnetic moment for several of our samples. We also expect to provide samples to groups at the Naval Research Laboratory (Dr. B. Jonker) and the University of Arizona (Dr. J. Dutcher) who will make measurements of other magnetic properties.

We plan to synthesize other novel or exotic crystal structures with other magnetic elements such as Co, Ni, Mn, and Cr on other non-magnetic substrates such as Ag, Au, and Pt. We believe that such structures hold considerable scientific promise and are an important source of new materials for technological applications.

3. Field-Ion Microscopy of High-Temperature Superconducting Materials

(A. J. Melmed, H. B. Elswijk*, and P. P. Camus)

A major activity during the past year has been an effort to use the special analytic capabilities of field-ion microscopy (FIM) and atom-probe (AP) mass analysis to obtain information towards the understanding of the atomic structure and physical properties of the new high-transition-temperature (T_c) superconducting oxides, a subject of intense worldwide interest. These superconductors are mostly produced in the form of ceramic wafers from compacted and heated powders, occasionally as small single crystals and most recently as thin films. They have, in general, a complex microstructure and most types are easily damaged by exposure to humidity in the environment or to many liquids. The mechanism of superconductivity is not known, and there are outstanding questions concerning the relationship between atomic structure and composition, microstructure, electronic structure, and superconductivity. The roles of grain-boundaries, twin planes, other defects, and composition variations are especially interesting.

The techniques of FIM and AP applied to metals, alloys and semiconductors provide real-space determinations of surface structure and qualitative bulk atomic structure, complementary to other microscopies and diffraction techniques. The unique capability of specimen dissection by controlled field evaporation enables elemental composition determinations to be made with sub-nanometer spatial resolution. Additionally, measurements of field-ion and field-electron energy distributions and electron work function provide probes of near-surface electronic structure. However, materials as complex as the high-T_c superconducting oxides have not in the past been studied by these techniques; new experimental methods were needed to enable such studies.

We have developed a new method of specimen preparation for FIM-AP and field electron emission microscopy (FEEM) of superconducting oxides. This method has proven to be applicable to other oxides, compound semiconductors, and probably a host of other non-ductile conducting materials, as well as to all of the presently known types of superconducting oxides. A small amount of material, typically about 10 cubic millimeters, is broken into fragments from which sharply pointed pieces are selected and attached to ends of tapered metal wires using an electrically conducting epoxy. The advantages of this technique compared to conventional methods of specimen preparation are: (1) no chemical or electrochemical artifacts occur, which is especially important for grain-boundary composition studies, (2) no weakening due to ion milling damage occurs, and (3) it is very rapid and conservative of sample material. We were initially concerned about the possibility of introducitng mechanical damage by the fracture process. However, transmission electron microscopy (TEM) results show that this does not occur. Also, if small-scale damage occurred on the fracture surface, we would normally remove such damage by field evaporation which allows probing through a depth of 1000 nm or more. This new method of specimen preparation heralds the application of FIM and associated measurements to a wide range of materials hitherto not amenable to such studies.

We have been able routinely to obtain FIM images of the other La-Sr-Cu-O type superconducting oxide, the R-Ba-Cu-O so-called "1,2,3" oxides (with R=Y, Yb, Sm, Gd, Dy, Ho, Er, Pr, Eu or La), and the newer Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O types. We have, however, mostly studied the "1,2,3" superconductors because the La-Sr-Cu-O type has proven to be too sensitive to degradation by laboratory humidity, and samples of the newer types have only recently become available. The work has progressed in collaboration with the following NIST scientists: Dr. C. K. Chiang of the Cermaics Division who prepares samples and measures resistivity; Dr. R. D. Shull of the Metallurgy Division who characterizes the samples by ac magnetic susceptibility; and Dr. H. A. Fowler of the Mathematical Analysis Division who provides computer-generated FIM images based on particular models. We also have two external collaborations: (1) Dr. M. K. Miller of the Oak Ridge National Labortory who is searching for defects and grain boundaries and determining microcomposition by AP; and (2) Dr. N. Ernst at the Fritz Haber Institute in Berlin who is measuring electron work functions and field-ion and field-electron energy distributions.

Our survey of the "1,2,3" superconductors has shown that a range of FIM image features occurs and that significant changes occur over a storage period of 8-10 months. Relatively fresh specimens made from wafers which had been shown by ac magnetic susceptibility meaurements to have sharp superconducting transitions at about 90 K and which had been stored in dry atmospheres for a few weeks or less yielded specimens whose FIM images had a totally unexpected character. The images consisted mostly of orderly parallel rows of brightly imaging atoms and molecules. These rows clearly are the intersections with the surface of parallel layers. This result was established from experiments in which several surface layers were field evaporated and photographically integrating the changing FIM image. As seen in Fig. 4.4, the image superposition results in approximately parallel bright stripes. These layers are perpendicular to the orthorhombic c-axis, demonstrated by TEM, and are spaced about 1.2 nm apart, measured from the FIM micrographs. The stripes are due to a very orderly and relatively rapid field evaporation of the atoms between the stripes. We are presently pursuing the identification of the atoms between the stripes, using an AP technique which selectively images a pre-chosen atomic species. The unusual, very orderly field evaporation suggests some special property of the layers, possibly enhanced electrical conductivity compared to the inter-layer material.

In addition to the striped images, we found some specimens whose images were mostly disordered and some with intermediate type images; that is partially ordered. Samples that were several months old yielded significantly fewer specimens which gave striped or partly striped images. The gradation of FIM images from striped through various decreasing amounts of striping can possibly be understood as the result of decreasing order of some elements in the oxide that would effect the field evaporation process. The most obvious correlation is with the known continuous variations in the stoichiometry and ordering of oxygen and oxygen vacancies in the Cu-O end-planes of the orthorhombic unit cell. Interestingly, a sample of Y-Ba-Cu-O which had been heated in nitrogen to remove some oxygen and which was shown by x-ray diffraction to be tetragonal, gave specimens which had mostly disordered FIM images. Some specimens, however, had images that were partly striped. These results indicate that the well-ordered tetragonal phase of Y-Ba-Cu-O also manifests some degree of ordered preferential field evaporation. It is difficult to produce bulk wafer samples with uniform oxygen doping. If we could, this would remove some of the variations in image types which we have observed. We hope to obtain improved material in order to better understand the FIM images.

We found no first-order effect in the FIM images going through the superconducing transition temperature, although there may be a second-order effect. This result is reasonable since the material is a layered electrinical conductor above T_c.

An exciting prospect arises from the fact that the striping of the FIM images provides a well-ordered atomic pattern, interruptions of which are easily detected. Thus, we have identified, with the help of TEM, the commonly occurring twin boundaries of the orthorhombic phase, grain-boundaries and other defects as well as various small inclusions of different material. We are beginning to apply our AP to the compositional analysis of local regions in and near such irregularities which may obstruct the transport of electrical current.

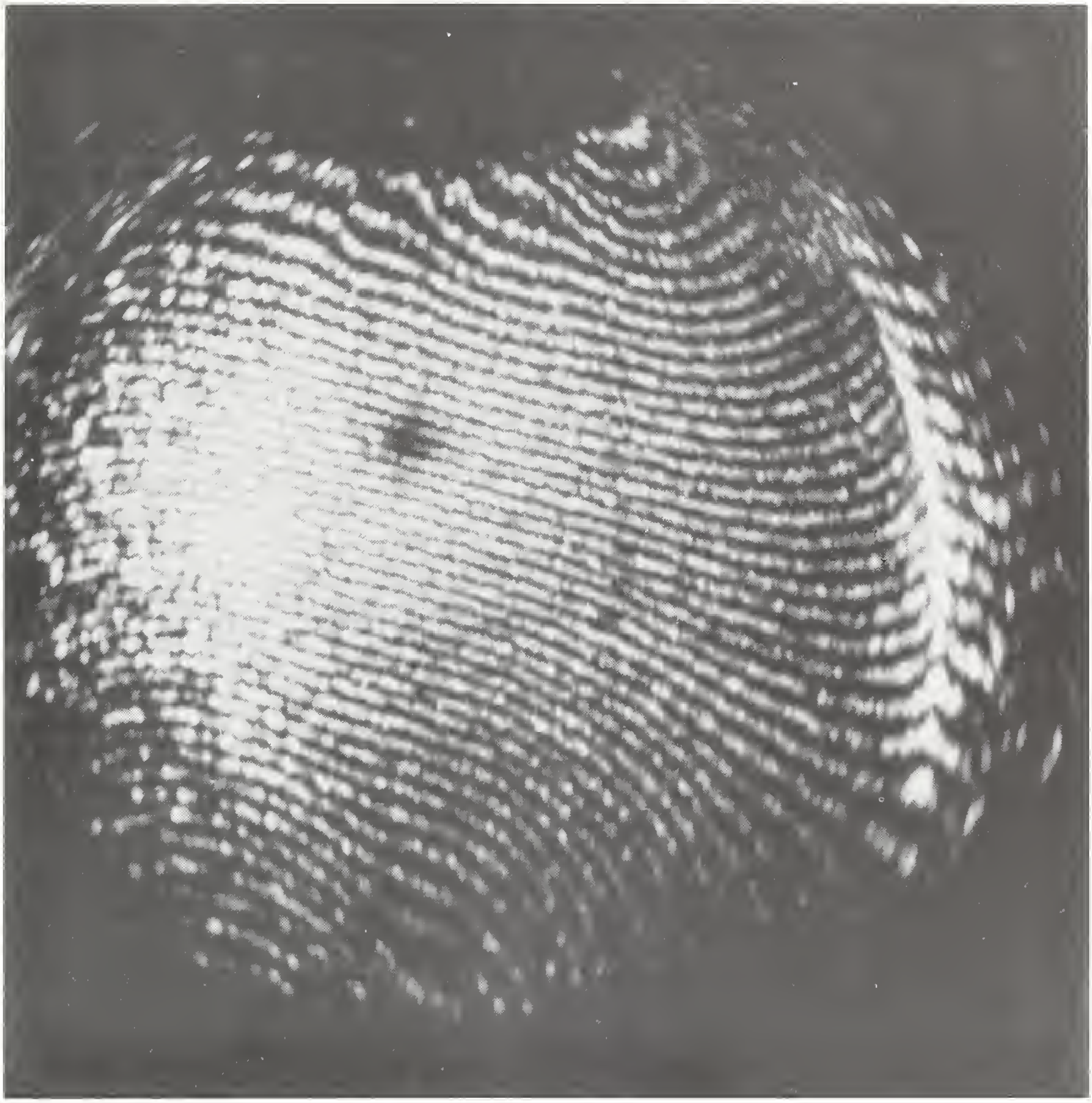

Fig. 4.4 Field-ion micrograph of the superconductor $YBa_2Cu_3O_{7-x}$ at 30 K. The orthorhomic c-axis is vertical. The separation of the layers (bright stripes) is about 1.2 nm. A twin boundary is seen on the right side as a vertical bright arc.

The problems of making good and durable electrical contacts and of applying protection overlayers for long-term storage of the superconducitng oxides are technologically important. Both problem areas involve questions of atomic diffusion between superconductors and adlayers. Therefore, we are beginning to study interdiffusion processes using our AP. We have done an experiment to learn how well our instrument could define a sharp interface. Copper was vapor-deposited onto an atomically smoothed and then air-exposed rhodium surface. Then, a composition depth-probe was made, going through the Cu and into the stepped surface adjacent to a Rh(111) plane. The results, shown in Fig. 4.5, shows two features of interst. First, the Cu/Rh(111) interface is defined within about a monolayer and second, the oxygen originally present on the Rh surface diffused several atomic layers into the Cu film. We intend to use several metals such as Ag, Rh and Al for overlayers on both clean and air-contaminated superconductors. An important advanatage of the AP compared to other composition probes for this type of study is its essentially single-atom sensitivity. This will allow us to investigate the important temperature regime between room temperature and, say, 100°C which is important in practical devices.

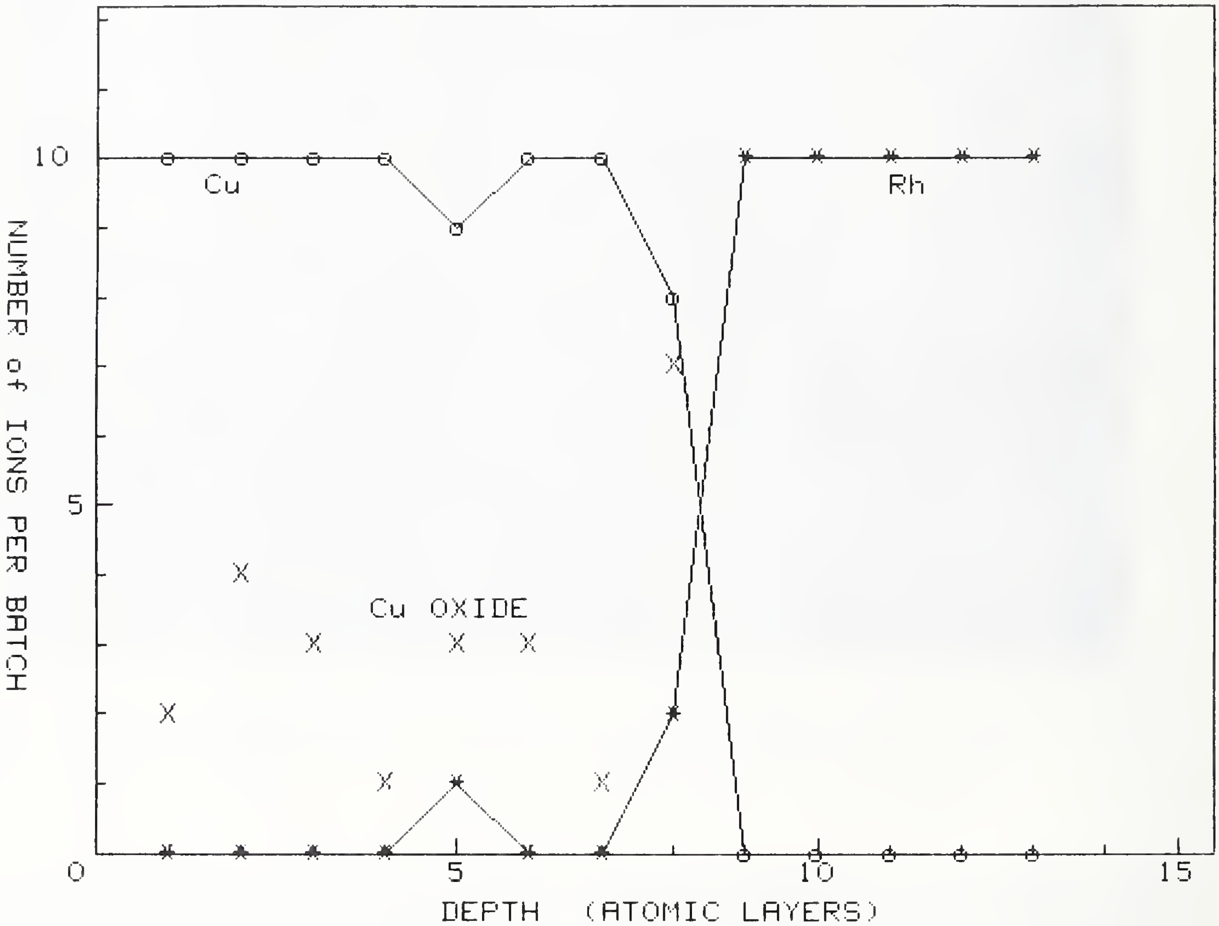

Fig. 4.5 An atom-probe depth profile for an air-exposed copper film on a Rh(111) surface showing the compositional variation of Cu(o), copper oxides (x), and rhodium (*) as a function of depth.

4. Microcomposition and Microstructure of Thin Films
(A. J. Melmed)

The nucleation and epitaxial growth of Cr crystalline overlayers were studied by vapor depositing chromium onto thermally annealed W field electron emitters. This procedure provided highly stepped substrates with low-index facets of various atomic configurations. Temperature and substrate morphology effects were identified and Cr/W epitaxial relationships were determined. In addition to the common Stranski-Krastanov (SK) nucleation mechanism (nucleation on top of a Cr overlayer) observed generally above ~ 500 K, low-temperature Cr nucleation and growth (~ 300 K) was observed on the W{110} planes. This process proceeded via either the SK or Volmer-Weber (VW) (nucleation directly on the substrate) mechanisms, depending upon the Cr deposition geometry.

Similar studies of Cr overlayer nucleation and crystal growth on Re substrates revealed that only bcc Cr (the normal structure) polycrystalline layers formed, in contrast to an earlier study of Eu/Re where both bcc and fcc structures occurred, depending on substrate crystallography. The difficulty of growing single crystals was attributed to the multiplicity of similar nucleation sites on the curved hcp substrate.

Our field-ion microscopy (FIM) studies of the Al/Mn icosahedral i-phase have agreed with transmission electron microscopy (TEM) determinations of long-range icosahedral symmetry. However, a consistent feature of the i-phase seen by FIM was short-range disorder, and this had not been reported in TEM results. In a collaboration with Dr. M. J. Kaufman, formerly of the NIST Metallurgy Division, we have conducted a careful TEM study to search for hitherto possibly overlooked evidence for structural disorder. Selected-area diffraction patterns from "off-axis" orientations showed not only sharp intensity maxima, but also a diffuse ring; overexposed diffraction patterns from axial orientations also showed the weak diffuse ring. These results were interpreted as evidence for structural disorder in the i-phase and support icosahedral cluster models with intercluster disorder. Our studies of the i-phase have been de-emphasized in favor of atom-probe FIM measurements of atomic interdiffusion across interfaces in metal/metal, metal-semiconductor, and metal/superconductor systems.

5. Theory of Novel Two-Dimensional Materials
(S. M. Girvin and M. J. DeWeert)

In this project, now concluded, we have investigated theoretically two problems concerning thin-film systems, the fractional quantum Hall effect and tunneling through a metal-insulator-metal junction.

In a collaboration with Dr. A. H. MacDonald, formerly with the Canadian National Research Council, we have investigated several aspects of the fractional quantum Hall effect (FQHE) and have demonstrated the existence of a peculiar type of off-diagonal long-range order (ODLRO) which gives rise to the FQHE.

In a superfluid, ODLRO is associated with Bose condensation. In the presence of a condensate, however, there is a non-zero amplitude that can destroy a particle in the condensate and create one far away. For the

FQHE, one can show that normally the density matrix is short-ranged and hence fails to exhibit ODLRO. This result occurs for two reasons, electrons are not bosons and so cannot Bose condense and even if they could, the magnetic field would destroy the long-range phase coherence. We have found nevertheless that there is a peculiar type of ODLRO hidden in this system. If one makes a singular gauge transformation which attaches a solenoid containing m flux quanta of a fake gauge field to each particle, two useful things occur. The statistics of the particles change from fermion to boson and the effect of the external magnetic field is eliminated. To see why the statistics change, consider exchanging two of the composite objects. In addition to the usual (-1) for fermions one obtains a Bohm-Aharanov phase factor from the charge of one particle seeing the flux tube on the other. This yields another factor of $(-1)^m$ which (m is odd) cancels the fermion sign leaving a (+1) as one would have for bosons. The singular-gauge density matrix exhibits ODLRO which we have been able to compute explicitly for the case of Laughlin's variational wave function. Thus the FQHE represents a condensation, not of ordinary particles, but of composite objects consisting of a particle and a gauge flux tube. It should be emphasized that this is not a tube of physical flux but rather a fake, non-dynamical gauge field.

This result extends the already deep analogies we have previously found between the FQHE and superconductivity and superfluidity. Both systems have dissipationless transport because of a remarkably low density of excited states at low energies. The collective mode is phonon-like at long wavelengths and exhibits a 'roton' minimum at intermediate wave lengths. Both types of systems exhibit quantized vortices. The vortices in a superconducting film carry quantized magnetic flux. In the FQHE, they carry quantized (fractional) charge. We have shown that one can develop a Landau-Ginsburg theory for the FQHE which is of the 'θ-vacuum' form of current interest in high-energy physics. This means essentially that charge and flux are mixed up in such a way that the natural objects in the theory carry both charge and flux.

The theory of the FQHE is now in excellent shape. Using Laughlin's wave function and the superfluidity analogy we have quantitatively accurate predictions for the collective mode dispersion, static susceptibility and related quantities which are amenable to experimental test.

In our second project, we have investigated the problem of what happens in a metal-insulator-metal tunnel junction when the insulator is ferromagnetic. The exchange field causes a spin asymmetry in the barrier height which allows only one spin to have a significant probability for tunneling. For example, typical parameters for a EuS barrier allow approximately 85% polarization of the tunnel current. The particular questions we have studied are: How large is the polarization that can be induced in the tunnel electrodes by this effect and what happens if the electrodes are superconducting? The steady-state polarization which builds up results from a competition between the tunneling time and the spin-flip relaxation time in the electrodes. For reasonable choices of parameters, it is possible to achieve polarizations equivalent to those which could be obtained in equilibrium only by application of magnetic fields of several

Tesla (fields much larger than those in the barrier for example). This polarization can affect the tunnel characteristics of the junction and can mimic the effect of field leaking out of the insulator into the electrodes.

A particularly interesting special case is that of superconducting electrodes. A polarizing barrier eliminates the possibility of Josephson tunneling for two reasons. First, only one spin member of the Cooper pair can tunnel easily. Second, the vector potential due to the ferromagnetic insulator destroys the phase coherence across the junction. This means that the tunnel characteristics are radically altered since only tunneling in the quasiparticle branch can be seen. It is then pertinent to ask how this injection of spin-polarized quasiparticles affects the superconductivity. This is a difficult non-equilibrium problem which we have chosen to attack in the following way. We assume a pseudo-equilibrium situation and seek that state which minimizes the free energy subject to the constraint that there is a given net spin polarization (so that not all electrons can be paired). This is handled by assuming a 'dead zone' in k-space in which the pair potential vanishes and the electrons are 100% polarized. The resulting modified BCS gap equation is then solved self-consistently. It turns out as expected that spin polarization weakens the superconductivity. If the polarization increases to the point that the width ν of the dead zone reaches

$$\nu = \Delta_0/2$$

where Δ_0 is the bare gap value, the superconductivity collapses and a normal Pauli spin-polarized state results. This leads to the prediction of a critical current in the tunnel junction above which superconductivity is destroyed. For lesser currents it may be possible to see the gap reduction optically (in the infrared absorption) although this may be a difficult experiment. It turns out that the dead zone produces a rather novel particle distribution which should also be detectable by spin resonance and related experiments.

B. State Characterization of Energetic Species Ejected from Surfaces

Specific state characterization of desorbed and ejected species from surfaces, whether induced by sputtering or by electron and photon bombardment, is still rare. It is now possible to address such dynamical surface interactions using laser techniques to determine the energy state, velocity, and angular distributions of <u>all</u> the ejected species--especially the neutrals which are the most abundant. Such studies can provide detailed microscopic information concerning energy transfer in these excitation-interaction processes.

The objective in this component of the program is to understand the excitation dynamics by which atoms and molecules are desorbed from surfaces in ion-sputtering processes as well as in electron- and photon-stimulated processes. Detailed characterization of the internal energy, kinetic energy, and desorption thresholds of desorbed species will provide a microscopic understanding of the nature of the electronic excitations leading to desorption due to collisions with electrons, photons, and ions.

Angular distributions will provide direct structural information concerning the surface geometry, as well as information concerning energy transfer during the collisional interaction.

We are performing work in two project areas. First, we are conducting an experiment in which laser-spectroscopic techniques will be used to determine the energy states of neutral atoms and molecules sputtered from surfaces by ion bombardment. Second, we are constructing a new type of display analyzer to measure angular and energy distributions of charged species desorbed from surfaces by electrons or photons to obtain surface-geometry information and to test theories of ejection mechanisms. Close contact is made with the related experimental and theoretical projects in the Division described in sections 3.A, 3.B, 3.J, 3.K, and 3.L.

1. Energy States of Neutral Species Sputtered from Surfaces
(J. Fine, P. Roncin*, R. Klein*, M. H. Mintz*, and M. H. Shapiro*)

Energetic ion-surface collisions generate extensive near-surface collision cascades in a solid. The energy transfer and atomic excitations that take place as a result of such collisions are not well understood in part because, until rather recently, the primary method for monitoring these collision phenomena was to measure macroscopic effects such as the total sputtering yield. The collision cascade causes the ejection of atoms, ions, electrons, and photons from the surface but it has only been in the past few years that measurements of the ejected particles or radiation have been utilized to obtain detailed information on specific atomic collisions that take place in condensed materials.

In recent experiments in which aluminum or silicon targets were bombarded by argon ions, we have shown that the Auger decay of collisionally excited Al or Si atoms can take place outside the solid depending on the distance from the surface (within the material) at which the excitation occurred, the atom's velocity, and the lifetime of the atomic excitation. As a result of our Monte-Carlo calculation to analyze these experiments, we expect that such sputtered atoms will have rather high kinetic energies - extending up to hundreds of electron volts. Collisions capable of transferring this much energy and creating inner-shell (2p) excitation can generate sputtered atoms (ions) which are in highly excited states. Such energy-transfer and excitation mechanisms are basic to our enhanced understanding of collisional processes in condensed materials. Information is required of those atomic processes which lead to electron promotion, excitation and ionization, and particle ejection. It is now possible to obtain this type of information by: (1) probing specific ejected (sputtered) atoms via resonant, multiphoton laser techniques; (2) monitoring the Auger-electron de-excitation of ejected atoms as well as those which decay inside the solid; and (3) computer calculations of the ion-solid collision cascade. Progress in each of these areas is described below.

(a) Laser Spectroscopy of Sputtered Atoms and Ions
(J. Fine, P. Roncin*, R. Klein*, and M. H. Mintz*)

In collaboration with Dr. J. D. Fassett of the NIST Inorganic Analytical Research Division, a new series of experiments has been designed to determine the kinetic energy distributions of specific sputtered atoms (ions) and their states of excitations. Measurements have been planned of: (1) the kinetic energy distributions of all the sputtered ions as a function of charge state, (2) the kinetic energy distributions of emitted electrons, (3) the collisional excitation of Rydberg states, (4) excited-state decay by photon emission, and (5) the kinetic energy distributions of sputtered atoms in specific excited states. Resonance multiphoton laser-ionization schemes have been developed to detect sputtered atoms in specific excited states.

During the past two years, a new instrument was constructed which consists of a sample manipulator, rapidly pulsed (50 ns) ion gun, pulsed time-of-flight (TOF) ion-extraction optics and detector, and windows for two laser beams. This instrument is now operational. Measurements have begun on the kinetic energy distributions of sputtered ions using the TOF spectrometer in an impulse-extraction mode together with pulsed ion-beam bombardment. Timing characteristics of the entire TOF impulse-mode extraction optics have been carefully analyzed. Timing of the ion pulse from ion gun to target has been established and observed flight times for sputtered ions have been found to be consistent with calculated flight times based on our analyzer geometry and potentials. TOF measurements were made as a function of the target potential and compared to calculations in order to establish an accurate kinetic energy scale for our energy distribution data. This turned out to be a non-trivial excercise and has resulted in an energy scale calibration which is probably accurate to < 3 eV.

Since it is critical that the impuse acceleration be applied just after all of the pulsed beam ions strike the target, we experimentally established optimum impulse extraction timing for various ion beam energies. This timing was verified by our calculations of flight times and trajectories for our high-collection-efficiency, large-aperture TOF analyzer. The transmission of this analyzer depends on both the emitted ion energy and the ion angle of emission for a given set of accelerting potentials. By varying these potentials, we can change the acceptance angle of our analyzer and so obtain information on the energy and angular distributions of collisionally ejected ions. Calculation of these critical ejection angles as a function of ion ejection energy for various TOF potentrals has been done and gives us a way of unfolding our ion kinetic energy distributions to obtain such energy/angle distributions.

Measurements have been made of the kinetic energy distributions of collisionally ejected ions from both polycrystalline Mg and Al due to the impact of 1.5 to 4 keV argon ions. The ions were incident on the target at 75°. Figure 4.6 shows the ion energy distributions obtained on polycrystalline aluminum as a function of bombarding ion energy; it is interesting to note the high abundance of ejected aluminum ions at energies greater

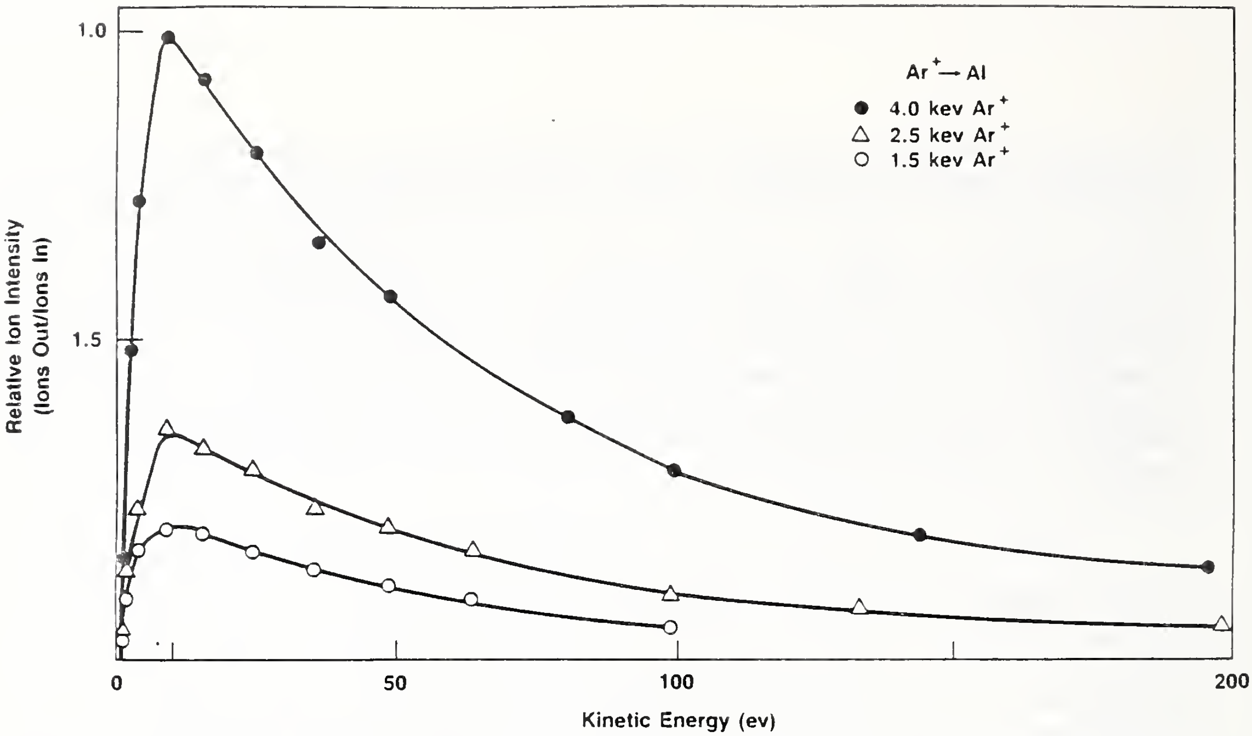

Fig. 4.6 Kinetic energy distributions of aluminum ions sputtered from an aluminum surface by argons ions of three different energies at an angle of incidence of 75°. These data have not been corrected for the enegy-dependence of the analyzer transmission function; the falloff in the distributions with increasing kinetic energy is less than that shown.

than 50 eV which is probably associated with collisional excitation and ionization mechanisms. Such measurements have also been made as a function of the TOF accelerating potentials; the data have been analyzed to obtain approximate emitted angular distributions for ions of 4, 9, 50, and 100 eV energy. Our results indicate that at higher energies, the emitted ions are strongly peaked toward the specular direction; at 4 eV the ions are emitted more uniformly but still peak near 50°. These results are consistent with computer calculations (such as those described below) which predict that collisionally excited, sputtered ions have high kinetic energy (~ 100 eV), are more probable for greater angles of incidence of the impacting ion beam, and are ejected with an angular distribution strongly peaked toward the specular direction. All of these angular/energy distribution results make it possible for us to proceed to the next phase of our research--to probe the charge and excitation state of collisionally excited ions and atoms using multiphoton resonance-ionization techniques.

We are currently measuring energy and angular distributions of sputtered ions from silicon and magnesium. We expect that a correlation of our results for Mg, Al, and Si with Auger-electron emission data for atomic-like collisional excitation should lead to a better understanding of the emission of singly and doubly charged, high-energy ions. We are also currently procuring a new high-current, pulsed ion gun and a tunable dye laser with frequency doubler.

(b) Auger-Electron De-Excitation of Sputtered Atoms
(J. Fine)

In collaboration with Drs. C. Le Gressus, J. P. Duraud, and D. Celier (Centre d'Etudes Nucleaires de Saclay, France), a series of measurements has been performed to investigate the Auger-electron emission from ion-bombarded single-crystal aluminum surfaces. Aluminum (100) and (111) surfaces were bombarded with argon ions and the dependence of atomic-like and band-like Auger-electron emission was monitored as the crystals were rotated about an axis normal to the surface. Our results indicate a very marked change in the total Auger-electrom emission intensity as a function of azimuthal angle. Intensity minima correspond to geometrical conditions where the incident ion beam is aligned with a string of atoms (i.e., there is a shadowing or underlying atoms by the outermost surface atom of a given string).

Similar measurements have now been obtained with incident xenon ions. Analysis of the data for both argon and xenon ions strongly suggests that collisional excitation and ejection of excited target atoms occur as a result of primary, asymmetric collisions (inert gas ion with target atom) and not because of secondary symmetric collisions (target atom with target atom) as previously suggested in the literature. This asymmetric model, developed in conjunction with Dr. G. Blaise (Orsay, France) is based on atom-atom scattering calculations and indicates that excited atoms are ejected from the outermost layer of surface atoms. Such excited atoms can be scattered directly (and ejected) or may be reflected by the second layer of atoms (and subsequently ejected) if the geometry of these second-layer atoms is appropriate.

(c) Simulation of Ion-Surfce Collisions
(M. H. Shapiro* and J. Fine)

Multiple-interaction calculations have been performed to simulate the ion-surface collisions occurring for typical sputtered conditions and to investigate the dynamical phenomena occurring in the resulting collision cascades. Preliminary results for argon ions bombarding an aluminum target indicate that asymmetric collisions are responsible for aluminum excitation and suggest that second-layer reflection is often important for ejection. Further analysis of the calculations should help to establish collisional-excitation mechanisms and trajectories and their dependence on atom geometry in the target.

2. Measurement of Angular, Energy and Mass Distributions of Desorbed Ionic Species
(R. L. Stockbauer, R. L. Kurtz, and T. E. Madey)

Several years ago we embarked on a program to design and construct a unique charged-particle energy analyzer which would have the capability of simultaneously measuring the energy, angular distribution, and mass of ions desorbed from surfaces. The design was based on an ellipsoidal mirror analyzer developed by Dr. D. E. Eastman of IBM. The construction of the analyzer is now complete and it will be installed on beamline 1 at SURF-II this autumn. This analyzer will play a key role in two areas of research, ion-desorption dynamics and angle-resolved photoemission.

We plan several experiments to elucidate the mechanisms of photon-stimulated desorption. One of the key questions which remains concerns the role of surfce geometry in the desorption process. With the new analyzer we will be able to tackle this problem. For instance, calculations of image-charge and reneutralization effects predict that the kinetic energy distributions of desorbed ions depend on the desorption angle. Since the new analyzer is capable of measuring kinetic energy as a function of angle, we will be able to assess the importance of these phenomena.

Likewise, the mass of the ions which make up the spots in the two-dimensional desorption pattern is also an important piece of information which has not been available to date. Hydrogen has a very large desorption probability and is present on most surfaces. Since it is the main background gas in an ultrahigh vacuum chamber, it is detected in almost all ion desorption studies. In our studies of O^+ desorption from different cyrstal faces of TiO_2, for example, almost as much H^+ was detected as was O^+. Without mass analysis, it was not possible to determine which spots or portions of spots in the pattern were due to H^+ and which to O^+. The new analyzer with its simultaneous mass and angle-resolving capabilities will be able to distinguish between the two ions and give separate patterns for each ion.

The analyzer will also play an important role in our photoemission studies of high-temperature superconductors (section 3.A). With its simultaneous energy and angle-resolving capability, we will be able to obtain angle-resolved photoelectron data on oriented thin films. This information can be compared directly to band-structure calculations which should lead to an understanding of the electronic interactions responsible for the superconductivity.

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Melmed, A. J., Shull, R. D., Chiang, C. K., and Fowler, H. A., "The Atomic Fingerprint of $YBa_2Cu_3O_{7-x}$ Type High-Temperature Superconductors Observed by Field Ion Microscopy," J. Mat. Sci. & Eng. (in press).

Miller, M. K., Melmed, A. J., and More, K. L., "Can APFIM Contribute to the Understanding of High Temperature Superconductors?" J. de Physique (in press).

Osofsky, M., Toth, L. E., Lawrence, S., Qadri, S. B., Shih, A., Mueller, D., Hein, R. A., Fuller, W. W., Rachford, F. J., Skelton, E. F., Elam, T., Gubser, D. U., Wolf, S. A., Gotaas, J. A., Rhyne, J. J., Kurtz, R. L., and Stockbauer, R., "Experimental Program on High T_c Oxide Superconductors at the Naval Research Laboratory," Proceedings of the Materials Research Society Symposium on High T_c Superconductors, Anaheim, CA, 1987 (in press).

Polak, M. and Madey, T. E., "The Structure of Molecular and Dissociated H_2O Adsorbed on Cu(110)," Surface Sci. (in press).

Powell, C. J., "Cross Sections for Inelastic Electron Scattering in Solids," Ultramicroscopy (in press).

Richter, L. J., Buntin, S. A., Cavanagh, R. R., and King, D. S., "Non-Boltzmann Rotational and Inverted Spin-Orbit State Distributions for Laser-Induced Desorption of NO from Pt(111)," J. Chem Phys. (in press).

Schmidt, W. A., Melmed, A. J., Lovisa, M. F., Naschitzi, M., and Block, J. H., "Field-Ion Energy Spectroscopy of Gold Overlayers on Silicon," Surface Sci. (in press).

Shivaprasad, S. M., Demmin, R. A., and Madey, T. E., "Characterization of Ultrathin Pt Overlayers on a W(110) Surface," Thin Solid Films (in press).

Steigerwald, D. A. and Egelhoff, Jr., W. F., "Structural Study of the Epitaxial Growth of fcc-Fe Films, Sandwiches, and Superlattices on Cu(110)," Surface Sci. (in press).

Steigerwald, D. A. and Egelhoff, Jr., W. F., "Two Simple, Metal Vapor Deposition Sources for a Downward Evaporation in Ultra-High Vacuum," J. Vac. Sci. Tech. (in press).

(c) Recent Publications of New Staff Members Resulting From Previous Positions (Buntin, Camus, Joyce, Richter, Robey, Stiles, and Yarmoff)

Buntin, S. A., Giese, C. F., and Gentry, W. R., "State-Resolved Differential Cross Sections for the Reaction D + H_2 → HD + H," J. Chem. Phys. 87, 1443 (1987).

Camus, P. P., "AP Analysis of Solute Clustering Above a Miscibility Gap," Journal de Physique, 48-C6, 331 (1987).

Gurney, B. A., Ho, W., Richter, L. J., and Villarrubia, J. S., "Multidetector Electron Energy-Loss Spectrometer for Time Resolved Surface Studies," Rev. Sci. Instr. 59, 22 (1988).

Himpsel, F. J., Karlsson, U. O., Morar, J. F., Rieger, D., and Yarmoff, J. A., "Microscopic Model for the Epitaxy of CaF_2 on Si(111)," Proc. of 1987 Spring Materials Research Society Meeting, Anaheim, CA.

Himpsel, F. J., Karlsson, U. O., McFeely, F. R., Morar, J. F., Rieger, D., Taleb-Ibrahimi, A., and Yarmoff, J. A., "Dielectrics on Semiconductors," Materials Science and Engineering B 1, 9 (1988).

Himpsel, F. J., Meyerson, B. S., McFeely, F. R., Morar, J. F., Taleb-Ibrahimi, A., and Yarmoff, J. A., "Core Level Spectroscopy at Silicon Surfaces and Interfaces," Proceedings of the Enrico Fermi School on "Photoemission and Absorption Spectroscopy of Solids and Interfaces with Synchrotron Radiation," Varenna, Italy, 1988 (North Holland, 1989).

Himpsel, F. J., Morar, J. F., and Yarmoff, J. A., "Surface Physics in Si MBE," in Proceedings of the Second International Symposium on Silicon Molecular Beam Epitaxy, 1987, edited by J. C. Bean and L.J. Schowalter (The Electrochemical Society, Pennington, NJ, 1988), p. 170.

Joyce, S., Langan, J. G., and Steinfeld, J. I., "Reactions of XeF_2 with Thermally Grown SiO_2," Surface Sci. 195, 270 (1988).

Joyce, S., Langan, J. G., and Steinfeld, J. I., "Chemisorption of Fluorocarbon free Radicals on Silicon and SiO_2," J. Chem. Phys. 88, 2027 (1988).

McFeely, F. R., Silverman, B. D., Yarmoff, J. A., and Karlsson, U. O., "The Structure of the Reaction Layer in the XeF_2-Si(111) System," in Proceedings of the Eighth International Symposium on Plasma Chemistry, Tokyo, 1987, edited by K. Akashi and A. Kinbara (International Union of Pure and Applied Chemsitry, Tokyo, Japan, 1987), p. 927.

Morar, J. F., Meyerson, B. S., Karlsson, U. O., Himpsel, F. J., McFeely, F. R., Rieger, D., Taleb-Ibrahimi, A., and Yarmoff, J. A., "Oxygen Removal From Si via Reaction with Adsorbed Ge," Appl. Phys. Lett. 50, 463 (1987).

Richter, L. J., Germer, T. A., and Ho. W., "Coadsorption Induced Site Changes: Bridging Hydrogen from CO and H on Rh(100)," Surface Sci. 195, L182 (1988).

Richter, L. J. Gurney, B. A., and Ho, W., "The Influence of Adsorbate-Adsorbate Interactions on Surface Structure: The Coadsorption of CO and H_2 on Rh(100)," J. Chem. Phys. 86, 477 (1987).

Richter, L. J. and Ho, W., "Vibrational Modes of Hydrogen Adsorbed on Rh(100) and Their Relevance to Desorption Kinetics," J. Vac. Sci. Tech. A 5, 453 (1987).

Richter, L. J. and Ho, W., "Vibrational Spectroscopy of H on Pt(111): Evidence for Universally Soft Parallel Modes," Phys. Rev. B 36, 9797 (1987).

Robey, S. W. and Oehrlein, G. S., "Valence Band Photoemission and Electron Energy Loss Studies of Reactive Ion Etched Silicon Dioxide," J. Vac. Sci. Tech. A 6, 1503 (1988).

Schrott, A. G., Cohen, S. L., Dinger, T. R., Himpsel, F. J., Yarmoff, J. A., Frase, K. G., Park, S. I., and Purtell, R., "Photoemission Study of Grain Boundary Segregation in $Y_1Ba_2Cu_3O_7$," in Proceedings of the Topical Conference on Thin Film Processing and Characterization of High-Temperature Superconductors, Anaheim, 1987, edited by J. M. E. Harper, R. J. Colton and L. C. Feldman (American Institute of Physics, Conference Proceedings No. 165, 1988), p. 349.

Stiles, M. D. and Hamann, D. R., "Ballistic Electron Transmission Through Interfaces," Phys. Rev. B 38, 2021 (1988).

Stiles, M. D. and Wilkins, J. W., "Inelastic Gas-Surface Scattering. II. Results," Phys. Rev. B 37, 7306 (1988).

Whitman, L. J., Gurney, B. A., Richter, L. J., Villarrubia, J. S., and Ho, W., "The Kinetics of CO Dissociation on Fe(111)," J. Vac. Sci. Tech. A 5, 538 (1987).

Yarmoff, J. A., Clarke, D. R., Drube, W., Karlsson, U. O., Taleb-Ibrahimi, A., and Himpsel, F. J., "Valence Electronic Structure of $Y_1Ba_2Cu_3O_7$," Phys. Rev. B 36, 3967 (1987).

Yarmoff, J. A. and McFeely, F. R., "Mechanism of Ion-Assisted Etching of Silicon by Fluorine Atoms," Surface Sci. 184, 389 (1987).

Yarmoff, J. A. and McFeely, F. R., "Constant Final-State Photoemission Study of Silicon Fluorine Reaction Layer Created During Etching: Morphology of the Reaction Layer," in *Photon Beam and Plasma Stimulated Chemical Processes at Surfaces*, edited by V. M. Donnelly, I. P. Herman and M. Hirose, (volume 75 of Material Research Society Symposium Proceedings, Pittsburgh, PA, 1987), p. 451.

Yarmoff, J. A. and McFeely, F. R., "Chemical Vapor Deposition of Tungsten on Silicon Studied with Soft X-Ray Photoemission," Proceedings of the Workshop on Tungsten and Other Refractory Metals for VLSI Applications IV, IBM, Yorktown Heights, NY, 1987.

Yarmoff, J. A., Clarke, D. R., Drube, W., Karlsson, U. O., Taleb-Ibrahimi, A., and Himpsel, F. J., "Electronic Structure of $Y_1Ba_2Cu_3O_7$," in *Proceedings of the Topical Conference on Thin Film Processing and Characterization of High-Temperature Superconductors*, Anaheim, 1987, edited by J. M. E. Harper, R. J. Colton, and L. C. Feldman (American Institute of Physics, Conference Proceedings No. 165, 1988), p. 264.

Yarmoff, J. A. and McFeely, F. R., "Chemical Vapor Deposition of Tungsten on Silicon and Silicon Oxide Studies with Soft X-Ray Photoemission," in *Proceedings of the Topical Conference on Deposition and Growth: Limits for Microelectronics*, Anaheim, 1987, edited by G. W. Rubloff (American Institute of Physics, Conference Proceedings No. 167, 1988).

Yarmoff, J. A. and McFeely, F. R., "Effect of Sample Doping Level During Etching of Silicon by Fluorine Atoms," Phys. Rev. B *38*, 2057 (1988).

Yarmoff, J. A. and McFeely, F. R., "Mechanism for Chemical-Vapor Deposition of Tungsten on Silicon from Tungsten Hexafluoride," J. Appl. Phys. *63*, 5213 (1988).

Yarmoff, J. A., Taleb-Ibrahimi, A., McFeely, F. R., and Avouris, Ph., "Chemical Selectivity in Photon-Stimulated Desorption of Fluorine from Silicon," Phys. Rev. Lett *60*, 960 (1988).

6. INVITED TALKS

Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation Rates (Metal Clusters)," Application of Lasers in Surface Science Conference, Trieste, Italy, August 15, 1988.

Demmin, R. A., "Structure and Adsorption Properties of Tungsten-Supported Platinum Films," Exxon Research and Engineering Company, Linden, NJ, June 9, 1988.

Demmin, R. A., "Structure and Adsorption Properties of Tungsten-Supported Platinum Films," W. R. Grace & Co., Columbia, MD, June 27, 1988.

Demmin, R. A., "Structure and Adsorption Properties of Tungsten-Supported Platinum Films," Air Products and Chemicals, Inc., Allentown, PA, July 7, 1988.

Egelhoff, Jr., W. F., "XPS Forward Scattering Studies of Epitaxial Growth," University of Colorado, Boulder, CO, November 13, 1987.

Egelhoff, Jr., W. F., "XPS and Auger Forward Scattering: A Structural Tool for Studying Ultrathin Films, Epitaxial Growth, Surface Segregation, and Interdiffusion," Fritz-Haber-Institut, Berlin, W. Germany, December 7, 1987.

Egelhoff, Jr., W. F., "XPS and Auger Forward Scattering: A Structural Tool for Studying Ultrathin Films, Epitaxial Growth, Surface Segregation, and Interdiffusion," Physics Institute, Clausthal University, Clausthal, W. Germany, December 9, 1987.

Egelhoff, Jr., W. F., "XPS and Auger Forward Scattering: A Structural Tool for Studying Ultrathin Films, Epitaxial Growth, Surface Segregation, and Interdiffusion," KFA, Jülich, W. Germany, December 10, 1987.

Egelhoff, Jr., W. F., "XPS and Auger Forward Scattering: A Structural Tool for Studying Ultrathin Films, Epitaxial Growth, Surface Segregation, and Interdiffusion," Cambridge, University, Cambridge, England, December 14, 1987.

Egelhoff, Jr., W. F., "XPS and Auger Forward Scattering: A Structural Tool for Studying Ultrathin Films, Epitaxial Growth, Surface Segregation, and Interdiffusion," Warwick University, Warwick, England, December 15, 1987.

Egelhoff, Jr. W. F., "XPS and Auger Forward Scattering: A Structural Tool for Studying Ultrathin Films, Epitaxial Growth, Surface Segregation and Interdiffusion," Department of Materials Sciences, University of Florida, Gainesville, FL, January 19, 1988.

Egelhoff, Jr., W. F., "XPS and Auger Forward Scattering: A Structural Tool for Studying Ultrathin Films, Epitaxial Growth, Surface Segregation, and Interdiffusion," Greater Washington Surface Science Seminar, National Institute of Standards and Technology, Gaithersburg, MD, May 20, 1988.

Egelhoff, Jr., W. F., "XPS and Auger Forward Scattering: A Structural Tool for Studying Ultrathin Films, Epitaxial Growth, Surface Segregation and Interdiffusion," Chemistry Department, Rutgers University, Piscataway, NJ, September 15, 1988.

Fine, J., "State Characterization of Collisionally Ejected Atoms from Surfaces," Division of Physical Chemistry, CEN-Saclay, France, October 10, 1987.

Gadzuk, J. W., "Molecular Aspects of Surface Chemical Dynamics," Workshop/ Symposium on Chemistry at Interfaces, Battelle Pacific Northwest Laboratories, Richland, WA, October 8, 1987.

Gadzuk, J. W., "Elementary Molecular Dynamics at Surfaces," Joint Institute of Laboratory Astrophysics Colloquium, University of Boulder, Boulder, CO, October 27, 1987.

Gadzuk, J. W., "Charge Transfer and Molecular Processes at Surfaces," Chemical Dynamics Seminar, Naval Research Laboratory, Washington, D.C., November 12, 1987.

Gadzuk, J. W., "Soluble Models in Surface Collision Dynamics," International Solvay Conference on Surface Science, University of Texas, Austin, TX, December 14, 1987.

Gadzuk, J. W., "Elementary Molecular Dynamics at Surfaces, Surface Science Seminar, University of Pittsburgh, Pittsburgh, PA, March 4, 1988.

Gadzuk, J. W., "Chaos in Surface Physics," Department of Physics Colloquium, Rice University University, Houston, TX, April 13, 1988.

Gadzuk, J. W., "Dynamics and Charge Transfer Processes at Surfaces," 173rd Meeting of the Electrochemical Society, Atlanta, GA, May 18, 1988.

Gadzuk, J. W., "Chaos in Surface Physics," Surface Physics, Physical Chemistry, and Theoretical Physics Departments, Fritz-Haber-Institut, Berlin, W. Germany, June 28, 1988.

Gadzuk, J. W., "Chaos in Surface Physics," Application of Lasers in Surface Science Conference, Trieste, Italy, August 22, 1988.

Jach, T., "Developments in X-Ray Standing Waves," Cornell Synchrotron Users Conference, Cornell University, Ithaca, NY, June 14, 1988.

Joyce, S., "Determination of Molecular Adsorbate Structures Using Electron Stimulated Desorption Ion Angular Distributions (ESDIAD)," Greater Washington Surface Science Seminar, National Institute of Standards and Technology, Gaithersburg, May 20, 1988.

Kurtz, R. L., "Photoemission Studies of High T_c Superconductors," American Vacuum Society Meeting, Anaheim, CA, November 4, 1987.

Kurtz, R. L., "Photoemission Studies of the Electronic Structures of High-T_c Superconductors," Yale University, New Haven, CT, April 8, 1988.

Kurtz, R. L., "Synchrotron Radiation Studies of High-T_c Superconductors," Greater Washington Surface Science Seminar, National Institute of Standards and Technology, Gaithersburg, MD, May 20, 1988.

Kurtz, R. L., "Surface Structure and Mechanisms in Ion Desorption from Oxide Surfaces," CSIC, Madrid, Spain, September 20, 1988.

Kurtz, R. L., "Electronic Structure of High-T_c Superconductors Studied Using Photoelectron Spectroscopy," IRIVA, 1st Iberian Vacuum Meeting, Braga, Portugal, September 29, 1988.

Madey, T. E., "The Interaction of Water with Surfaces," Rutgers University, Brunswick, NJ, October 29, 1987.

Madey, T. E., "Electron and Photon Stimulated Desorption as Probes of Structure and Bonding at Surfaces," Department of Materials Science, University of Virginia, Charlottesville, Virginia, November 16,1987.

Madey, T. E., "Electron and Photon Stimulated Desorption as Probes of Structure and Bonding at Surfaces," 7th International Conference on Thin Films, New Delhi, India, December 10, 1987.

Madey, T. E., "Interaction of H_2O with Surfaces," Solar Energy Research Institute, Golden, CO, January 14, 1988.

Madey, T. E., "Recent Advances in Electron Stimulated Desorption Ion Angular Distributions (ESDIAD) of Positive and Negative Ions," Brookhaven National Laboratory, Upton, NY, March 7, 1988.

Madey, T. E., "Structure and Reactivity of Chemisorbed Species," Engelhard Corp., Newark, NJ, March 8, 1988.

Madey, T. E., "Recent Advances in Electron Stimulated Desorption Ion Angular Distributions (ESDIAD) of Positive and Negative Ions," Sandia National Laboratory, Albuquerque, NM, March 18, 1988.

Madey, T. E., "Electron and Photon Stimulated Desorption: Benefits and Pitfalls," European Vacuum Conference, Salford (Manchester), England, April 14, 1988.

Madey, T. E., "The Interaction of H_2O with Surfaces," University of Warwick, Warwick, England, April 19, 1988.

Madey, T. E., "The Interaction of H_2O with Surfaces," University of Liverpool, Liverpool, England, April 20, 1988.

Madey, T. E., "Radiation Damage in Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy," 10th Symposium on Applied Surface Analysis, Topical Conference of the American Vacuum Society, Lakewood, CO, April 29, 1988.

Madey, T. E., "Electron and Photon Stimulated Desorption as Probes of Structure and Bonding at Surfaces," Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA, May 10, 1988.

Madey, T. E., Series of 5 lectures on "Electron and Photon Stimulated Desorption as Probes on Structure and Bonding at Surfaces," International Center for Theoretical Physics, Trieste, Italy, May 30-June 3, 1988.

Madey, T. E., "The Adsorption of Water on Surfaces: Basic Aspects," International Conference on the Chemistry and Physics of Electrified Surfaces, Bologna, Italy, August 30, 1988.

Madey, T. E., "The Adsorption of Water on Surfaces: Basic Aspects," Fourth Joint Vacuum Conference, Portoroz, Yugoslavia, September 23, 1988.

Madey, T. E., "IUVSTA - Past, Present, and Future," Swedish Academy of Engineering Sciences, Stockholm, Sweden, September 27, 1988.

Madey, T. E., "Direct Determination of the Structure of Surface Molecules," Swedish Academy of Engineering Sciences, Stockholm, Sweden, September 27, 1988.

Marton, D., "Ion-Bombardment Induced Surface Roughness of Thin Metallic Layers," Fourth International Conference on Metrology and Properties of Engineering Surfaces, National Institute of Standards and Technology, Gaithersburg, MD, April 14, 1988.

Melmed, A. J., "The Atomic Fingerprint of High-T_c Superconductors Observed by FIM," Physics Department Seminar, Michigan State University, Lansing, MI, January 26, 1988.

Powell, C. J., "Dependence of Inelastic Electron Mean Free Paths on Electron Energy and Material," European Conference on Applications of Surface and Interface Analysis, Schwabenlandhalle, Fellbach, W. Germany, October 19, 1987.

Powell, C. J., "Observation of Recoil Energy Losses in Elastic Scattering of Electrons from Surfaces," European Conference on Applications of Surface and Interface Analysis, Schwabenlandhalle, Fellbach, W. Germany, October 20, 1987.

Powell, C. J., "Surface Chemical Analysis: Report on the VAMAS Project," European Conference on Applications of Surface and Interface Analysis," Schwabenlandhalle, Fellbach, W. Germany, October 22, 1987.

Powell, C. J., "The International Development of Standards for Surface Analysis," Topical Conference on Quantitative Surface Analysis, Monterey, CA, October 31, 1987.

Powell, C. J., "Accomplishments of the VAMAS Surface Chemical Analysis Working Party," Versailles Project on Advanced Materials and Standards (VAMAS) International Steering Committee, Brussels, Belgium, February 17, 1988.

Powell, C. J., "Comparison of L_3-Shell Binding Energies in Six 3d Metals by X-ray Photoelectron Spectroscopy, Appearance-Potential Spectroscopy, and Electron Energy-Loss Spectroscopy," Physics Institute, University of Odense, Odense, Denmark, February 18, 1988.

Powell, C. J., "Cross Sections for Inelastic Electron Scattering in Solids," U.S.-French Workshop on Electron Beam Induced Spectroscopies at Very High Spatial Resolution, Aussois, France, February 29, 1988.

Powell, C. J., "Appearance Potential Spectroscopy of Solids and Comparisons of L_3-Shell Binding Energies of Ti-Ni as Measured by APS, EELS, and XPS," Workshop on Electron-Beam Induced Spectroscopies at Very High Spatial Resolution, Aussois, France, March 1, 1988.

Powell, C. J., "Comparison of L_3-Shell Binding Energies of Six 3d Metals by X-ray Photoelectron Spectroscopy, Appearance-Potential Spectroscopy, and Electron Energy-Loss Spectroscopy," University of Liverpool, Liverpool, England, April 14, 1988.

Powell, C. J., "Recent Developments in Applied Surface Science," Research Highlights Seminar of the International Union of Vacuum Science, Technique and Applications, University of Salford, Manchester, England, April 15, 1988.

Powell, C. J., "Calculations of Electron Inelastic Mean Free Paths for 31 Materials," Greater Washington Surface Science Seminar, National Institute of Standards and Technology, Gaithersburg, MD, May 20, 1988.

Richter, L. J., "Laser Induced Desorption of NO from Pt(111): Dynamics of Excitation and Desorption," Application of Lasers in Surface Science Conference, Trieste, Italy, August 25, 1987.

Stockbauer, R., "Electronic Structure and the Surface Chemistry of High T_c Superconductors and Related Compounds," An International Symposium on the Uses of Synchrotron Radiation in Chemistry, Upton, NY, November 6, 1987.

Stockbauer, R., "Surface Chemistry of High T_c Superconductors," NIST Gaithersburg-Boulder Superconductivity Meeting, December 7, 1987.

Stockbauer, R., "Recent Photoemission Results on High-T_c Superconductors," NIST Boulder-Gaithersburg Superconductivity Meeting, Boulder, CO, July 14, 1988.

Stockbauer, R., "Photoemission Studies of High Temperature Superconductors," Department of Physics, Louisiana State University, Baton Rouge, LA, September 29, 1988.

Yarmoff, J. A., "The Interaction of Fluorine with Silicon Surfaces," Gordon Research Conference on the Chemistry of Electronic Materials, Ventura, CA, March 8, 1988.

Yarmoff, J. A., "Synchrotron Radiation Studies of the Fluorine-Silicon Interaction," Xerox Webster Research Center, Rochester, NY, June 10, 1988.

7. SURFACE SCIENCE DIVISION SEMINARS

Amirav, A., Tel Aviv University, Tel Aviv, Israel, "Molecular Ionization and Dissociative Ionization in Hyperthermal Molecular Surface Scattering," September 21, 1988.

Ballentine, C., University of Texas, Austin, TX, "Magnetic Properties of Epitaxial Fe, V, and Ni Films on Ag(100)," June 10, 1988.

Bloch, J. M., Argonne National Laboratory, Chicago, IL, "Studies of Interfaces and Thin Films Using X-Ray Grazing Incidence Techniques," February 25, 1988.

Camus, P. P., Oak Ridge National Laboratory, Oak Ridge, TN, "Atom Probe Field Ion Microscopy of Fe-Cr-Co Alloys," March 18, 1988.

Doren, D., AT&T Bell Labortories, Murray Hill, NJ, "Precursors to Chemisorption: What Difference Do They Make?" December 4, 1987.

Dutcher, J., Simon Fraser University, Vancouver, Canada, "Brillouin Light Scattering of Magnetic Surface Anisotropy," June 3, 1988.

Heinrich, B., Simon Fraser University, Burnaby, Canada, "MBE Studies and Magnetic Properties of Ultrathin Films and Sandwiches of bcc Ni(001) and bcc Fe(001) Epitaxially Grown on fcc Ag(001)," Joint seminar with Electron Physics Group, March 17, 1988.

Henrich, V. E., Yale University, New Haven, CT, "Bulk and Surface Electronic Structure of Rock Salt Transition-Metal Monoxides," November 24, 1987.

Holloway, S., Liverpool University, Liverpool, England, "Time-Dependent Quantum Approach to Gas-Surface Dynamics and Rust-Busting," April 19, 1988.

Kevan, S. D., University of Oregon, Eugene, OR, "Intuition and Surface Electronic Structure," October 8, 1987.

Kiskinova, M., University of Pittsburgh, Pittsburgh, PA, "CO and NO Adsorption on Pt(111) and Modified Pt(111) Surfaces," August 12, 1988.

McFeely, F. R., IBM T. J. Watson Research Center, Yorktown Heights, NY, "Photoemission Studies of Selective Tungsten CVD on Silicon and SiO_2," September 6, 1988.

Mundschau, M., University of Clausthal, Clausthal, Germany, "Low-Energy Electron Microscopy," January 19, 1988.

Paul, J., Royal Institute of Technology, Sweden, "Adsorption on Aluminum," November 18, 1987.

Richmond, G. L., University of Oregon, Eugene, OR, "Non-Linear Optics as a Probe of Interfacial Structure and Dynamics," October 13, 1987.

Robey, S. W., IBM Watson Research Center, Yorktown Heights, NY, "Photoemission Studies of Plasma Etched Surfaces," March 15, 1988.

Ross, P., Department of Energy, Germantown, MD, "Structure Determination at Liquid-Solid Interfaces Using Grazing Incidence X-Ray Scattering," February 3, 1987.

Sault, A., Sandia National Laboratories, Albuquerque, NM, "Dissociation of Alkanes on Ni(100)," January 11, 1988.

Shapiro, M. H., National Science Foundation, Washington, DC, "Molecular Dynamics Simulations of Ion/Surface Collisional Excitation," June 15, 1988.

Stiles, M., AT&T Bell Laboratories, Murray Hill, NJ, "Ballistic Electron Transmission Through Interfaces," May 26, 1988.

Stuve, E., University of Washington, Seattle, WA, "The Adsorption of Solvent and Ionic Species on Metal Surfaces," November 20, 1987.

Tatar, R. C., General Electric R&D Center, Schenectady, NY, "Electron Correlation and Valence Bonds in Metals and Intermetallic Compounds," September 21, 1987.

Whitman, L. J., Cornell University, Ithaca, NY, "Kinetics and Mechanisms of K-Promoted Surface Reactions," March 30, 1988.

8. CONFERENCES ORGANIZED OR HOSTED

Workshop on Quantitative Surface Analysis, NIST, October 24, 1986 (cosponsored by the Applied Surface Science Division of the American Vacuum Society, ASTM Committee E-42 on Surface Analysis, and the Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards).

Meeting of ASTM Committee E-42 on Surface Analysis, Gaithersburg, MD, October 25, 1986.

10th International Vacuum Congress/6th International Conference on Solid Surfaces/33rd National Symposium of the American Vacuum Society, Baltimore, MD, October 27-31, 1986.

Symposium on Surface Analysis, 22nd Annual Meeting of the Microbeam Analysis Society, Kona, HI, July 13-17, 1987.

6th Department of Energy, Catalysis and Surface Chemistry Research Conferences, NIST, October 14-16, 1987.

2nd Topical Conference on Quantitative Surface Analysis, Monterey, CA, October 30-31, 1987 (cosponsored by the Applied Surface Science Division of the American Vacuum Society, ASTM Committee E-42 on Surface Analysis, and the Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards).

Greater Washington Surface Science Seminar, NIST, May 20, 1988.

9. TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Cavanagh, R. R.

Treasurer, General Committee of the Physical Electronics Conference

Local Co-Chairman, Physical Electronics Conference in 1990

Member (1987) and Chairman (1988) of the NIST Research Advisory Committee

Egelhoff, Jr., W. F.

NIST Representative to SEMATECH Planning Workshop on Physical Vapor Deposition, San Francisco, CA, September 21-22, 1987.

Erickson, N. E.

Member, ASTM Committee E-42 on Surface Analysis

Fine, J.

Chairman, Subcommittee E-42.09 on Standard Reference Materials of ASTM Committee E-42 on Surface Analysis

Gadzuk, J. W.,

Member, Editorial Advisory Board, "Progress in Surface Science"

Member, International Steering Committee, 5th International Conference on Vibrations at Surfaces, Garmisch-Partenkirschen, FRG, September, 1987

Member, Organizing Committee, 6th International Conference on Vibrations at Surfaces, 1990

Madey, T. E. .

Member, American Institute of Physics Subcommittee on Intellectual Property Rights

Program Chairman, 10th International Vacuum Congress/6th International Conference on Solids Surfaces/33rd National Symposium of the American Vacuum Society, Baltimore, MD, October, 1986

Secretary General, International Union for Vacuum Science, Technique and Applications

Member, Program Advisory Committee for the Synchrotron Radiation Center of the University of Wisconsin, Madison, Wisconsin

Member, International Advisory Committee, Beijing Laboratory of Vacuum Physics, Peoples Republic of China

Member, Advisory Committee for Laboratory of Surface Science and Technology at the University of Maine, Orono, ME

Member, Policy Board for High Resolution Electron Microscope Facility, Arizona State University

Member, International Advisory Committee, Second International Conference on the Structure of Surfaces, Amsterdam, The Netherlands, June, 1987.

Member, International Advisory Committee, Workshop on Desorption Induced by Electronic Transitions, DIET-III, Long Island, NY, May, 1987 and DIET-IV, Austria, October, 1989

Member, ASTM Committee E-42 on Surface Analysis

Member, Editorial Board, "Methods of Surface Characterization"; co-editor of two volumes in series

Melmed, A. J.

President (7/86 through 7/87), International Field Emission Society

Division Safety Officer (2/86 through 1/88)

Chairman, Organizing Committee, International Field Emission Symposium, 1990

Powell, C. J.

Member, Executive Committee, and International Liaison, ASTM Committee E-42 on Surface Analysis

Chairman (through 10/87) and Vice-Chairman (from 11/87), Surface Chemical Analysis Working Party, Versailles Project on Advanced Materials and Standards

Member, Board of Trustees, Gordon Research Conferences

Member (from 1/88), Board of Directors, American Vacuum Society

Member (through 11/87), Ad Hoc Committee on Topical Conferences, American Vacuum Society

Chairman, Applied Surface Science Division Steering Committee, International Union of Vacuum Science, Technique, and Applications

Chairman, Applied Surface Science Program Committee for the 11th International Vacuum Congress and 7th International Conference on Solid Surfaces, Cologne, FRG, September 25-29, 1989

National Representative, Commission I.6 on Colloid and Surface Chemistry including Catalysis, International Union of Pure and Applied Chemistry

Co-Opted Member, Subcommittee on Surface Analysis of Commission V.2 on Microchemical Techniques and Trace Analysis, International Union of Pure and Applied Chemistry

Chairman, Organizing Committee, Workshop on Quantitative Surface Analysis, NIST, October 24, 1986

Co-Chairman, Symposium on Surface Analysis, Microbeam Analysis Society, Kona, HI, July 13-17, 1987.

Chairman, Organizing Committee, 2nd Topical Conference on Quantitative Surface Analysis, Monterey, CA, October 30-31, 1987

Member, Editorial Board, "Applications of Surface Science"

Member, Editorial Board, "Surface and Interface Analysis"

Member, Editorial Board, "Methods of Surface Characterization"; co-editor of one volume in series

NIST Representative, SEMATECH Workshop on DoE National Laboratories and the US Semiconductor Industry, Albuquerque, NM, May 26-28, 1987

Stockbauer, R.

Assistant Program Chairman, 10th International Vacuum Congress/6th International Conference on Solid Surface/33rd National Symposium of the American Vacuum Society, Baltimore, MD, October, 1986

Member, Office Automation Committee, American Vacuum Society

Division Safety Officer (from 2/88)

10. PROFESSIONAL INTERACTIONS, CONSULTING AND ADVISORY SERVICES

Cavanagh, R. R.

Collaborating with Drs. J. J. Rush, T. J. Udovic and J. M. Nicol of the NIST Reactor Radiation Division on measurements of vibrational, torsional, and re-orientational dynamics of molecular species in and on high-surface-area materials.

Collaborating with Drs. J. C. Stephenson, T. E. Heilweil and M. P. Casassa of the NIST Molecular Spectroscopy Division on time-resolved measurements of vibrational relaxation of molecules bound to surfaces.

Collaborating with Dr. D. S. King of the NIST Molecular Spectroscopy Division on the dynamics of molecular desorption from surfaces.

Collaborating with Dr. J. B. Beckerle, contractor, on the electronic density of states of small metal particles and the importance of these states on the vibrational relaxation properties of adsorbates.

Demmin, R. A.

Collaborated with Dr. N. H. Turner of the Naval Research Laboratory in scanning Auger microprobe experiments on thin films.

Collaborated (with R. L. Kurtz and R. L. Stockbauer) with Drs. D. R. Mueller and A. Shih of the Naval Research Laboratory in a photoemission study of thin films.

Egelhoff, Jr., W. F.

Collaborating with Dr. J. E. Rowe of AT&T Bell Laboratories in investigations of the diffusion of nickel into GaAs(110) using the XPS searchlight effect.

Collaborating with Dr. B. Heinrich of Simon Fraser University, Canada to measure magnetic properties of novel crystal structures.

Collaborating with Dr. R. F. Willis of Cambridge University, England to make neutron spin-flip measurements of novel crystal structures.

Collaborated with Prof. S. Bauer of Cornell University to make synchrotron x-ray diffraction measurements of the structural quality of superlattices fabricated at NIST.

Fine, J.

Collaborating with Dr. I. Terzic of the Boris Kidric Institute, Belgrade, Yugoslavia on electronic excitation and electron emission for ion-bombarded surfaces. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Drs. L. and N. Tanovic of the University of Sarajevo, Yugoslavia on characterizing surface topography changes that result from ion bombardment. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. T. Nenadovic of the Boris Kidric Institute, Belgrade, Yugoslavia on the surface topography effect of both particle and laser-beam interactions with thin solid films. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. J. D. Fassett of the NIST Inorganic Analytical Research Division on the use of laser multiphoton-ionization techniques to identify sputtered atoms and to determine their kinetic energies.

Collaborating with Dr. W. Kirchhoff of the Department of Energy on a data analysis procedure for sputter-depth-profile interface characterization.

Collaborating with Drs. C. Le Gressus and J. P. Duraud of the Centre d'Etudes Nucleaires, Saclay, France on the collisional excitation and electron decay of atoms at single-crystal surfaces.

Collaborating with Dr. P. Roncin of the Universitė Paris, CNRS/Orsay, France on the use of laser multiphon-ionization techniques to identify sputtered atoms and to determine their kinetic energies.

Collaborating with Dr. G. Blaise of the Universitė Paris, CNRS/Orsay, France on the collisional excitation and sputtering of atoms at surfaces.

Collaborating with Dr. M. H. Shapiro of the California State University at Fullerton on multiple-interaction calculations of collisional atomic excitation and ejection at single-crystal surfaces.

Collaborating with Dr. G. P. Chambers of the Naval Research Laboratory, Washington, D.C. on the compilation and evaluation of absolute sputtering yield data.

Collaborating with Dr. M. Szymonski of the Jagellonian University, Krakow, Poland on energy distributions of collisionally excited and ejected atoms at surfaces.

Gadzuk, J. W.

Collaborating with Prof. M. Sunjic of the Ruder Boskovic Institute and the University of Zagreb, Yugoslavia on theories of electron spectroscopies and dynamics of molecular processes at surfaces. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology.

Collaborating with Dr. S. Holloway, University of Liverpool, England on theories of molecular processes at surfaces. This collaboration is assisted by a grant from the NATO Scientific Affairs Division.

Collaborating with Dr. N. Sathyamurthy, Indian Institute of Technology, Kanpur, India, and serving as monitor for a project "Chemical Dynamics and Laser Spectroscopy", under the auspices of the India-U.S. Materials Science Program funded via the provisions of PL-480.

Mini-course on "Chemical Dynamics at Surfaces," presented at Workshop on Fast Chemical Processes organized by Tata Institute of Fundamental Research, Bombay, India.

Consulted for Battelle Pacific Northwest Laboratory Symposium on New Frontiers in Surface Science.

Invited participant in the First Joint Physics and Chemistry Solvay Conference: Surface Science.

Collaborating with Prof. J. T. Yates, Jr., University of Pittsburgh on problem of resonant electron-stimulated desorption.

Collaborating with Dr. C. W. Clark of the NIST Radiation Physics Division on atomic physics aspects of oxygen chemisorption related to resonant electron-stimulated desorption.

Collaborated with NIST Center for Applied Mathematics in presentation of a Mini-Course on Chaos.

Consulted with Dr. J. Harris and other members of the Solid State Theory Group, KFA (Nuclear Research Organization) Julich, W. Germany on problems associated with molecular dynamics at surfaces.

Jach. T.

Collaborating with Drs. R. D. Deslattes, P. L. Cowan, D. Lindle, R. Lavilla and J. Cooper of the NIST Quantum Metrology Division on gas-phase x-ray fluorescence experiments at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. R. C. C. Perera, Lawrence Berekely Laboratory on the measurements and interpretation of the x-ray spectra of chlorinated molecules.

Consulting with Drs. M. B. Bedzyk and Q. Shen of Cornell University to investigate superficial waves in surface dynamical x-ray diffraction.

Collaborated with Drs. J. Geist, G. Carver, and D. Novotny, of the NIST Semiconductor Electronics Division on the design and fabrication of silicon x-ray detectors.

Consulted by Drs. W. R. Ott, D. L. Ederer, and R. Canfield of the NIST Radiation Physics Division on the extension of silicon photodiode calibrated into the far ultraviolet and soft x-ray region.

Consulted by Dr. J. Comas of the NIST Semiconductor Electronics Division on incorporating silicon x-ray detector development into the program for the silicon process line.

Consulted by the NIST Research Advisory Committee on the procurement of unified computer-aided design (CAD) software for personal computers and organized, under the auspices of the Center for Applied Mathematics, a meeting to determine the need for such procurement.

Collaborated with Drs. J. P. Kirkland and R. A. Neiser of the Naval Research Laboratory on the characterization of commercial silicon photodiodes as x-ray detectors.

Collaborated with Dr. R. Spal of the NIST Ceramics Division on characterization of the x-ray monochromator crystal with integrated detector.

Joyce, S. A.

Collaborating (with J. Yarmoff) with Dr. F. R. McFeely of the IBM Watson Research Center on measurements of electron attenuation lengths in SiO_2.

Kurtz, R. L.

Collaborating (with R. L. Stockbauer and T. E. Madey) with Drs. A. Shih, D. R. Mueller, L. Toth, M. Osofsy, and S. Wolf of the Naval Research Laboratory on studies of high T_c superconductors.

Collaborating (with R. L. Stockbauer and T. E. Madey) with Drs. A. Shih and D. R. Mueller of the Naval Research Laboratory in photoemission and ion desorption studies of Ba and BaO on W and Ir as models for high-emission dispenser cathodes.

Collaborating (with R. L. Stockbauer and T. E. Madey) with Prof. J. L. de Segovia and Dr. E. Roman of the Instituto Ciencia de Materiales, CSCIC, Madrid on a study of the electronic structure and molecular adsorption of H_2O at low temperatures on transition-metal oxide surfaces.

Collaborating (with R. L. Stockbauer) with Drs. J. Rife, W. Hunter, and M. Kabler of the Naval Research Laboratory to instrument a surface science beamline at the Brookhaven National Synchrotron Light Source to extend the photon energy range of experiments beyond what is available at SURF-II.

Collaborating with Prof. V. E. Henrich, Yale University on investigations of the interaction of molecules of catalytic interest with $Fe_2O_3(0001)$.

Collaborating with Dr. R. Walkup of IBM in studies of ion desorption using molecular dynamics calculations to predict surface reconstructions, stability of various defect structures, and ion-desorption trajectories.

Madey, T. E.

Collaborating with Drs. I. Terzić, J. Vukanić and Z. Misković of the Boris Kidrić Institute, Belgrade, under the auspices of the U.S.-Yugoslav Agreement for Cooperation in Science and Technology, on theoretical and experimental studies of electron-stimulated desorption and scattering of alkali ions from surfaces.

Collaborated with Dr. C. Benndorf of the University of Hamburg, under the auspices of a NATO grant, on studies of the influence of surface additives on local molecular structure.

Collaborated with Prof. P. A. Thiel of Iowa State University in writing a comprehensive review article on the interaction of water with solid surfaces.

Collaborating (with R. L. Kurtz and R. L. Stockbauer) with Dr. J. L. de Segovia of the Instituto de Fisica de Materiales, Madrid, Spain, under the auspices of the U.S.-Spain Joint Committee for Technical Cooperation, on experimental studies of adsorption on metals and oxides using electron-stimulated desorption and synchrotron radiation methods.

Collaborating (with C. J. Powell) with Drs. J. K. N. Sharma and S. M. Shivaprasad of the Indian National Physical Laboratory, under the auspices of the U.S.-Indo Cooperative Program, on experimental studies of metal-semiconductor interfaces.

Collaborating (with A. J. Melmed) with Prof. R. Meclewski and Drs. A. Cizewski and R. Blasczyszyn of the University of Wroclaw, Poland on problems concerning ultrathin films of metals on metals, and the adsorption on water on these films. This work is conducted under the auspices of the Maria Sklodowska Curie Foundation.

Melmed, A. J.

Collaborating with Dr. C. K. Chiang of the NIST Ceramics Division who has provided samples of high-T_c superconducting materials for field-ion microscopy.

Collaborating with Dr. R. D. Shull of the NIST Metallurgy Division on magnetic susceptibility and x-ray diffraction measurements of high-T_c superconducting materials used for field-ion microscopy.

Collaborating with Dr. H. A. Fowler of the NIST Mathematical Analysis Division on simulations of images by field-ion microscopy.

Collaborating with Dr. M. K. Miller of the Oak Ridge National Laboratory on field-ion microscopy and atom-probe micro-composition measurements of high-T_c superconducting materials.

Collaborating with Dr. N. Ernst of the Fritz Haber Institute, West Berlin, FRG on field-ion and field-electron energy-distribution measurements of high-T_c superconducting materials.

Powell, C. J.

Collaborating (with T. E. Madey) with Drs. J. K. N. Sharma and S. M. Shivaprasad of the Indian National Physical Laboratory, under the auspices of the U.S.-Indo Cooperative Program, on experimental studies of metal-semiconductor interfaces.

Collaborating with Dr. D. R. Penn of the NIST Electron Physics Group and Dr. S. Tanuma of the Nippon Mining Company, Japan on calculations of the inelastic mean free paths of low-energy electrons in solids.

Collaborating with Dr. M. P. Seah of the UK National Physical Laboratory on an analysis of the factors affecting the accuracy and precision of quantitative surface analyses by Auger-electron spectroscopy and x-ray photoelectron spectroscopy.

Collaborating with Dr. M. P. Seah of the UK National Physical Laboratory on the development of plans and programs for the Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards.

Adjudicator for the Science Prize of the UK ESCA and Auger Users Group.

External examiner for a Doctor of Science candidate, Odense University, Denmark.

Consulted with the Office of Naval Research on a review of selected FY90 Basic Research Options.

Consulted with the Canadian National Sciences and Engineering Research Council on a site visit to the Surface Science Western Laboratory of the University of Western Ontario.

Stockbauer, R. L.

Collaborating (with R. L. Kurtz and T. E. Madey) with Drs. A. Shih, D. R. Mueller, L. Toth, M. Osofsky, and S. Wolf of the Naval Research Laboratory on studies of high-T_c superconductors.

Collaborating (wtih R. L. Kurtz and T. E. Madey) with Drs. A. Shih and D. R. Mueller of the Naval Research Laboratory in photoemission and ion-desorption studies of Ba and BaO on W foil and W(100) as models for high-emission dispenser cathodes.

Collaborating (with R. L. Kurtz and T. E. Madey) with Prof. J. L. de Segovia and Dr. E. Roman of the Instituto Ciencia de Materiales, CSIC, Madrid, on a study of the electronic structure and molecular adsorption of H_2O at low temperatures on transition-metal oxide surfaces.

Collaborating (with R. L. Kurtz) with Drs. J. Rife, W. Hunter, and M. Kabler of the Naval Research Laboratory to instrument a surface science beamline at the Brookhaen National Synchrotron Light Source to extend the photon energy range of experiments beyond what is available at SURF-II.

Consulted with the staff of the American Vacuum Society and the program chairman for the National Symposia on the data base of meeting abstracts and related software.

Yarmoff, J. A.

Collaborating with Dr. J. W. Hudgens of the NIST Chemical Kinetics Division on reactive scattering of molecular and free-radical beams with semiconductor surfaces using multiphoton ionization for detection.

Collaborating with Dr. J. Stroscio of the NIST Radiation Physics Division on electron energy-loss spectroscopy studies of Cs adsorbed on GaAs (110).

Collaborating with Dr. F. R. McFeely of the IBM Watson Research Center on mechanistic studies of the selective chemical vapor deposition of tungsten on silicon and SiO_2 via WF_6 and measurements of the attenuation lengths of very low energy electrons in silicon oxide, and of the relative Si 2p photoemission cross sections at the SiO_2/Si interface as a function of oxidation state and final-state energy.

Collaborating with Dr. J. R. Lince of The Aerospace Corporation on studies of the surface chemistry of MoS_2.

MOLECULAR SPECTROSCOPY DIVISION
A. Weber, Chief

SUMMARY OF ACTIVITIES
Fiscal Year 1988

1. INTRODUCTION

A. Goal

This Division is a discipline oriented unit and its goal is to be at the forefront of modern theoretical and experimental molecular spectroscopy in order to:

Advance spectroscopic measurement methods and techniques.

Develop models, theoretical concepts and quantum theoretical methods for predicting molecular properties and energetics of molecules and clusters.

Obtain reliable reference spectroscopic data for NIST, government, research community and industrial needs.

Understand and model fundamental chemical processes.

Provide state-of-the-art frequency standards.

Transfer forefront spectroscopic expertise to other NIST Divisions, other government agencies, industry and the research community.

Within the framework of these general goals the Division also follows several specific objectives which have been part of the overall program of the Center for Chemical Physics - Properties of Weakly Bonded Systems, Biotechnology, and Energy Transfer. Properties of weakly bonded systems are obtained for small atomic and molecular complexes held together by van der Waals and hydrogen bond forces in order to determine the structure, conformation, thermodynamics, and reactivity of such systems. The objective of the biotechnology quantum mechanical effort is the development of an ab initio reaction field program for studies of complex systems such as clusters, proteins, and surfaces. In the third area the major effort involves the study of vibrational energy transfer in the spectroscopy and kinetics of molecules.

This report contains descriptions of these activities and other related studies of each of the three groups.

B. Organization

The Molecular Spectroscopy Division is organized into three working groups: High Resolution Spectroscopy (HRS), Molecular Dynamics Group (MD), and Quantum Chemistry (QC). The permanent Division staff is augmented by that of postdoctoral fellows and guest scientists. During the past year we have had ten guest scientists and one post doctoral fellow engaged in Division projects. In addition four members of the Surface Science Division participated in the work of the MD group. A list of the guest scientists, their permanent affiliations, and their activities is given in Section 10 of this report.

C. Division Programs

To be able to respond to the present and projected needs of NIST, the Center for Atomic, Molecular and Optical Physics (CAMOP), and the user community, a significant fraction of the Division's effort is directed toward achieving and maintaining the expertise of its staff in their discipline oriented fields, and into maintaining its experimental facilities at the state-of-the-art level. We must remain at this level of expertise in spectroscopic measurements, theory, and interpretation in order to respond quickly to provide standards, serve national technical needs, and to insure adequate response to future problems. Remote sensing for industrial and atmospheric monitoring, laser chemistry and physics and combustion diagnostics are a few of the many important high technology areas that depend on modern spectroscopic techniques. These applications also provide much of the direction and motivation for our efforts.

As described in Section 2, the work of the HR group involves experimental and theoretical applications of molecular spectroscopy for characterizing gas phase molecules, primarily in the infrared (rotation-vibrational) and microwave (rotational) spectral regions, the development of frequency standards for the infrared, and the development and application of new experimental techniques for high resolution spectroscopy. The emphasis of these studies is in the applications of our expertise to problems in structural chemistry, atmospheric chemistry, chemical analysis, radio astronomy and the properties of weakly bound molecular species.

The environmental problem posed by the pollutants of the earth's atmosphere, especially the role played by trace constituents in the chemistry of the upper atmopshere, are of major concern and a portion of the group's activities is devoted to providing critically needed data to help solve some of these problems. In this effort our activities are guided by the needs of the environmental research community, and are conducted with the support of NASA. These efforts will continue to play an important role in the work of the HR group during the coming years.

Weakly bound molecular complexes, i.e., van der Waals and hydrogen bonded molecules have received considerable attention in our laboratory with major progress in characterizing large amplitude tunneling effects and structural information on trimeric complexes. The Division is in a unique position of having available personnel and instrumentation that permits such studies to be performed using any and all of the facilities from the microwave to the near infrared region of the spectrum in a concerted attack on the problems posed by these weakly bound systems. These experimental efforts are augmented by the analytical and computational theoretical expertise available in the Division.

The Division is the home of the Molecular Spectra Data Center. This Center, supported by the Office of Standard Reference Data and staffed by members of the HR group provides evaluated data on molecular rotational spectra in the microwave region with special emphasis on spectra of interstellar species. A more recent effort is the development of evaluated vibrational frequency and electronic band center data for transient molecules. Closely related to these activities is the measurement and evaluation of infrared spectra to be used as standards in calibrating diode lasers and infrared laser spectrometers. The work on infrared standards is a response to requests from the instrumentation industry, industrial research laboratories, applied technological user groups, government agencies and laboratories. Improvements in the stability of diode lasers have emphasized the need for accurate calibration standards. New absorption frequencies of N_2O, CS_2, and OCS have been obtained by heterodyne methods to produce tables of accurate frequencies in spectral regions not covered previously. This work has been made possible through the joining of the unique facilities of the Time and Frequency Division of NIST/Boulder with our spectroscopic expertise. Other collaborations, with non-U.S. research groups exist as well in an effort to develop the most extensive and accurate set of frequency calibration data. Section 2.A of the HR group report describes these activities in greater detail.

The MD group primarily does quantum-state specific studies of molecular dynamics. A common factor in the research of this group is the role of energy transfer in the spectroscopy and kinetics of molecules. Three major activities are pursued: Condensed Phase Energy Transfer, Laser Diagnostics of Surface Dynamics, and Dynamics of van der Waals Molecules. As described in Section 3.A, in the first of these, the direction taken is the study of condensed phase vibrational energy transfer from vibrationally excited chemical bonds in liquids, solids, and on molecules bound to surfaces or small clusters.

Time resolved spectroscopic measurements at the picosecond level have been employed in thorough studies of vibrational predissociation of weakly bound molecular clusters and overtone photodissociation of the HN_3 molecule. Since the measurements are performed in the time domain, a direct measure of the lifetimes of the predissociating states is obtained. These studies are described in Section 3.B of the MD group report.

In the third major activity the goal is to obtain an understanding of the energy transfer and chemical dynamics occurring at metal surfaces at a fundamental level. This work is done in close collaboration with staff members of the Surface Science Division. This collaboration has resulted in the ability to perform state-resolved studies of thermally and laser desorbed molecular processes at well characterized surfaces. Details about recent accomplishments are presented in Section 3.C.

Several of these studies are supported by AFOSR and DOE as indicated in the report.

The Quantum Chemistry group continues to develop and extend the range of reliable and useful calculations to complex polyatomic systems. The stabilities, conformations spectroscopy and reactivity of complex molecules, clusters, ions, radicals, and transition states, among others, are successfully investigated by the Quantum Chemistry group.

Electronic structure calculations are described in Section 4.B. The first version of an ab initio reaction field computer program has been developed and tested on a variety of hydrogen bonded complexes and further tests are in progress on larger more complex systems such as proteins. Several ab initio SCF calculations have been performed on molecular complexes, which have been experimentally investigated in the HR group, to obtain a more detailed interpretation of their structures, binding energies and electronic properties.

A second major effort in the QC group is in the area of scattering theory with the goal of understanding the spectroscopy of colliding molecular fragments. Two approaches are employed: (1) numerical state-to-state close coupled quantum scattering methods and (2) analytic tools based on the generalized form of the multichannel quantum defect theory (MCQDT). The application of this theory to molecular photodissociative effects, generalized MCQDT applications and ultracold atomic collision phenomena are described in Section 4.C. The problems which may be treated arise in a variety of areas of molecular physics, e.g., laser spectroscopy, laser development, chemistry of planetary atmospheres and ultracold collision phenomena.

D. Collaborations

The Division staff conducts its research in collaboration with postdoctoral associates, members of the Surface Science and Time and Frequency Divisions as well as with many visiting scientists. Some of these use the facilities of the Division and are appointed guest scientists at NIST. Section 10 of this report lists the names, affiliations, and activities of the guest scientists who collaborated with us during the past year. Further collaborations exist with other scientists associated with universities from the U.S. and abroad whose names are given in the various project descriptions and appear as co-authors of many of the publications and talks listed in Sections 5 and 6 of this report.

E. Other Agency Support

Among the several goals of the Division are the services provided to various agencies of the government which in turn support some of the work done in the Division. The various agencies of the Department of Defense (USARO, AFOSR, Hanscom AFB), NASA, DOE are among those that sponsored some of the research done during the past year.

In the remainder of this Annual Report are the individual group reports (Sections 2, 3, 4), the listings of publications and talks (Sections 5 and 6), Division seminars (Section 7), outside professional activities by the staff (Section 8), professional interactions and consultations by the Division staff (Section 9), and visiting scientists (Section 10).

2. HIGH RESOLUTION SPECTROSCOPY GROUP

A. Introduction

The work of this group spans a variety of spectroscopic topics, many of which are part of programmatic efforts. Accordingly the activity reports are grouped into six separate sections: Calibration and Data Center Activities, Spectroscopy for Environmental Studies, Spectroscopy of Hydrogen-bonded and van der Waals Complexes, Rare Gas-Molecular Complexes, Matrix Isolation Spectroscopy, as well as General Spectroscopy and Theory. Each section is concluded with a brief statement of work planned for the coming year. The descriptions list the scientists active on the projects. These include NBS staff, guest scientists, as well as outside collaborators.

B. Calibration and Data Center Activities

We collect under this heading the work of the group connected most closely with the core mission of NBS, namely the production and dissemination of compilations of accurately measured frequencies or wavenumbers for use as secondary standards, and of critically evaluated molecular constants for use in other disciplines. Occasionally, spectral fitting programs, for use in reducing data by investigators in other laboratories, are also provided. The group devotes a significant portion of its effort each year to this program, and frequently collaborates with workers in other laboratories. Outputs of the program serve needs spanning the microwave to the ultraviolet spectral regions.

1. Heterodyne Frequency Measurements on CS_2 to Cover the 1460 to 1550 cm^{-1} Region

(A. G. Maki, J. S. Wells*, and M. Schneider*)

In order to provide frequency calibration benchmarks in the 1460 to 1550 cm^{-1} region, we have made heterodyne frequency measurements on 15 absorption lines for the 00^01-00^00 band of $^{12}CS_2$ and $^{13}CS_2$. Since these absorption lines are very strong, the data on $^{13}CS_2$ are quite useful even if isotopically enriched samples are not used. This is part of a continuing collaboration between the NIST-Boulder and the NIST-Gaithersburg laboratories to provide frequency calibration benchmarks based on heterodyne frequency measurements throughout the infrared region. These measurements were combined with other data to get improved rotational constants which were used to produce tables of accurate transition frequencies (or wavenumbers) such as Table I.

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*Guest Scientist or Collaborator

Table I. Wavenumbers (in cm^{-1}) Calculated for the ν_3 Band of $^{13}CS_2$

P-BRANCH	J"	R-BRANCH	P-BRANCH	J"	R-BRANCH
---	0	1485.54812(09)	1471.00438(10)	56	1495.49568(13)
1484.89334(09)[a]	2	1485.97778(09)	1470.41377(10)	58	1495.77074(13)
1484.44997(09)	4	1486.40194(09)	1469.81773(10)	60	1496.04025(14)
1484.00111(09)	6	1486.82062(09)	1469.21627(10)	62	1496.30421(14)
1483.54677(09)	8	1487.23380(09)	1468.60940(11)	64	1496.56261(15)
1483.08696(09)	10	1487.64148(09)	1467.99711(11)	66	1496.81545(15)
1482.62166(09)	12	1488.04366(09)	1467.37940(11)	68	1497.06272(15)
1482.15090(09)	14	1488.44034(08)	1466.75629(11)	70	1497.30443(15)
1481.67466(09)	16	1488.83152(08)	1466.12777(11)	72	1497.54058(15)
1481.19295(08)	18	1489.21719(08)	1465.49384(11)	74	1497.77115(15)
1480.70578(08)	20	1489.59735(08)	1464.85451(11)	76	1497.99615(15)
1480.21314(08)	22	1489.97200(08)	1464.20978(11)	78	1498.21558(15)
1479.71504(08)	24	1490.34113(08)	1463.55965(12)	80	1498.42943(15)
1479.21148(08)	26	1490.70475(08)	1462.90412(12)	82	1498.63770(15)
1478.70246(08)	28	1491.06286(08)	1462.24320(12)	84	1498.84039(14)
1478.18799(08)	30	1491.41544(08)	1461.57688(13)	86	1499.03750(14)
1477.66806(07)	32	1491.76250(08)	1460.90518(14)	88	1499.22903(14)
1477.14268(07)	34	1492.10404(08)	1460.22808(15)	90	1499.41496(13)
1476.61185(08)	36	1492.44005(08)	---	92	1499.59531(13)
1476.07558(08)	38	1492.77053(09)	---	94	1499.77006(13)
1475.53386(08)	40	1493.09548(09)	---	96	1499.93922(14)
1474.98670(08)	42	1493.41489(10)	---	98	1500.10278(14)
1474.43410(08)	44	1493.72877(10)	---	100	1500.26075(16)
1473.87606(08)	46	1494.03711(10)	---	102	1500.41311(17)
1473.31259(09)	48	1494.33992(11)	---	104	1500.55987(19)
1472.74368(09)	50	1494.63718(11)	---	106	1500.70103(22)
1472.16934(09)	52	1494.92889(12)	---	108	1500.83657(25)
1471.58957(09)	54	1495.21506(12)	---	110	1500.96651(29)

a) The uncertainty (twice the estimated standard error) in the last digits is given in parentheses. In spite of the small uncertainty given by the statistics of the fits, the absolute frequency uncertainty should not be less than ±0.0001 cm^{-1} (3 MHz).

2. New Heterodyne Frequency Measurements on OCS

(A. G. Maki, W. B. Olson, and J. S. Wells*)

At this time we can not make accurate heterodyne frequency measurements on absorption features located in arbitrary regions of the infrared spectrum. We therefore have been engaged in a program to accurately measure the lower energy levels of the OCS molecule so that we may calculate accurate frequencies for transitions where direct measurements are not possible. One of the levels that has, until now, been missing from our measurements is the ν_2, or 01^10, level. By using a long-path absorption cell, Joe Wells (NIST-Boulder) has now been able to measure the 01^11-00^00 and 02^01-01^0 bands near 1375 cm^{-1}. When these heterodyne measurements are combined with heterodyne measurements on the 01^11-01^10 and

02^01-00^00 bands, we have two different paths for evaluating the 01^10 energy levels. Furthermore, these measurements will enable us to accurately calculate the transition frequencies for the 01^10-00^00 band of OCS near 520 cm^{-1}.

In a similar fashion we have measured a number of hot band transitions in the region from 1866 to 1919 cm^{-1} in order to determine accurate frequencies for energy levels that can be used to provide calibration tables for the region from 2700 to 3000 cm^{-1}. These heterodyne measurements were supplemented with new FTS measurements which we made to help determine some of the effects of centrifugal distortion and ℓ-type resonance.

3. New Heterodyne Measurements of N_2O
(A. G. Maki, J. S. Wells*, and L. R. Zink*)

In another part of our collaboration with NIST-Boulder, we have continued to make heterodyne measurements of transitions of N_2O that will help to locate accurately the energy levels of N_2O that are involved in transitions useful for calibration. Heterodyne measurements have been made on the 10^00-02^00 band near 1060 cm^{-1} and the 10^00-01^10 band near 1635 cm^{-1}. These measurements allowed us to prepare calibration tables for the 02^00-00^00 band near 1168 cm^{-1}, the 01^10-00^00 band near 589 cm^{-1}, and the 02^01-00^00 band near 2462 cm^{-1}.

4. Microwave Spectral Tables - III. Hydrocarbons, CH to $C_{10}H_{10}$
(F. J. Lovas and R. D. Suenram)

All of the rotational spectral lines observed and reported in the open literacture for 91 hydrocarbon molecules have been tabulated. The isotopic molecular species, assigned quantum numbers, observed frequency, estimated measurements uncertainty and reference are given for each transition reported. In addition to correcting a number of misprints and errors in the literature cited, the spectral lines for many normal isotopic species have been refit to produce a comprehensive and consistent analysis of all the data extracted from various literature sources. The derived molecular properties, such as rotational and centrifugal distortion constants, hyperfine structure constants, electric dipole moments, and rotational g-factors are listed (see J. Phys. Chem. Ref. Data, in press).

5. Vibrational and Electric Energy Levels of Transient Molecules
(M. E. Jacox)

With partial support from the Office of Standard Reference Data, a compilation of the electronic energy levels of polyatomic transient molecules with from three to six atoms has been prepared and published. This major work represents a critical evaluation of optical and photoelectron spectral data for approximately 500 free radicals, molecular ions, and other highly reactive molecules. While most of the data were obtained from gas-phase studies, spectral observations in rare-gas and nitrogen matrices, for which matrix interactions are relatively weak, were also included. Radiative lifetimes, vibrational energy levels, and the principal rotational constants were tabulated. Because new observations are accumulating rapidly and because ground-state vibrational data were included, this new publication updates an important subset of the ground-state vibrational data complitation for small polyatomic transient molecules which was published four years ago (M. E. Jacox, J. Phys. Chem. Ref. Data 13, 945 (1984)).

In April 1988, support was received from the Office of Standard Reference Data for the preparation of computer-accessible versions of these spectral tables. The first stage of this project, conversion of the tables to ACSII files suitable for distribution on floppy disks or to network transmission to users, has recently been completed. With help from a summer worker, work is well along on the preparation of the data on band origins and vibrational energy levels for conversion to a pair of dBase III+ files, TDATA and VDATA, which can be used for range searches. When this conversion has been completed, compiled dBase files will be prepared, removing the need for the user to possess the dBase III+ software package.

The vibrational and electronic spectral data are constantly being updated. Preparation of a supplement to the earlier ground-state vibrational data tables is in progress. These new tables, which will be submitted for publication in the Journal of Physical and Chemical Reference Data, will include new spectral data for transient molecules with from 7 to 16 atoms, as well as for transient molecules with from 3 to 6 atoms for which no electronic spectral data have been reported. The forthcoming publication will also include a master index, to facilitate location of spectral data for a given molecule in the three compilations.

6. Compilation of Bond Distances of Molecules in the Gas Phase
(W. J. Lafferty)

This project has the goal of compiling the best molecular structural parameters reported in the literature. It is part of a long standing collaboration with J. H. Callomon (University College, London), K. Kuchitsu (University of Tokyo), and E. Hirota (Institute for Molecular Science, Japan) under the auspices of Landolt-Börnstein and includes gas phase structural studies determined by electron diffraction methods, visible spectroscopy, microwave spectroscopy as well as infrared techniques. Evaluation of structures determined by IR techniques is done at NIST. The first publication of this effort was in 1976 (Landolt-Börnstein, New Series, Group II, Volume 7). A supplement to update the original work was completed in 1986 and should appear in print this year. Since a flood of new studies on ions, van der Waals complexes, and hydrogen bonded molecules has appeared since the completion of the last literature search in 1985, it has been decided to issue an additional supplement. The cut-off date for the literature search will be at the end of 1988 and the manuscript will be submitted by June 1989.

7. Future Plans

a. Calibration Efforts

(A. G. Maki)

In our efforts to use heterodyne techniques to measure all the lower energy levels of OCS we would like to locate the 10^00 level to within a few MHz. Several possible schemes for doing that are under consideration. One would be to make a direct measurement of the 10^00-00^00 band using doubled CO_2 laser transitions as the frequency standard. Since we have no strong local oscillator lasers at 2060 cm^{-1}, this would require measuring the beat frequency between the diode laser and the doubled CO_2 laser. This has been done successfully before for the region around 1900 cm^{-1} in the NIST-Boulder lab., but success for the scheme proposed here is not guaranteed.

Other possibilities would be to measure the 10^00-02^00 band at 1020 cm^{-1} or the 10^00-01^10 band at 1540 cm^{-1}. These are weak bands that occur in regions where there are a great many stronger lines either from OCS or, in the case of the 1540 cm^{-1} region, from CS_2 which is present as an impurity in most OCS samples.

The N_2O band 11^10-00^00 at 2800 cm^{-1} and the 10^01-00^00 band at 3480 cm^{-1} are strong enough to use for calibration if we could measure the 11^10 and the 10^01 levels. With the long-path absorption cell it may be possible to measure the 11^10-01^11 transition at 940 cm^{-1} and the 10^01-10^00 transition near 1260 cm^{-1}.

There is a particular need for calibration data in the 3000 to 4000 cm^{-1} region. Since Joe Wells' laboratory at NIST-Boulder is not equipped to make direct heterodyne measurements on transitions in that region, it is necessary to attempt to measure energy levels appropriate to transitions in that region. In addition to the N_2O 10^01 level mentioned above, the 12^00 level of N_2O and the 10^01 and 12^00 levels of OCS would be good candidates if the heterodyne measurements can be made. It may also be possible to make some heterodyne measurements on CO_2 which will be useful for filling gaps in our calibration tables.

b. Molecular Spectra Data Center

(F. J. Lovas)

The first revision of the paper originally entitled "Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions - 1985 Revision" was published in the January 1986 issue of J. Phys. Chem. Ref. Data.

Work has begun on the next revision of this paper, and completion is planned for 1989. The literature search of radio astronomy papers and data evaluation of new microwave studies of these species will continue throughout this period. Since the last revision was published, 15 new interstellar species have been identified, bringing the number of identified molecules to 74. Many new transitions of the previously known species have also been reported, which represents about a 15 increase in the observational data.

During FY88 we started work on Part IV of the Microwave Spectral Tables which will treat organic species containing oxygen. Our reprint collection currently contains 157 species in this class with empirical formulas CHO through $C_7H_{12}O$. Spectral data for the first 25 species (130 isotpic forms) have been coded for spectral fitting and table generating programs. This review is projected to be completed in the fall of 1990.

c. Vibrational and Electronic Energy Levels of Transient Molecules (M. E. Jacox)

During FY89 it is planned to complete the conversion of the vibrational frequency and electronic band center data to compiled dBase III+ files. The electronic spectral tables will continue to be updated, and a supplement to the 1984 ground-state vibrational energy level tables will be prepared for publication.

C. Spectroscopy for Environmental Studies

Many small molecules play a significant role in the chemistry of the earth's atmosphere. As such, they are of significant interest to agencies like NASA, DOD and the CMA (Chemical Manufacturer's Association). The interest of these agencies generally focusses on molecular spectroscopy as a remote sensing tool and for the determination of concentration profiles. Consequently, the emphasis in this section is on band analyses as well as the important information on line intensities, line widths, line shapes, and the effect of pressure on these quantities. As in all branches of spectroscopy, the very narrow band width of infrared laser sources now permits quite reliable studies of phenomena involved in spectroscopic concentration determinations.

1. Absorption Bands of Nitric Acid Below 1250 cm^{-1} (A. G. Maki, W. B. Olson, R. Escribano, A. Goldman, J. Burkholder, and C. J. Howard)

All of the infrared absorption bands of nitric acid (HNO_3) below 1250 cm^{-1} have been measured and analyzed in our continuing study of the spectrum of this important atmospheric molecule. The lowest frequency band, the ν_9 band at 458 cm^{-1}, has been studied in collaboration with three other laboratories, A. Goldman at the University of Denver, J. Burkholder and C. J. Howard at NOAA in Boulder, Colorado, and R. Escribano at the Instituto de Estructura de la Materia, Madrid, Spain. This is the strongest low frequency band of HNO_3 but four other weaker bands have been studied in our laboratory, ν_6, ν_7, ν_8, and $\nu_8 + \nu_9$, because they also are observed in atmospheric spectra.

Relative intensity measurements were also made to compare the intensity of the ν_7 band to that of the ν_6 band for which we have a value for the absolute intensity. Our measurements also provide information on the direction of the transition moment with respect to the rotational axes of the molecule for all the observed bands.

The goal of this work is to provide constants that allow one to accurately calculate the spectrum of nitric acid under different conditions of temperature and pressure in order to quantitatively account for the observed atmospheric spectrum. In Fig. 2.1 the comparison of the observed and calculated spectrum of the central part of the ν_6 band. For the low frequency bands of nitric acid the agreement between the observed and calculated spectrum is very good.

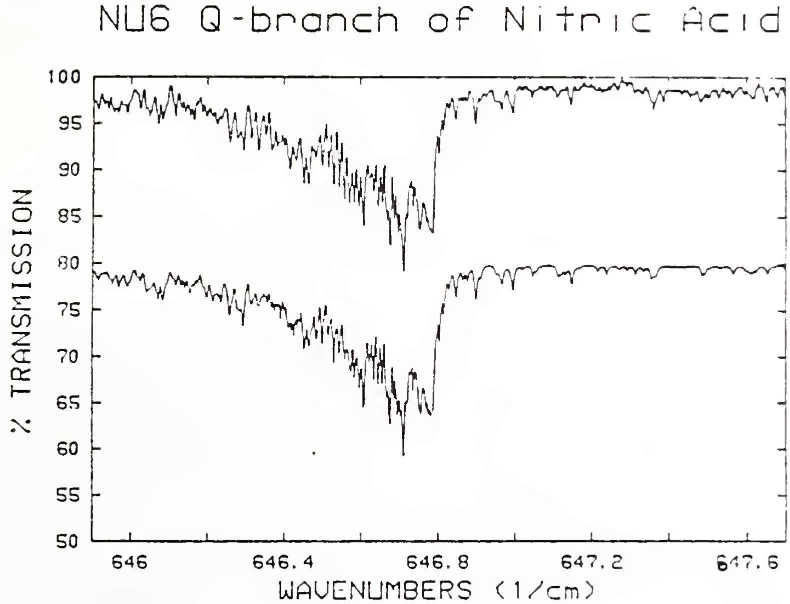

Fig. 2.1 Spectrum of the central part of the ν_6 band of HNO_3. The upper curve is the observed spectrum and the lower curve is the calculated spectrum. The calculated spectrum is displaced for greater clarity.

The ν_8 band is shown in Fig. 2.2. This band has an intensity anomaly that results in weaker than expected absorption in the low frequency part of the band (the P-branch) and stronger than expected intensity in the high frequency part (the R-branch). By making relative intensity measurements we are able to obtain two empirical parameters that account for this intensity anomaly.

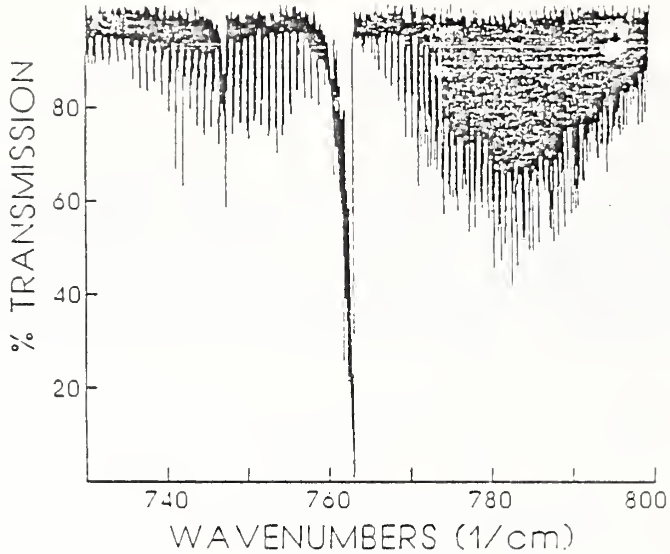

Fig. 2.2 A compressed view of the entire ν_8 band of HNO_3 showing the difference in intensity of the P-branch and R-branch transitions. Note the hot band Q-branch at 747.5 cm^{-1}.

The band at 1205 cm^{-1} was of particular interest because it occurs in an important part of the atmospheric spectrum and the exact vibrational assignment was uncertain. From our analysis of the ν_6, ν_7, ν_8, and ν_9 bands we have shown that the 1205 cm^{-1} band must be due to the combination $\nu_8 + \nu_9$. Knowing the correct assignment was helpful in assigning the fine structure for this band and we now have most of the lines assigned. Fig. 2.3 shows the observed spectrum of $\nu_8 + \nu_9$ and the spectrum calculated assuming it can be described by simply combining the constants for the ν_8 and ν_9 bands (and shifting the center to allow for an anharmonic vibrational term). An alternative assignment is $\nu_6 + \nu_7$ and the expected spectrum for that possibility is also given in Fig. 2.3.

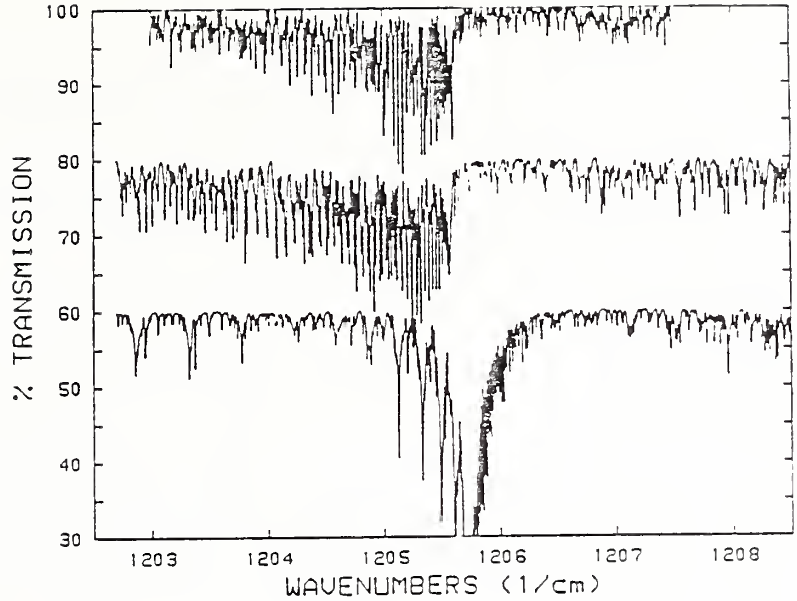

Fig. 2.3 Spectrum of the Q-branch region of the 1205 cm^{-1} band of HNO_3. The upper curve is the observed spectrum. The middle curve is calculated from the constants for ν_8 and ν_9. The lower curve is calculated from the constants for ν_6 and ν_7. The curves are displayed for clarity.

The results of this work have been transmitted to various laboratories that are involved in measuring and analyzing atmospheric spectra.

2. The Low Frequency Band of Sulfur Dioxide
(A. G. Maki, W. B. Olson, and L. Coudert)

One of the important gases involved in the chemistry of acid rain is, of course, sulfur dioxide (SO_2). Most of the sulfur in the atmosphere that comes from industrial processes is originally in the form of SO_2. Prior to this work the lowest frequency fundamental band of SO_2 had not been studied with high resolution.

To understand all the observed features of the high resolution spectrum of SO_2 it is necessary to remember that several different states and isotopic species are normally present. At room temperature a normal sample of SO_2 has the following population distribution:

000 state (ground state) of $^{32}S^{16}O_2$	86.5%
000 state (ground state) of $^{34}S^{16}O_2$	3.8%
010 state of $^{32}S^{16}O_2$	7.0%.

The remaining 2.7% of the molecules are other isotopic species and/or other vibrationally excited states. The intensity of the first hot band, $2\nu_2-\nu_2$, has an additional factor of 2 that comes from the transition moment so the intensity ratio of the ground state transitions to those of the first hot band is only 86.5/2x7.0 = 6.2 at room temperature.

We have measured and analyzed the ν_2 fundamental band and the $2\nu_2$-ν_2 hot band for $^{32}SO_2$ and $^{34}SO_2$. In the analysis we have combined the FTS infrared measurements with microwave measurements given in the literature to obtain band centers and rotational constants. These constants can be used to produce a synthetic spectrum which accounts for all the observeable features in the spectrum of SO_2 between 400 and 600 cm^{-1}.

3. High Resolution Measurements on the Two Low Frequency Fundamentals of Sulfur Trioxide

(A. G. Maki, W. B. Olson, and R. Escribano*)

The spectrum of sulfur trioxide (SO_3) is also of interest because it is a possible intermediate in the conversion of SO_2 to H_2SO_4. In a collaboration with Rafael Escribano of the Instituto de Estructura de la Materia, Madrid, Spain, we have measured and analyzed the two fundamental bands of SO_3 between 400 and 600 cm^{-1}. These two bands are coupled by a Coriolis resonance which complicates the analysis and makes it necessary to analyze both bands at the same time. In order to fit the spectrum a special computer program was developed that would use all the necessary elements in the Hamiltonian. Similar analyses had already been made in both the Madrid laboratory and at NIST so the assignment and analysis of the spectrum was fairly easy for us. Our measurements also allowed us to improve the rotational constants for the ground state of SO_3. This project is part of a program for scientific cooperation between the U.S. and Spain sponsored by the U.S. State Department.

4. Analysis of the Infrared Spectrum of Chlorine Dioxide (OCℓO)

(A. G. Maki, J. Burkholder*, C. J. Howard*, and R. Escribano*)

A new endeavor in our collaboration with R. Escribano of the Instituto de Estructura de la Materia, Madrid, Spain, is the analysis of all the fundamental bands of OCℓO. This molecule is an intermediate in the chlorine chemistry that relates to the ozone composition in the atmosphere. At the present time only two papers have described moderately high resolution measurements on OCℓO in the infrared and much better measurements and a better analysis are required before one can claim to understand the complete infrared spectrum.

There are two complicating features of the COℓO spectrum. One is the existence of two chlorine isotopes. At present only one isotopic species has been studied. The other complication is caused by the unpaired spin of the odd electron on the chlorine atom. This spin couples with the angular momentum of the molecule to give rise to a doublet structure for which the spacing varies from 0.0 to 0.2 cm^{-1}, depending on the transition involved.

To analyze the spectrum it is necessary to take into account the spin-splitting by either an approximation calculation, or by an exact calculation. For many transitions the approximation formulae are not adequate so a complete analysis requires that we use a computer program that fits the spectrum to a Hamiltonian with the appropriate spin coupling matrix elements. Such a program has been developed by Escribano for the analysis of the three fundamental bands. The spectra that we are using were measured by Burkholder and Howard in the NOAA laboratory in Boulder, Colorado.

5. Line Coupling Studies in the Spectrum of CO_2 in the ν_2 Region

(W. J. Lafferty and W. B. Olson)

The spectra of several Q-branches of the CO_2 molecule have been used for some time in atmospheric temperature sounding studies. Recently, it has been determined that shapes of Q-branch envelopes in a pressure broadened spectrum can not be simply accounted for by using sums of simple Lorentzian line shapes. This is due to the fact that molecules in states of appropriate symmetry can be collisionally mixed if the resulting transitions overlap (1,2). The effect on the spectrum is to make the Q-branch envelopes appear to be sharper than expected from the simple model so frequently this effect is referred to as collisional narrowing. Using perturbation theory, the shape of a given line can be expressed as:

$$S_J = 1/\pi \sum_k d_k^2 \rho_k \left[\frac{P w_{kk}}{(\nu - \nu_k^\circ)^2 + (P w_{kk})^2} + \frac{P (\nu - \nu_k^\circ) Y_k}{(\nu - \nu_k^\circ)^2 + (P w_{kk})^2} \right]$$

where d_k is the line intensity, P is the pressure, ν_k° is the transition frequency, ρ_k is the Boltzmann factor and

$$Y_k = \sum_{j \neq k} (d_j/d_k) w_{jk}/(\nu_k - \nu_j)$$

where w_{jk} is the collisional rate matrix. The first term is the conventional Lorentz expression; the second term is due to collisional mixing.

In collaboration with M. L. Hoke and S. A. Clough of the AF Geophysical Lab., we are studying collisional narrowing effects in the N_2 broadened CO_2 spectrum in the ν_2 region around 650 cm^{-1} with the ultimate goal being the determination of the temperature dependence of the Y_k coefficients. About 30 spectra have been obtained with our BOMEM FT-spectrometer with the total pressure varying from 250 Torr to one atmosphere. In order to obtain reliable intensity data from the BOMEM interferometer, it was necessary to make a number of modifications to the instrument including placing a secondary aperture in the He-cooled detector Dewar to remove spurious modulated radiation. In order to check the intensity accuracy of the instrument, line strengths and pressure broadening measurements have been made on 150 P- and R-branch transitions of the fundamental as well as a number of "hot band" transitions. Work is currently in progress to determine the Y_k coefficients not only for the fundamental band but for the $2\nu_2^0 - \nu_2^1$ and $\nu_1 - \nu_2^1$ bands as well. An illustration of the effect of collisional narrowing is shown in Fig. 2.4. Work on the spectra of cold samples will begin shortly.

1. G. J. Rosasco, W. Lempert, W. S. Hurst, and A. Fein, Chem. Phys. Letters 97, 436 (1982).

2. L. L. Strow and B. M. Gentry, J. Chem. Phys. 84, 1149 (1986).

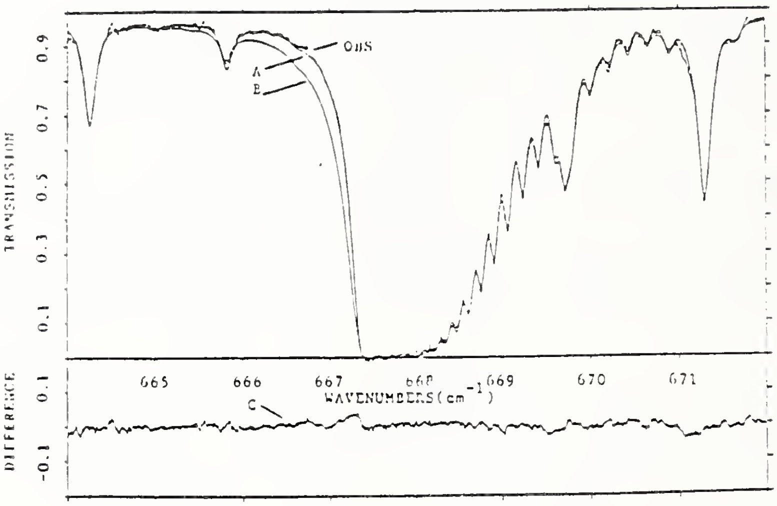

Fig. 2.4 Observed, calculated and difference spectra of the Q-branch of the fundamental ν_2^1 band of CO_2. The spectra were taken in a 10 cm cell with 6.2 Torr of CO_2 and 641 Torr of N_2 at a temperature of 296 K and a resolution of 0.006 cm^{-1}. Curve B is a spectrum calculated without line broadening while Curve A is calculated with line broadening effects included. Curve C is the difference between the observed spectra and Curve A.

6. Doppler-Limited Spectra of the C-H Bending Overtone of Fluoroform (A. S. Pine and J. M. Pliva*)

The parallel (A_1) and perpendicular (E) bands of the C-H bending overtone, $2\nu_4$, of CHF_3 have been recorded at Doppler-limited resolution at room temperature using a difference-frequency laser spectrometer. The $\ell=0$ component, $2\nu_4^0$ (A_1), and the $\ell=+2$ component, $2\nu_4^{+2}$(E), (accessed by $\Delta K=-1$ transitions) are only weakly perturbed by a mutual ℓ-type resonance near the K'=31 and 33 levels respectively; they can be fit to ≤ 0.0002 cm^{-1}, approaching the experimental precision. The $2\nu_4^{-2}$ (E) component (accessed by $\Delta K=+1$ transitions) is strongly perturbed, principally by anharmonic and Coriolis resonances with $2\nu_3+\nu_4^{\pm 1}$ (E). This perturbing state, though not observed directly, can be well specified by its influence on $2\nu_4^{-2}$. Additional localized resonances, arising from a multitude of possible combinations of lower frequency vibrations, are also observed in the high K levels of $2\nu_4^{-2}$. These increase the rms deviation of the fit to the $\Delta K=+1$

transitions, but a reliable set of deperturbed constants can be obtained by judicious selection of the data.

7. Molecular Beam Spectrum of the Highly Perturbed C-H Stretching Region of Fluoroform

(A. S. Pine, G. T. Fraser, and J. M. Pliva*)

Assignments of the C-H stretching fundamental of fluoroform, CHF_3, have been obtained from a spectrum recorded near 3035 cm^{-1} at sub-Doppler resolution (~10 MHz FWHM) and low effective temperature (~4 K) in an adiabatically-cooled molecular beam using bolometric detection of molecules excited by a color-center laser. This fundamental band is highly perturbed and has resisted analysis at higher temperatures, even at Doppler-limited resolution, whereas its overtones have been the subject of several studies of intramolecular vibrational relaxation. Under molecular beam conditions, the central Q-branch, which dominates the spectrum at room temperature, almost vanishes, while the bulk of the intensity is equally shared by two "sidebands" with Q-branches symmetrically displaced by ~±5 cm^{-1} from the suppressed central Q-branch. This peculiar structure is due to a close anharmonic and Coriolis resonance between the fundamental ν_1 (species A_1) and the combinations $\nu_4^{\pm} + \nu_5^{\pm} + \nu_6^{\mp}$ ($A_1 + A_2$) located only 1.40 cm^{-1} above ν_1, whose origin is at 3033.55 cm^{-1}. The coupling constant of the resonance is $\kappa_{1456}/2\sqrt{2} = 3.68$ cm^{-1}. Additional severe perturbations by the E components of $\nu_4 + \nu_5 + \nu_6$ as well as by $\nu_2 + \nu_4 + \nu_6$ have been identified in the spectrum.

8. N_2 and Air Broadening in the Fundamental Bands of HF and HCl

(A. S. Pine and J. P. Looney*)

There have been many measurements reported of N_2, O_2, or air broadening of HF and HCl, but none with sufficient resolution to obtain detailed line profiles near the Doppler limit at pressures below ~1 atm[1] and temperature below ~300 K. We therefore determined the N_2- and air-broadened lineshapes of HF and HCl transitions in the $\nu = 1 \leftarrow 0$ bands measured at T = 295 and 202 K with a high-resolution difference-frequency laser spectrometer. Pressure broadening, shift and collisional narrowing parameters have been extracted by least-squares fitting of several collisional profiles to the spectra. At low pressures, the collisional, or Dicke, narrowing effect causes deviations from the Voigt profile having a Doppler-fixed Gaussian component and yields a measure of the diffusion constants for the hydrogen halides in the buffer gases. At high J, where the pressure shifts are comparable to or larger than the broadenings, a slight asymmetry is observed in the lineshapes which is attributed to statistical correlation between velocity- and state-changing collisions. The ratio of air-to-N_2 broadening is roughly given by the relative quadrupolar contributions of O_2 and N_2, though it varies systematically with rotational level. The temperature variations in the broadening coefficients are also J dependent, deviating significantly from $T^{-1/2}$ and exhibiting opposite behavior for HF and HCl.

9. Q-branch Line Mixing in N_2O: Effects of ℓ-type Doubling
(A. S. Pine and L. L. Strow*)

Rotational collisional narrowing, or line mixing, has been observed in the Q-branch of the $\nu_2 + \nu_3$ Π-Σ band of N_2O near 2798 cm^{-1} using a difference-frequency spectrometer. Self-broadening spectra were recorded at pressures ranging from 20 to 747 Torr. The broadening coefficients, derived from the lower pressures before the lines significantly overlap, are in close agreement with prior measurements of P- and R-branch widths in Σ-Σ bands. At higher pressures where Q-branch lines are blended, the band contours deviate from purely additive component line shapes, exhibiting stronger peak absorptions and weaker wings characteristic of line mixing. A simple rotational energy gap scaling law is used to model the off-diagonal relaxation matrix elements needed to calcuate the observed collisional narrowing. Spectra calculated using several trial sets of collisional selection rules are presented. We find evidence for a parity conserving collisional selection rule and/or elastic-reorientation collisions.

10. Future Plans

As indicated above, the work on the analysis of the infrared spectrum of $OC\ell O$ has just begun and we expect the analysis to take much of the coming year even though the spectra are all in hand. There is still more work to be done on the analysis of the $2\nu_9$ band of HNO_3. Our analysis of the resonance between $2\nu_9$ and ν_5 needs improving. Frank DeLucia of Duke University would like us to help them identify the $2\nu_9$ transitions in their millimeter and sub-millimeter wave spectrum of HNO_3. Aaron Goldman of the University of Denver also needs the best calculation we can give him for the positions and intensities of the absorption lines in the $2\nu_9$ and ν_5 bands.

Another molecule that has been found in the atmosphere and that results from fluorocarbon chemistry is F_2CO. Carl Howard of NOAA has measured a number of infrared bands that do not seem to be too badly affected by perturbations and we hope to find time to analyze some of them.

The optothermal molecular-beam color-center laser spectrometer, built for the investigation of molecular complexes and used for the low temperature, subDoppler resolution study of fluoroform mentioned above, will continue to be applied to the spectra of large or heavy molecules of atmospheric interest with previously unresolved or undeciphered structure. In particular, we will examine the hydrogen stretching vibrations in nitric acid, $HONO_2$, and the two chlorofluorocarbons, CHF_2Cl and $CHFCl_2$.

The high-power single-frequency broadly-tunable color-center laser developed for optothermal spectroscopy is also ideal for precision photoacoustic studies of collisional lineshapes. Photoacoustic spectroscopy has the advantage over transmission measurements because of reduced uncertainties in the zero absorption baseline, since only the power absorbed by the molecules is registered. This method will be applied to the study of differential broadening of the Λ-doublets in NO and to search for collisional interference (line mixing) in the Q branches of CH_4 and NH_3.

D. Spectroscopy of Hydrogen-Bonded and van der Waals Complexes

In the past several years the structures of a large number of dimer and heterodimer van der Waals complexes have been evaluated by high resolution spectroscopic methods. In the microwave spectroscopic work the lowest energy configuration is generally observed providing structural information; some vibrational information can also be obtained. For example, van der Waals stretching frequencies can be estimated from the centrifugal distortion constants. For some complexes, evidence for internal motions are indicated and analysis of the spectra can lead to information concerning the barriers to those motions. Even more dynamical information is often obtained for those complexes studied by infrared spectroscopy. The result of this research, combined with theoretical studies, is that a better description of intermolecular interactions is being developed.

In this section we report the tunneling-rotation and vibrational spectra for the dimers of water, formaldehyde, acetylene, hydrogen fluoride, ammonia hydrogen sulfide, and carbon dioxide. in addition to these pure dimers, we report spectroscopic studies of mixed species, e.g., N_2-H_2O, H_2S-H_2O, etc.

A complete understanding of intermolecular interactions requires some information concerning the effects of a third body on the interaction between two molecules. If bimolecular interactions alone were important, no further information would be needed to predict the properties of condensed phases. Certainly many body interactions are present but the importance of their contribution needs to quantified. It is possible to make a further step in this direction by experimentally determining the structure of trimeric van der Waals complexes. The effect of a third molecule can then be analyzed by noting structural changes of dimer-type bonding within the larger complex.

Until recently, measuring the microwave spectra of large clusters was hampered by difficulties in obtaining sufficient concentrations in a supersonic expansion these being ultimately due to limited vacuum pumping speeds. The use of a pulsed source, which is naturally included in a Fourier transform microwave spectrometer, has dramatically changed this situation. Stronger expansions and, consequently, lower expansion temperatures can be produced with very little loading of reasonably sized diffusion pumps. This advantage has allowed microwave spectra to be obtained for a growing number of trimeric van der Waals complexes. The list of trimeric complexes which have been studied in the last few years by microwave spectroscopy is so far fairly short and includes Ar_2HF, $Ar_2HC\ell$, $(HCN)_3$ and $(HCN)_2Ar$. The structures for all of these have been determined by Professor H. S. Gutowsky and his coworkers at the University of Illinois. An important observation that is evident in their work is that the trimers are composed of sets of dimer-type structures. That is, the concept of pairwise additivity in the interaction of molecules seems to be reasonable. This is shown by the fact that the bond length of the dimers are about the same as the relevant bond lengths within the trimers. For example, in the Ar_2HF trimer, the Ar-F bond distance is only 0.04 A longer than in ArHF. On the other hand, the angular orientations are somewhat different; the HF is pointed toward the Ar in ArHF but is pointed between the Ar atoms in Ar_2HF.

Our studies of dimeric complexes in the CO_2/H_2O systems has led us to pursue an investigation of trimeric van der Waals complexes which incorporate these two molecules. Three trimers have been observed, $(CO_2)_3$ in the infrared, and $CO_2(H_2O)_2$ and $H_2O(CO_2)_2$ in the microwave regions. These studies are described below.

Complexes formed by rare gas-atoms and molecules are also held together by van der Waals forces and could be described here. Since, however, they do compose a separate category, our work with these systems is presented in Section E. The program of study of hydrogen-bonded and van der Waals complexes initiated several years ago now represents a significant fraction of the group's total effort. Continuning studies using a difference frequency laser spectrometer in the 3 micron region, the optothermal beam spectrometer and the pulsed beam Fourier transform microwave spectrometer are reported. The major efforts during the past two years deal with structural determinations of weakly bound dimers and trimers from microwave spectra and potentials derived from extensive infrared spectra. This program has benefitted greatly this past year from collaborations with guest scientists. We certainly plan to continue work in this direction for the forseeable future.

1. Pulsed FT Microwave Spectrometer - Improvements
(R. D. Suenram and F. J. Lovas)

A major improvement in the design of the pulsed FT microwave spectrometer has been made. The innovation greatly improves the scanning speed under manual operation and will make computer automation much simpler. In addition, the amount of equipment necessary for operation has been reduced which results in considerable cost savings over the previous version.

The design change involves the use of a microwave single sideband modulator in lieu of a second microwave source and the associated electronics necessary for phase locking and counting of the second source. The new design is shown in the accompaning block diagram (Fig. 2.5). As can be seen in the diagram only one synthesized microwave source is necessary. The output of the microwave synthesizer is split by a power divider. Part of the microwave signal is used to bias the LO part of a microwave mixer. The other half of the signal is used to drive the microwave input of a single sideband modulator. A 30 MHz sideband is generated by using the 10 MHz reference crystal output of the synthesizer to drive a X3 multiplier which generates an extremely clean, filtered, and amplified 30 MHz signal which is phase coherent with the microwave output. This 30 MHz signal is used to generate a 30 MHz sideband on the microwave frequency, ν_{syn} in the single sideband. The single sideband modulator

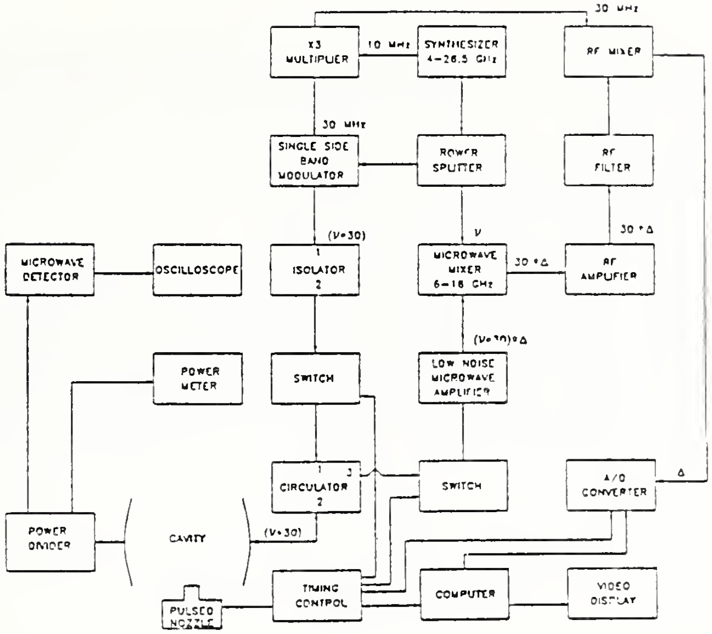

Fig. 2.5 Block diagram of the single sideband Fourier transform microwave spectrometer.

output is concentrated in either a ν_{syn} + 30 MHz or ν_{syn}-30 MHz (selectable) sideband with the fundamental frequency ν, and all other related sidebands and higher harmonics being suppressed. This signal (usually ν_{syn} + 30 MHz) is used to pump the molecules in the molecular beam in the cavity. The novel aspect of this is that the microwave cavity further suppress all the unwanted signals since it is tuned to ν_{syn} + 30 MHz also. The molecular signal which emanates from the cavity returns through the circulator and is sent to the RF port of the microwave mixer while the LO port receives the clean ν_{syn} to generate the 1F signal. The IF signal (30 MHz + Δ, the shift in ν caused by the molecular transition frequency) is sent to the RF port of an RF mixer. The LO drive for this mixer is the same ultra clean 30 MHz signal from the X3 multiplier. All the other aspects of the data collection scheme remain unchanged.

2. New Measurements of Microwave Transitions in the Water Dimer
(L. H. Coudert*, F. J. Lovas, R. D. Suenram, and J. T. Hougen)

New measurements of ten K = 1 lines, including six Q-type and four R-type, were made on the completely protonated species of the water dimer. For some of these lines, as well as for some K = 0 transitions known from the literature, Stark coefficients were determined, and these Stark coefficients provide a confirmation of the assignments. The new K = 1 measurements show that the splitting associated with the $(HF)_2$-like tunneling motion decreases from about 19.5 GHz for K = 0 to about 16.2 GHz for K = 1. To understand the fact that K = 1 lines are populated in our 1 K beam, we must assume, in accordance with the results of beam studies on other molecules, that levels of different nuclear spin modification relax separately. In an attempt to gain information on tunneling splittings other than that caused by the $(HF)_2$-like motion, we have made new measurements on 1-0 and 2-1 transitions with K = 0 for several partially deuterated species, in which the $(HF)_2$-like motion cannot occur. Small splittings ranging from 4 to 145 MHz were observed. Because of the nature of the tunneling motions involved, these new data yeild only the difference of the tunneling splitting in the upper and lower states of the transition.

We have also observed spectra for $(HOD)_2$, two singly substituted ^{18}O species, two singly substituted ^{17}O species and the doubly substituted ^{17}O species. For $(HOD)_2$, the unshifted E-states of $(H_2O)_2$ are absent, leaving only A and B states present. The 1-0 and 2-1 K = 0 transitions have been observed for these levels. The tunneling frequency corresponding to the HF dimer like motion (exchanging of D atoms in the hydrogen bond) for this species is 2643 MHz. A schematic diagram of the energy levels is given in Fig. 2.6.

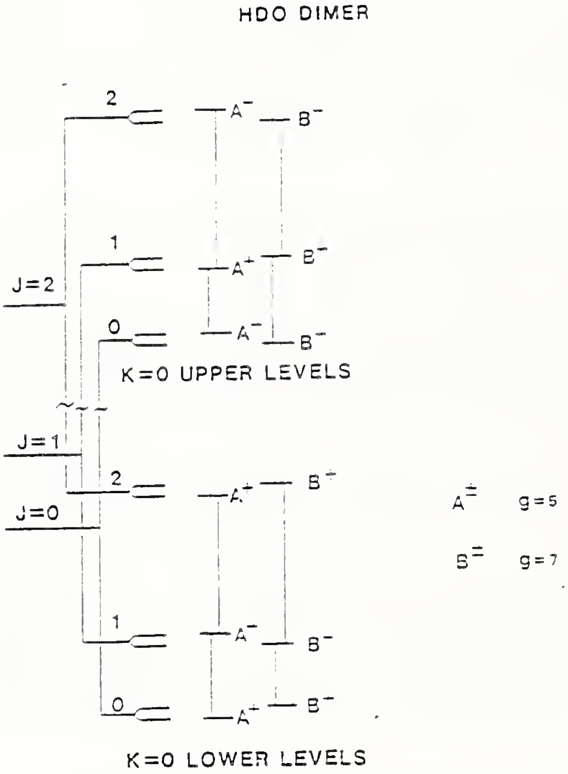

Fig. 2.6 Schematic diagram of the energy levels for $(HDO)_2$. The vertical lines indicate the observed microwave transitions.

The nuclear quadrupole coupling constants for the ^{17}O species have been determined from measurements on the J = 1-0 transitions. The values determined are shown in Fig. 2.7.

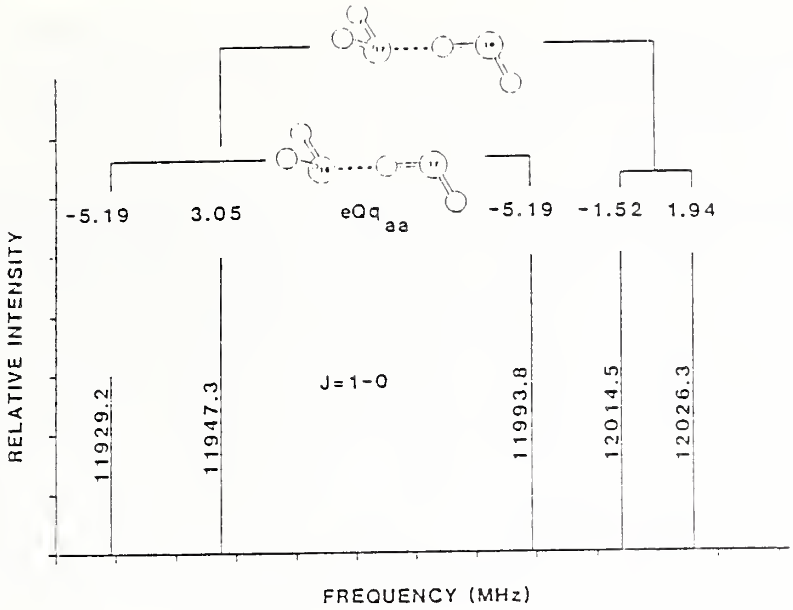

Fig. 2.7 Stick diagram of the observed J=1-0 transitions of H_2O-$H_2{}^{17}O$ and $H_2{}^{17}O$-H_2O. The nuclear electric quadrupole coupling constants of ^{17}O are shown above each transition.

3. Tunneling Splittings in the Water Dimer: Further Development of the Theory

(L. H. Coudert* and J. T. Hougen)

Energy level expressions were derived for the hydrogen-bonded water dimer complex and some of its deuterated species, using a previously reported Internal-Axis-Method-like formalism development for high-barrier tunneling problems involving several large amplitude motions. First, the feasibility of various tunneling motions was considered, using a potential surface given by Coker and Watts, and three main tunneling paths for $(H_2O)_2$ were chosen. We assumed that the most feasible path corresponds to a 180° rotation of the acceptor monomer; that the next most feasible path corresponds to a geared-type rotation of the two monomers, leading to an exchange of donor and acceptor monomer roles; and that the third most feasible path corresponds to an exchange of donor hydrogen atoms in the hydrogen bond, accompanied by an umbrella motion of the acceptor monomer. As the second step, the J and K dependence of the purely vibrational tunneling splittings, which arise in the IAM-like formalism because angular momentum is generated during the tunneling motions, was taken into account by computing sets of angles χ, θ, ϕ for Wigner $D^{(J)}(\chi, \theta, \phi)_{K,K'}$ expressions appearing as factors in the vibrational tunneling matrix elements. Symmetry relations determined for the angles χ, θ, ϕ greatly simplify the calculations. Finally, the Hamiltonian matrix was set up and diagonalized to obtain the desired energy level expressions. For the most symmetric species $(H_2O)_2$ and $(D_2O)_2$ we also treated the J and K dependence of the tunneling splittings arising from the presence of rotational terms in the effective Hamiltonian operator.

4. The Torsional-Rotational Spectrum and Structure of the Formaldehyde Dimer

(F. J. Lovas, R. D. Suenram, L. H. Coudert*, T. Blake*, K. J. Grant*, and S. E. Novick*)

The microwave spectra of $(H_2CO)_2$ and $(D_2CO)_2$ have been observed with a pulsed beam Fabry-Perot cavity Fourier transform microwave spectrometer. Both species exhibit a-type spectra which are split by internal rotation of each momomer unit and an interchange of donor-acceptor bonding roles analogous to the water dimer. A rotational analysis of each spectrum provides the constants A = 18554. (40) MHz, B = 1887.133(25) MHz, and C = 1384.576(25) MHz for $(H_2CO)_2$ and A = 14862. (4) MHz, B = 1760.607(10) MHz, and C = 1269.629(10) MHz for $(D_2CO)_2$. Stark effect measurements yielded the following components of the electric dipole moments: μ_a = 0.858(4) D and μ_b = 0.027(10) D for $(H_2CO)_2$, and μ_a = 0.908(4) D and μ_b = 0.095(4) D for $(D_2CO)_2$. The geometry obtained from fitting the derived moments-of-inertia, shown in Fig. 2.8, has the planes of the two monomer units perpendicular to one another with a nearly antiparallel orientation of the CO groups and a carbon to oxygen distance of 2.84Å.

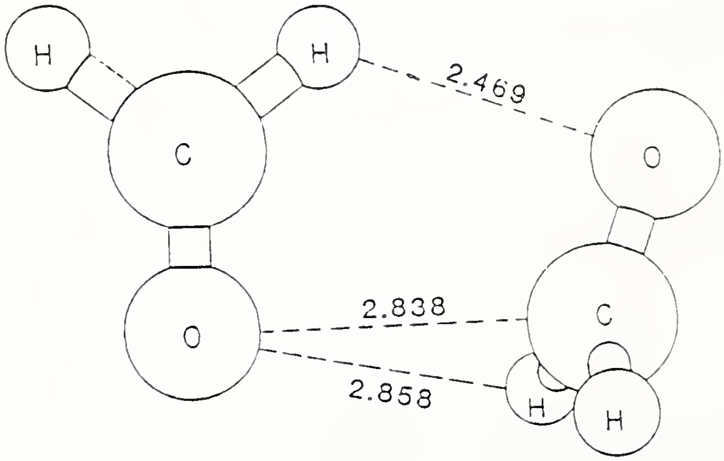

Fig. 2.8 Molecular structure of formaldehyde dimer.

5. Infrared and Microwave Investigations of Interconversion Tunneling in the Acetylene Dimer

(G. T. Fraser, R. D. Suenram, F. J. Lovas, A. S. Pine, J. T. Hougen, W. J. Lafferty, and J. S. Muenter*)

A sub-Doppler infrared spectrum of $(HCCH)_2$ has been obtained in the region of the acetylene C-H stretching fundamental using an optothermal molecular-beam color-center laser spectrometer. Microwave spectra were obtained for the ground vibrational state using a pulsed-nozzle Fourier-transform microwave spectrometer. In the infrared spectrum, both a parallel and perpendicular band are observed with the parallel band having been previously assigned to a T-shaped C_{2v} complex by Prichard, Nandi, and Muenter and the perpendicular band to a C_{2h} complex by Bryant, Eggers, and Watts. The parallel band exhibits three K_a=0 and three asymmetry-doubled K_a=1 series. The transitions show a clear intensity alternation with K_c with two of the K_a=0 series missing every other line. In addition, the perpendicular band has the same ground-state combination differences as the parallel band. To explain these apparent anomalies in the spectrum, we invoked a model consisting of a T-shaped complex with interconversion tunneling between four isoenergetic hydrogen-bonded minima as illustrated in Fig. 2.9. In this model, the parallel and perpendicular bands arise from excitation of the acetylene units parallel and perpendicular to the hydrogen bond. The observation of rotation-inversion transitions in the microwave spectrum, in addition to the pure rotation transitions of Prichard, Nandi, and Meunter, verifies the model. The measured microwave splittings yield a tunneling frequency of 2.2 GHz which is consistent with a ~33 cm^{-1} barrier separating the four minima.

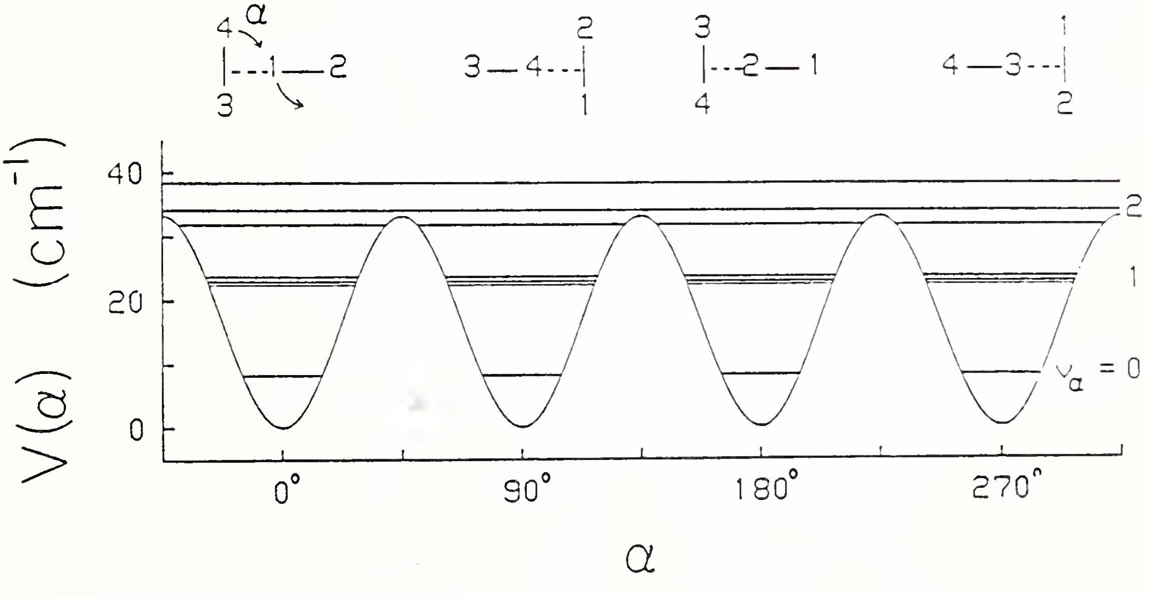

Fig. 2.9 Model potential for the internal-rotation tunneling in the acetylene dimer. The potential energy is taken as $V(\alpha) = V_4(1-\cos 4\alpha)/2$ where $V_4 = 33.2\ cm^{-1}$ and α is defined in the figure. The $\nu_\alpha = 0$ level is split into A_1^+, E^+, and B_1^+ tunneling sublevels with the B_1^+-A_1^+ splitting determined by microwave spectroscopy to be 2207 MHz (0.07362 cm^{-1}).

6. Vibrational, Rotational, and Tunneling Dependence of Vibrational Predissociation in the HF Dimer

(A. S. Pine and G. T. Fraser)

Vibrational predissociation linewidths have been resolved in the two H-F stretching bands of the HF dimer using an optothermal (bolometer-detector) molecular-beam color-center laser spectrometer. In addition to the strong vibrational mode dependence reported earlier by several groups, we observe a substantial K-rotational and tunneling dependence on the longer-lived mode, ν_1, which is associated with the "free-H" stretching vibration. The predissociation linewidths (FWHM in MHz) for this vibration are 6.4(5) for $K=0^+$, 9.5(5) for $K=0^-$, 10.2(5) for $K=1^+$ and 11.8(5) for $K=1^-$, where the +/- superscripts refer to the symmetric/antisymmetric tunneling states. The J dependence (at low J) is negligible compared to the K dependence. The K=0 levels of the "bound-H" stretch have tunneling-independent widths of 330(30) MHz. Extraneous broadening due to saturation effects was observed and corrected for in these measurements.

7. Vibrational Exchange upon Intercoversion Tunneling in $(HF)_2$ and $(HCCH)_2$

(G. T. Fraser)

Model calculations were undertaken to interpret the large H-F and C-H stretching vibrational dependencies of the interconversion tunneling splitting and the corresponding infrared vibration-tunneling state selection rules in $(HF)_2$ and $(HCCH)_2$. The model consists of two potential curves, $V_a(\rho)$ and $V_b(\rho)$, with $V_a(\rho)=V_b(-\rho)$, where ρ is the tunneling coordinate. For $(HF)_2$, $V_a(\rho)$ and $V_b(\rho)$ correspond to having the vibrational excitation localized in submolecules H_aF_a and H_bF_b, respectively (see Fig. 2.10). The two potential curves are coupled by an interaction term, $V_{ab}(\rho)$, that allows the vibrational excitation to be exchanged between the two monomer units, permitting tunneling to occur. The interaction term is approximated by resonant infrared transition-dipole coupling. The magnitudes of the calculated vibrational dependencies and the predicted selection rules are in agreement with previous experimental observations.

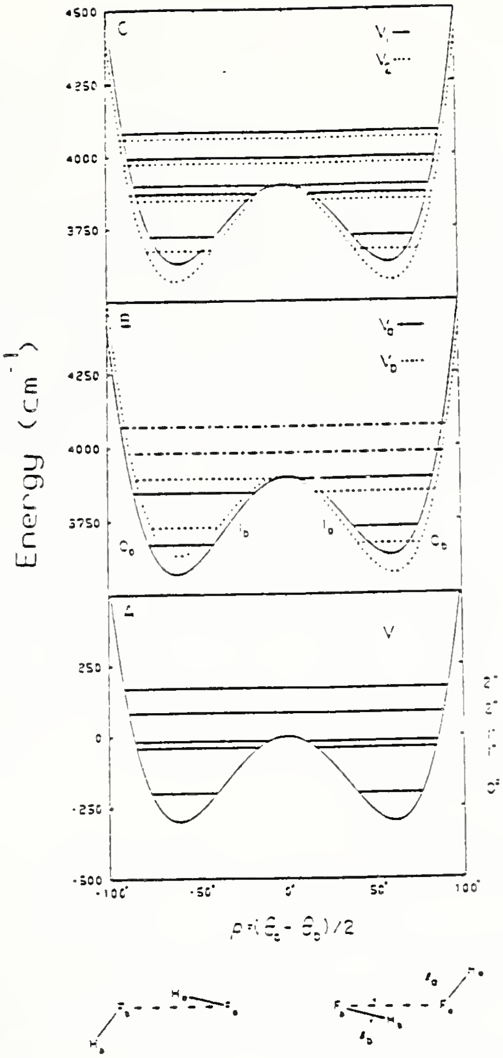

Fig. 2.10 Potential curves and tunneling pathway used to model the vibrational dependence of the interconversion tunneling splittings in $(HF)_2$. Here, ρ is the tunneling coordinate. Figures A-C show the ground-state potential $V(\rho)$, the two excited-state curves $V_a(\rho)$ and $V_b(\rho)$, which correspond to having the HF excitation in H_aF_a and H_bF_b, respectively, and the effective (adiabatic) potentials $V_1(\rho)$ and $V_2(\rho)$ for the ν_1 and ν_2 vibrational states of the dimer. Also shown are vibrational states calculated for these potentials.

8. Ammonia Dimer: Further Structural Studies

(D. D. Nelson, Jr.*, W. Klemperer*, G. T. Fraser, F. J. Lovas, and R. D. Suenram)

New experimental results on the structural and dynamical properties of NH_3 dimer were obtained with the NIST pulsed beam Fourier transform microwave spectrometer. The J = 1-0, K = 0 transitions of $^{14}NH_3$-$^{15}NH_3$, $^{15}NH_3$,-$^{14}NH_3$, ND_3 dimer, and ND_3-ND_2H have been measured at high resolution and ^{14}N electric quadrupole coupling constants determined. The NH_3 subunits comprising the dimer are inequivalent. The quadrupole coupling constant associated with the first ammonia subunit eqQ^1_{aa}, is measured in $^{14}NH_3$-$^{15}NH_3$ [- 627(8) kHz], in the ND_3 dimer [- 531(15) kHz], and in ND_3-ND_2H [- 991(18) kHz]. For the other subunit, eqQ^2_{aa} was found for $^{15}NH_3$-$^{14}NH_3$ [892(8) kHz], the ND_3 dimer [745(13) kHz], and NH_2H [1013 (18) kHz]. These numbers can be used to estimate the vibrationally averaged polar angles of these isotopomers of NH_3 dimer. The result is (including the primary isotopomer) θ_1 for $^{14}NH_3$-$^{14}NH_3$ is 48.6°, for $^{14}NH_3$-$^{15}NH_3$ is 48.7°, for ND_3 dimer is 49.6° and for ND_3-ND_2H is 45.3°; while θ_2 for $^{14}NH_3$-$^{14}NH_3$ is 64.5°, for $^{15}NH_3$-$^{14}NH_3$ is 64.3°, for ND_3 dimer is 62.6°, and for ND_3-ND_2H is 65.8°. The remarkable invariance of these values rules out the possibility of large vibrational averaging or tunneling averaging in this system and establishes that the angles $\theta_1 = 49°$ and $\theta_2 = 65°$ are near equilibrium. The isotope effect in the component of the electric dipole moment along the a inertial axis μ_a, correlates well with the trend in polar angles given by the quadrupole coupling constants. The absence of interchange tunneling effects in the observed states of NH_3 dimer implies that these states are asymmetrically excited internal rotor states of the complex. These experimental structural results are in disagreement with all previous theoretically determined structures for NH_3 dimer except one. A recent electronic structure calculation which incorporates correlation through the coupled pair functional approach (while systematically varying geometry) obtains a compact, asymmetric structure for the dimer; this is in close accord with our observations.

9. Microwave Spectrum and Molecular Structure of the N_2-H_2O Complex

(H. O. Leung*, M. D. Marshall*, R. D. Suenram, and F. J. Lovas)

We observed the a-type, K = 0 microwave spectrum of the N_2-H_2O complex using a pulsed molecular beam Fabry-Perot cavity microwave spectrometer. Seven isotopic species have been studied in the range of 5-23 GHz. The N_2-H_2O complex exhibits tunneling motions similar to the 1 → 2 tunneling motion of the H_2O-DOD complex which gives rise to four components for each rotational transition. The molecular constants obtained for $^{14}N_2$-HOH are (in MHz):

Constant	A_2-State	A_1-State	B_1-State	B_2-State
B	2906.3618(2)	2906.9252(2)	2914.1457(2)	2914.2520(2)
D_J	0.041806(15)	0.043486(15)	0.042625(15)	0.043300(15)
$eQq(^{14}N)$	-4.253(2)		-4.227(3)	

The structure has a nearly linear N-N-HO geometry with a N-H distance of 2.42(4) Å and an OHN angle of 169° (R_{O-N} = 3.37(4) Å). The electric dipole moment along with a principal axis of inertia was determined for the $^{15}N_2$-HOH species with $\mu_a = 0.833(3)$ Debye. Unlike the H_2O-D_2O species, all four expected transitions are observed and exhibit the singlet and triplet spin-spin hypderfine structure expected for both $^{15}N_2$-HOH and $^{14}N_2$-HOH.

10. Rotational Spectra and Structures of the H_2S-H_2O and $(H_2S)_2$ Complexes

(F. J. Lovas, R. D. Suenram, and L. H. Coudert)

A pulsed-beam Fabry-Perot cavity microwave spectrometer has been employed in the measurement of rotational spectra of H_2S-H_2O and $(H_2S)_2$. The a-type K = 0 rotational transitions of both species have been observed in the 6-21 GHz range. The spectrum of H_2S-H_2O is expected to be analogous to that $H_2{}^{18}O$-H_2O and $^{15}N_2$-H_2O (described above) for which two tunneling motions give rise to four components for each transition. For H_2S-H_2O and its ^{34}S and ^{18}O isotopic forms, only 3 of the 4 components have been observed as illustrated in Fig. 2.11. The molecular parameters for H_2S-H_2O are:

State		1	2	3
(B+C)/2	(MHz)	3443.899(1)	3450.712(1)	3450.777(2)
D	(kHz)	28.71(5)	21.20(4)	24.67(4)
μ	(D)	0.551(3)	0.702(3)	0.697(6)

The energy levels of H_2S dimer and its isotopic forms are expected to be similar to those of water dimer. While hoping to observe a wider range of states than presently known for water dimer, at present only the K = 0 states for the E levels for $(H_2S)_2$, $(H_2{}^{34}S)$ and $(D_2S)_2$, and the similar levels of the mixed isotopic forms have been observed. For $(H_2S)_2$ the rotational constants are: B (E^+) = 1749.310(1) MHz and B (E^-) = 1748.109(1). The structures of both complexes are shown in Fig. 2.12. The fact that only three of the four expected transitions have been observed remains unexplained, as it is for the deuterated and ^{18}O species of water dimer.

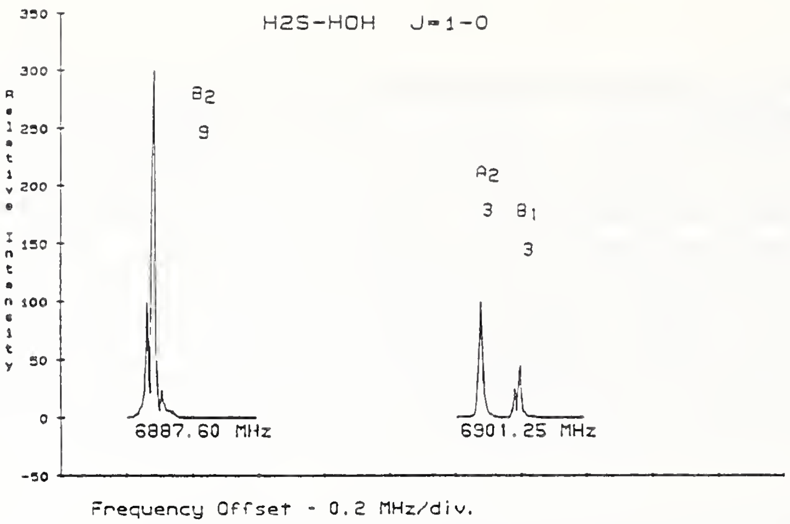

Fig. 2.11 The three observed components for the J=1-0 transition are shown. Two of the transitions have a triplet pattern.

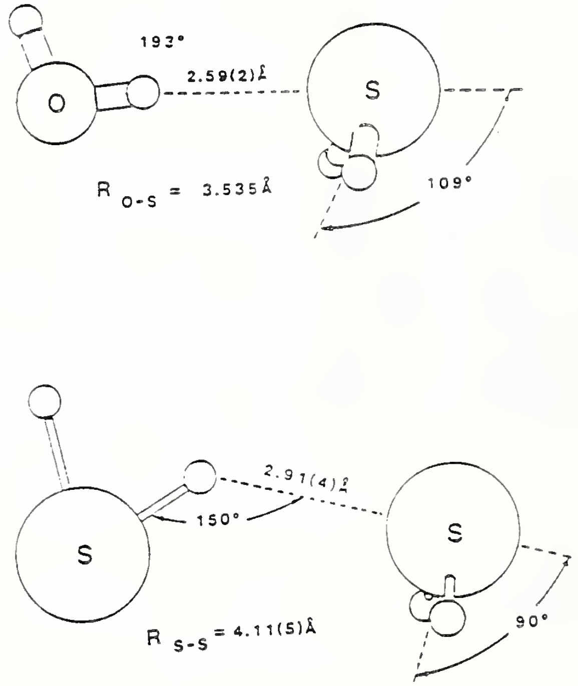

Fig. 2.12 Molecular Structures of H_2O-H_2S and H_2S dimer.

11. Microwave Spectrum of the Ozone-Water Complex

(R. D. Suenram, F. J. Lovas, J. Gillies*, and C. W. Gillies*)

The microwave spectrum of the ozone-water complex has been observed using a pulsed molecular beam microwave spectrometer. The spectra for normal species, $H_2{}^{18}O$, and one deuterated species have been assigned. Both a- and c-type transitions have been observed and fit using a centrifugal distortion Hamiltonian. For the O_3-H_2O species the rotational constants are A=11960.584(5), B=4174.036(8) and C=3265.173(8) MHz. The measured components of the dipole moment for the complex are μ_a=1.014(2)D, μ_b=0D, and μ_c=0.52(3)D which gives for the total dipole moment μ_T=1.14(1)D. From the available data several structural conclusions can be drawn, but details of the conformation are, at present, somewhat uncertain. The inertial defect ($\Delta \equiv I_c - I_b - I_a$) is -8.55uÅ^2 which indicates that the complex has a non-planar heavy atom structure. From Ray's asymmetry parameter $\kappa \equiv (2B-A-C)/(A-C)$ ($\kappa \equiv -0.8$) we conclude that the observed conformation must have a sandwich (H_2O and O_3 monomer planes parallel) or T-shaped (H_2O and O_3 monomer planes perpendicular), as opposed to an elongated structure with water bound to one end of the ozone molecule.

The dipole moment of the complex indicates that the two monomer subunits must be arranged such that substantial cancellation of the monomer dipoles occurs since μ_{water} = 1.85D and μ_{ozone} = 0.53D. This is also consistent with a T-shaped structure as shown in Fig. 2.13. Additional work is in progress involving the second deuterated isotope and $H_2{}^{17}O$.

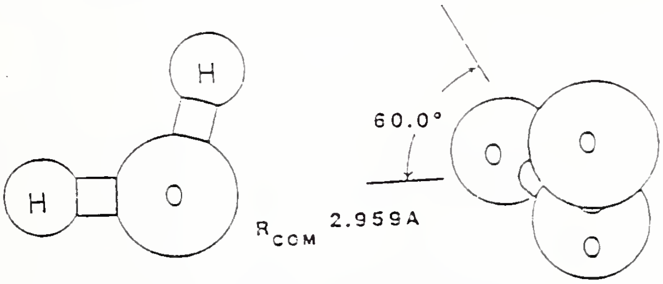

Fig. 2.13 Structure of the water-ozone complex.

12. The Structure of the CO_2-CO_2-H_2O van der Waals Complex Determined by Microwave Spectroscopy

(K. I. Peterson*, R. D. Suenram, and F. J. Lovas)

The rotational spectra of CO_2-CO_2-H_2O, CO_2-CO_2-D_2O, $^{13}CO_2$-$^{13}CO_2$-H_2O and CO_2-CO_2-$H_2{}^{18}O$ were measured using a pulsed molecular beam Fabry-Perot Fourier transform microwave spectrometer. The rotational constants of the normal species are A=3313.411(5) MHz, B=1470.548(3) MHz, C=1308.850(3) MHz, Δ_J=0.00341(4) MHz, Δ_{JK}=-0.0016(1) MHz, Δ_K=0.020(5) MHz, δ_J=0.000179(2) MHz, and δ_K=0.0005(7) MHz. The dipole moment, μ_b, is 1.989(2) D. Only b-type transitions are observed and the $J_{K-K+'}$ - J''_{K-K+} = J'_{ec}-J''_{oe} transitions are three times more intense than the others. This indicates a structure with two-fold symmetry with the C_{2v} axis of the water subunit aligned with the C_2 axis of the complex. The CO_2 subunits lie in a plane perpendicular to the C_2 axis located 2.47 Å below the oxygen atom in the water subunit. The C-C bond distance is 3.41(5) Å. Their orientation is very similar to that observed for the CO_2-CO_2 dimer although the C-C bond length is 0.19 Å shorter in the trimer. The C-O bond distances between the H_2O and two CO_2 subunits are both 3.00(5) Å which is 0.16 Å longer than that found in the CO_2-H_2O dimer. The hydrogens of the H_2O subunit are directed away from the CO_2-CO_2 plane; their angular orientation around the b axis is not well-determined. Two views of the structure are shown in Fig. 2.14.

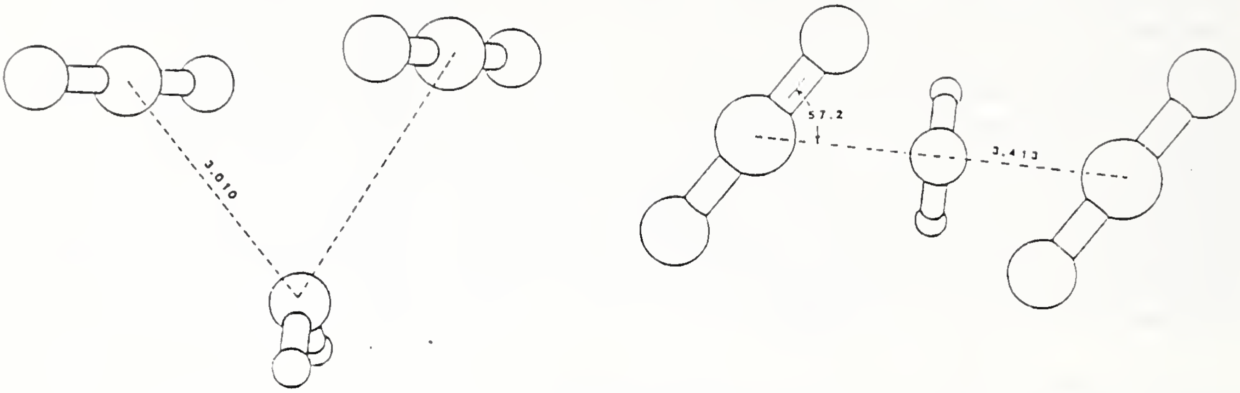

Fig. 2.14 Two views of the molecular structure of $(CO_2)_2H_2O$.

13. Structural Study of the H_2O-H_2O-CO_2 Trimer
(K. I. Peterson*, R. D. Suenram, and F. J. Lovas)

The microwave spectrum of the trimeric species H_2O-H_2O-CO_2 was studied in the 7-18 Ghz frequency range using a pulsed molecular beam Fabry-Perot Fourier transform microwave spectrometer. Each transition is doubled because of energy level splitting due to coupling of an internal rotation of one of the H_2O subunits with the overall rotation of the complex. Both states can be fit using a centrifugal distortion Hamiltonian. The rotational constants and inertial defects are:

	Lower State	Upper State
A	6163.576(5) MHz	6164.068(7) MHz
B	2226.156(3) MHz	2226.677(3) MHz
C	1638.972(2) MHz	1638.839(3) MHz
Δ	-0.66197 $uÅ^2$	-0.57724 $uÅ^2$

The electric dipole moment has also been measured yielding μ_a=1.57D, μ_b=0.76D and μ_c<0.1D. Several isotopically substituted species have been studied with various ^{13}C, ^{18}O and deuterium substitutions. All except a singly deuterated species exhibit doubled spectra. We conclude that the species has a nearly-planar triangular structure with dimer-type structures evident within the trimer complex (see Fig. 2.15). The oxygen of one of the H_2O subunits is bonded to the CO_2 carbon with a bond length of 2.8Å, within 0.1Å of that found in the H_2O-CO_2 dimer. The other H_2O has its oxygen bonded to one of the hydrogens of the first H_2O; the bond distance is 2.0Å, within 0.1Å of that found in the H_2O-H_2O dimer. This second H_2O is also hydrogen bonded to one of the oxygens in the CO_2 subunit with a bond distance of 2.0Å which is what one would expect for a hydrogen bonded

H_2O-CO_2 dimer (this species has not been observed). Evidence suggests that this H_2O subunit is involved in the internal rotation.

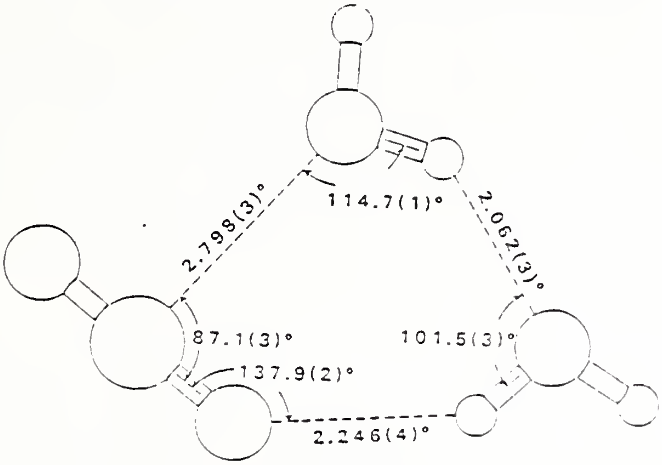

Fig. 2.15 Molecular structure of $(H_2O)_2CO_2$.

14. Microwave Spectrum of the CH_3OH-NH_3 Complex
(G. T. Fraser, R. D. Suenram, F. J. Lovas, and W. J. Stevens)

Microwave spectra of CH_3OH-NH_3 and $^{13}CH_3OH$-NH_3 have been obtained using a pulsed-nozzle Fourier-transform microwave spectrometer. The spectra, which are complicated by the internal rotation of the CH_3 and NH_3 groups, exhibit five K = 0 states at the ≈ 1 K rotational temperature of the expansion. Four of these are metastable, excited internal rotor states and correlate to E states of free CH_3OH or NH_3. For the two states in which the NH_3 top is in its ground internal rotor state, $\Delta J=1$, $K = 0$ progressions are observed and fit to linear-molecule-type frequency expressions to obtain effective spectroscopic constants. For CH_3OH-NH_3 these constants are: $(B + C)/2=3690.119(2)$ and 3686.114(2) MHz; $eQq_{aa}=-3.184(10)$ and -3.182(9) MHz; and $\mu_a=2.854(9)$ and 2.956(14) D. The complexes are hydrogen bonded with an OH-N bond length of 2.02Å. This bond length is similar to that found by Herbine and Dyke in the related HOH-NH_3 complex, 1.97Å. Ab initio SCF calculations have also been carried out for the CH_3OH-NH_3 and HOH-NH_3 complexes in order to compare interaction-energy components and origins of the dipole moment enhancements.

15. Determination of the Structure of OCS-CO_2
(S. E. Novick*, R. D. Suenram, and F. J. Lovas)

The rotational spectrum of the weakly bound complex OCS-CO_2 has been measured using a pulsed beam Fourier transform microwave spectrometer. The rotational constants of the major isotopomer are A = 4454.606 MHz, B = 1517.7788 MHz, and C = 1129.666 MHz. The molecule is planar with a "slipped near parallel" structure analogous to the structure of the dimer of carbon dioxide. The sulfur atom occupies the "inner" position; this is the obtuse rather than the acute vertex of the O-O-O-S quadrangle. The distance from the center-of-mass (c.m.) of CO_2 to the c.m. of OCS is 3.552Å which is slightly shorter than the C-C distance in CO_2 dimer (3.599Å).

16. Microwave Spectrum and Structure of H_2CO-CO_2

(T. A. Blake*, S. E. Novick*, R. D. Suenram, and F. J. Lovas)

The rotational spectrum of the H_2CO-CO_2 van der Waals complex has been measured using a pulsed beam Fourier transform microwave spectrometer. Each rotational line is split into a "strong" and "weak" intensity component due to the internal rotation of the formaldehyde moiety about its C_2 axis. The "strong" transitions are assigned to a B symmetry internal rotor state with the rotational constants A = 10.399.1(2) MHz, B = 2678.215(1) MHz, and C = 2128.340(1) MHz. The "weak", or A state lines were assigned with the rotational constants A = 10.400.5(2) MHz, B = 2678.271(1) MHz, and C = 2128.312(1) MHz.

The complex has a planar structure analogous to the "near slipped parallel" structures of $(CO_2)_2$ and CO_2-OCS, with the oxygen of H_2CO interacting with the carbon of CO_2 as illustrated in Fig. 2.16. The structural parameters and dipole moments of both the A and B states are the same within the stated uncertainties. The C-O (formaldehyde)-C (carbon dioxide) angle is 102.90(5)°, the O (formaldehyde)-C-O (carbon dioxide) angle is 83.23(3)°, and the O (formaldehyde)-C (carbon dioxide) distance is 2.980(1) A. The measured dipole moments are μ_a=1.661(2) D, and μ_b=1.671(2) D.

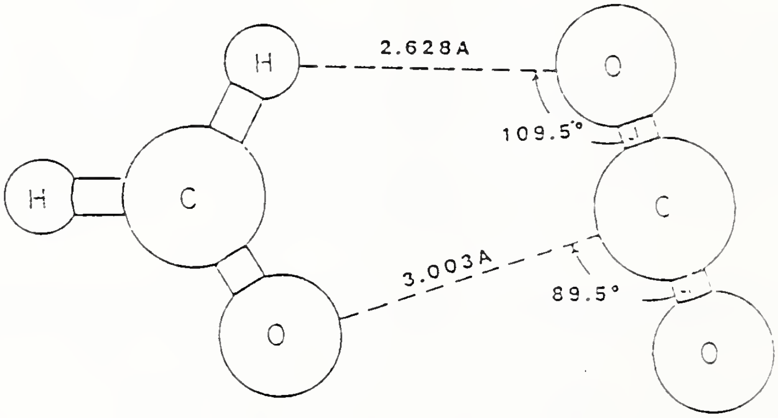

Fig. 2.16 Structure of the Formaldehyde-Carbon-Dioxide Complex

17. Structure and Vibrational Dynamics of the CO_2 Dimer from the Sub-Doppler Infrared Spectrum of the 2.7 μm Fermi Diad

(K. W. Jucks*, Z. S. Huang*, R. E. Miller*, G. T. Fraser, A. S. Pine, and W. J. Lafferty)

Sub-Doppler infrared spectra of two Fermi resonance coupled bands of carbon dioxide dimer have been obtained at 3611.5 and 3713.9 cm^{-1} using an optothermal molecular beam color-center laser spectrometer. The band origins for the complexes are red shifted by approximately 1 cm^{-1} from the corresponding $\nu_1 + \nu_3/2\nu_2^0 + \nu_3$ CO_2 bands. The higher frequency band is perturbed while the lower frequency band appears free of extraneous perturbations as determined from a precision fit to a Watson asymmetric rotor Hamiltonian. This fit and the observed nuclear spin statistical weights reveal that the complex is planar with C_{2h} symmetry (see Fig. 2.17). The C--C separation and C--C-O angle are determined to be 3.599(7)Å and 58.2(8)°, respectively. The nearest neighbor O--C distance is 3.14Å which is the same as that found in the crystal. From the centrifugal distortion analysis the weak bond stretching and symmetric bending frequencies are estimated to be 32(2) and 90(1) cm^{-1}. No interconversion tunneling is observed.

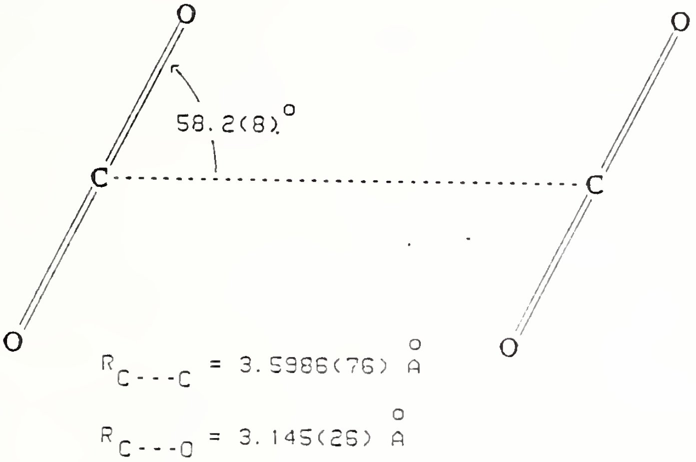

Fig. 2.17 Molecular structure of the CO_2 dimer determined from the ground state rotational constants. The complex is planar with C_{2h} symmetry.

18. Sub-Doppler Infrared Spectrum of the Carbon Dioxide Trimer

(G. T. Fraser, A. S. Pine, W. J. Lafferty, and R. E. Miller*)

A spectrum of the carbon dioxide trimer van der Waals species has been recorded near 3614 cm^{-1} at sub-Doppler resolution using an opthothermal (bolometer-detected) molecular-beam color-center laser spectrometer. A planar, cyclic structure with C_{3h} symmetry (see Fig. 2.18) has been determined for the complex with a carbon-carbon separation of 4.0382(3)Å. The observed perpendicular band, corresponding to an in-plane E'-symmetry vibration of the trimer, has been attributed to a localized excitation of the $2\nu_2^0 + \nu_3$ combination mode of a CO_2 subunit by virtue of its small blue shift (~0.98 cm^{-1}) from that of the isolated monomer.

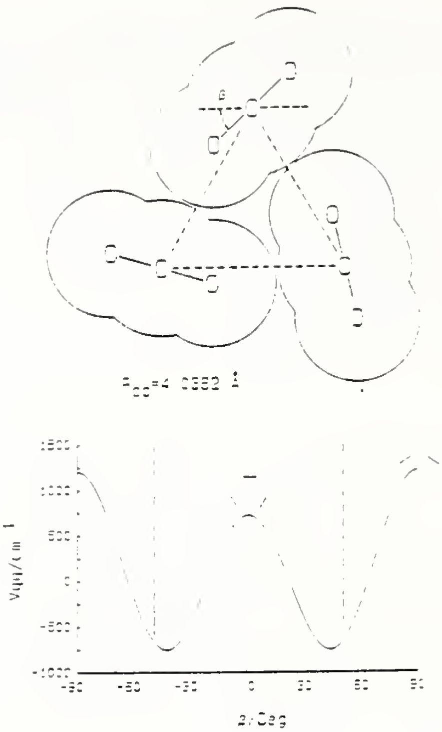

Fig. 2.18 Structure of the CO_2 trimer obtained from the spectrum assuming zero inertial defect and angle, $\beta \sim 43°$, from minimum of the electrostatic quadrupole-quadrupole potential pictured below. The dashed lines on the potential are drawn for contact of the van der Waals radii; the D_{3h} transition state geometries are indicated at $\beta = 0°$ and 90°.

19. Vibrational Predissociation in the CO_2 Dimer and Trimer and Rare Gas-CO_2 Complexes

(A. S. Pine and G. T. Fraser)

Vibrational predissociation linewidths for the CO_2 dimer and trimer and the Ne-CO_2 and Ar-CO_2 complexes have been resolved using a bolometer-detected (optothermal) molecular-beam color-center laser spectrometer. Observations were made on the pair of vibrations near 3715 and 3613 cm^{-1} corresponding to the $\nu_1 + \nu_3/2\nu_2^0 + \nu_3$ Fermi diad of CO_2. Homogeneous linewidths of from ~0.5 to ~22 MHz (FWHM) were measured for these related complexes, with Ne-CO_2 exhibiting both the broadest and the sharpest lines for the upper and lower bands, respectively. Ar-CO_2 and $(CO_2)_2$ showed mode-independent intermediate predissociation rates while only the lower band of $(CO_2)_3$ could be found. The results indicate that V → V energy transfer processes are the dominant predissociation channels with symmetry selection or propensity rules and specific resonances playing a role. The observed and calculated spectrum of the 3613 band is shown in Fig. 2.19.

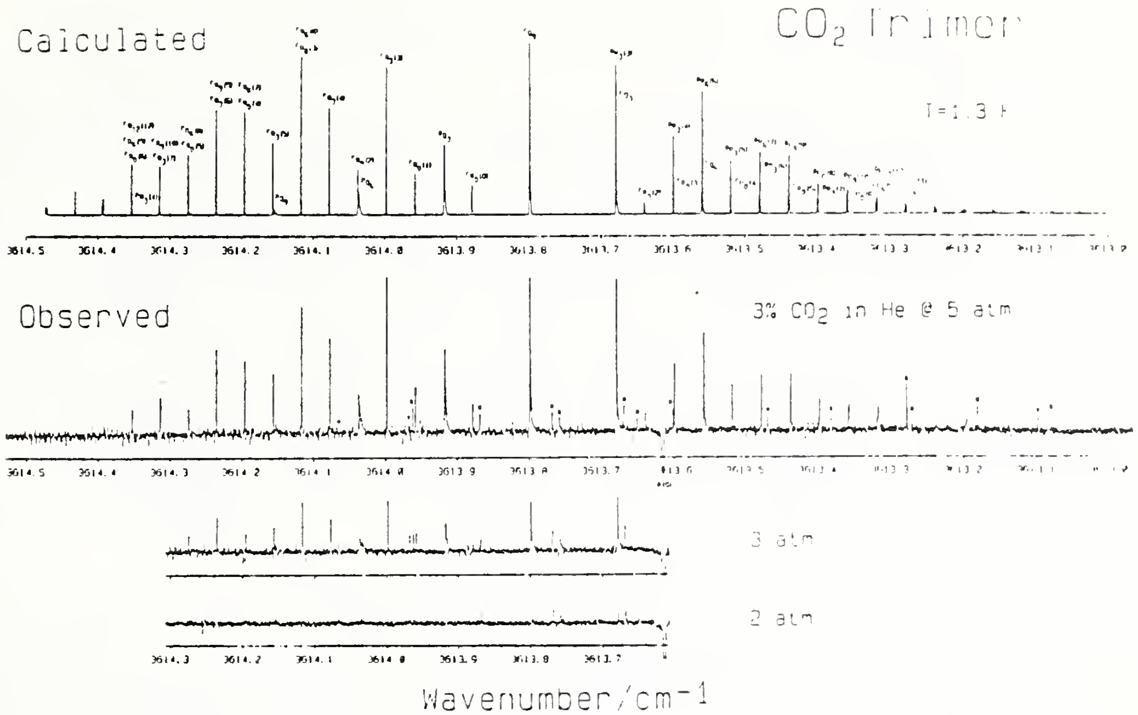

Fig. 2.19 Observed and calculated spectra of the CO$_2$ trimer in the region of the $2\nu_2^0 + \nu_3$ combination band of the monomer indicated by the negative-going R(0) line. Observed spectra for 3% CO$_2$:He mixture and 5 atm driving pressure. Asterisks indicate transitions attributed to the CO$_2$ dimer. Calculated transitions are simulated with Gaussian profiles of 20 MHz FWHM and an effective rotational temperature of 1.3 K.

20. Rotational Spectrum and Structure of H_2CO-HCl

(G. T. Fraser, C. W. Gillies*, J. Zozom*, F. J. Lovas, and R. D. Suenram)

Rotational spectra of H_2CO-$H^{35}Cl$, H_2CO-$H^{37}Cl$, D_2CO-$H^{35}Cl$, and D_2CO-$H^{37}Cl$ have been observed using a pulsed-nozzle Fourier transform microwave spectrometer. For H_2CO-$H^{35}Cl$ the following spectroscopic constants have been determined (in MHz): B = 2687.856(23), C = 2527.412(23), Δ_J = 0.0105(12), Δ_{JK} = - 0.233(10), eQq_{bb} = 14.106(19). HCl is bonded to the oxygen of H_2CO through a nonlinear hydrogen bond. For the H_2CO-$H^{35}Cl$ complex, the distance between the centers of masses of the HCl and H_2CO moieties is 3.3487Å giving an O--Cl distance of 3.21Å. From the quadrupole coupling constant, eQq_{aa}, an effective vibrationally averaged angle between the HCl axis and the a-axis of the complex is determined to be 30.5°. Centrifugal distortion analysis yields estimates of the weak bond stretching force constant and stretching frequency as 0.069(8) mdyn/Å and 85(4) cm^{-1}, respectively.

21. Electric Dipole Moments of HCl- and HCN-Hydrocarbon Complexes
(A. Weber, G. T. Fraser, and R. D. Suenram)

Electric dipole moments of several hydrocarbon-HCN and hydrocarbon-HCl complexes have been measured using a pulsed-nozzle Fourier-transform microwave spectrometer. The dipole moments (μ) and complexation-induced dipole moments ($\Delta\mu$) are (in D):

	HCl		HCN		HF[1,2]	
	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$
Acetylene	1.6032(29)	0.57	3.4130(42)	0.50	2.3681(28)	0.65
Ethylene	1.6167(15)	0.58	3.4023(27)	0.49	2.3839(45)	0.67
Benzene	1.688(10)	0.67			2.244(4)	0.59
Cyclopropane	1.7405(16)	0.71	3.5875(41)	0.67	2.5084(28)	0.78

The dipole moments for the HF complexes have been measured previously[1,2] using molecular-beam electric-resonance spectroscopy. The HCl-benzene result is in good agreement with the 1.6(1) D moment determined by Gandhi et al.[3] using electric deflection techniques. The induced dipole moments show a number of interesting features. With the same acid binding partner, the acetylene and ethylene complexes give similar induced moments while the cyclopropane complexes give the largest induced moments. Except for the benzene complexes, the induced dipole moments increase as: X-HCN < X-HCl < X-HF and do not follow the dipole moments of the acid binding partners which are ordered: HCl < HF < HCN.

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1. D. D. Nelson, Jr., G. T. Fraser, and W. Klemperer, J. Chem. Phys. 82, 4483 (1985).
2. F. A. Baiocchi, J. H. Williams, and W. Klemperer, J. Am. Chem. Soc. 87, 2079 (1983).
3. S. R. Gandhi and R. B. Bernstein, Chem. Phys. Lett. 143, 332 (1988).

22. Isotope Effects in the High-Resolution Infrared Spectrum of OC-HF
(G. T. Fraser and A. S. Pine)

High-resolution infrared spectra of H-F stretching bands of natural OC-HF and enriched $O^{13}C$-HF and ^{18}OC-HF have been recorded under thermal equilibrium conditions near 195 K with a tunable difference-frequency laser. The rotational constants of the three isotopic species are consistent with the linear C-H van der Waals bond as determined by microwave spectroscopy. The isotope shifts for the band centers exhibit a curious staggering with total CO mass which we attribute to anharmonic coupling of the zero-point CO bending motion. Resolved splitting of the ℓ doublets in a hot band originating in the CO bending vibration yield tentative assignments and rotational constants for this low frequency van der Waals mode.

23. Infrared and Microwave Spectra of OCO-HF and SCO-HF

(G. T. Fraser, A. S. Pine, R. D. Suenram, D. C. Dayton*, and R. E. Miller*)

The H-F stretching bands of the OCO-HF and SCO-HF complexes have been studied by optothermal (bolcmeter-detected) molecular-beam spectroscopy. Both species exhibit spectra of a quasilinear molecule red-shifted from free HF by 52.1 and 57.5 cm^{-1}, respectively. The principal band in both molecules is accompanied by a slightly red-shifted doublet-type subsidiary band that can be interpreted as a hot band of a low frequency bending vibration or a K=1 subband of a bent molecule. Accurate doublet splittings in the ground H-F vibrational state have been measured by pulsed-nozzle Fourier-transform microwave spectroscopy.

24. Pulsed Beam Rotational Study of the CH_2CH_2-O_3 van der Waals Complex

(C. W. Gillies*, J. Gillies*, W. Stahl*, R. D. Suenram, and F. J. Lovas)

We have recently completed a structural study of the primary ozonide of ethylene (see section on General Spectroscopic Studies). Our studies of the primary ozonide indicated that the reaction path involved a concerted 1,3-cycloaddition of ozone to the two carbon atoms of ethylene. If this were true it appeared that the van der Waals complex of ethylene-ozone would reflect this geometry and represent the transition state in the ethylene-ozone reaction which produces the cyclic primary ozonide. Using independent gas inlets to a pulsed solenoid valve, one for the Ar/CH_2CH_2 mixture and the second for the Ar/O_3 mixture, and mixing the two gases close to the nozzle exit, we have observed the rotational spectrum of O_3-CH_2CH_2 with the Fourier transform microwave spectrometer.

A geometry in which the ethylene plane is approximately parallel to the ozone plane with a C•••O distance of 3.25Å is consistent with the microwave data (see Fig. 2.20). This structure has the same symmetry (C_s) as ethylene primary ozonide. Since ethylene primary ozonide is the thermally labile 1,3-dipolar cycloaddition product of ozone plus ethylene, both species lie along the reaction coordinate predicted by orbital symmetry rules. Isotopic work is planned to further define the geometry of this complex. Future experiments will include other classical examples of 1,3-dipolar cycloadditions.

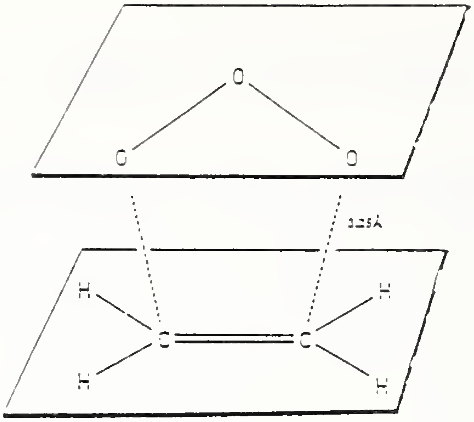

Fig. 2.20 Approximate geometry of ethylene-ozone complex showing the parallel planes of ethylene and ozone with a C···O distance of 3.25Å.

25. Future Plans

The major emphasis of the microwave studies during the past two years has been on structural studies of molecular complexes containing water, H_2S and formaldehyde. Since water is the most important solvent, we plan to continue investigations of water complexes. A preliminary identification of the spectrum of H_2O-H_2CO has been obtained recently and will be investigated further. Several of the experiments described above are still incomplete and these will be carried to completion next year.

A laser ablation source is now under construction and will be ready for initial tests early next fiscal year. With this source we plan to investigate complexes containing metal atoms and refractory materials.

Several modifications are planned to the optothermal molecular-beam spectrometer initially developed and successfully demonstrated for the probing of molecular complexes with a tunable color-center laser. A tunable sideband CO_2 laser system is under construction to provide access to the important 10 μm spectral region for the study of predissociation in a number of molecular complexes. The sideband generator operates by nonlinear optical mixing of microwave radiation from 8 to 18 GHz with a stabilized line-tunable CO_2 laser in a CdTe electooptic crystal. This should provide substantial coverage (>50%) throughout the 9 to 11 μm range with powers in excess of 1 mW. In conjunction with the color-center laser, this will also enable us to use infrared-infrared double resonance techniques to help identify and sort out spectra of previously uninterpreted rovibrational bands.

We are also installing quadrupole focussing fields in the drift chamber of the molecular-beam apparatus to permit us to examine the microwave spectrum of polar molecules and to provide microwave-infrared double resonance capabilities to aid in species identification and spectral assignments.

E. Rare Gas - Molecule Complexes

Since complexes involving the rare gas atoms comprise a separate category we describe our work on these in this section.

1. Optothermal-Infrared and Pulsed-Nozzle Fourier-Transform Microwave Spectroscopy of Rare Gas-CO_2 Complexes

(G. T. Fraser, A. S. Pine, and R. D. Suenram)

Sub-Doppler infrared spectra of Ne-CO_2, Ar-CO_2, and Kr-CO_2 have been recorded near 3613 and 3715 cm^{-1}, in the region of the $2\nu_2^0 + \nu_3/\nu_1 + \nu_3$ Fermi diad of CO_2, using an optothermal molecular-beam color-center laser spectrometer. In addition, pulsed-nozzle Fourier-transform microwave spectra are reported for the ground vibrational states of the complexes. The infrared and microwave spectra are consistent with T-shaped complexes as shown originally by Steed, Dixon, and Klemperer for Ar-CO_2. The infrared band origins for the Ar and Kr complexes are red shifted, from that of free CO_2, by 1.09 and 0.95 cm^{-1} for Ar-CO_2 and by 1.97 and 1.76 cm^{-1} for ^{84}Kr-CO_2. For Ne-CO_2, blue shifts of 0.15 and 0.19 cm^{-1} are observed. The lower Fermi components are free of perturbations, whereas the upper components of Ar-CO_2 and Kr-CO_2 are perturbed. For Ar-CO_2 the perturbation is strong, shifting the positions of the observed Q-branch lines of the $K_a = 1 \leftarrow 0$ subband by as much as 500 MHz.

2. Rotational-Tunneling Spectrum of Ar-H_2O and Ar-H_2S

(F. J. Lovas and R. D. Suenram)

Recently Cohen et al.[1] reported the far infrared spectrum of Ar-H_2O. They observed c-type transitions from the ground state to the upper component of a hydrogen exchange tunneling doublet (internal rotation of H_2O in the complex). Based on their rotational analysis we have confirmed their ground state assignments by observing the a-type transitions in the ground state. In order to determine the structure of the complex we have also measured the a-type spectrum of Ar-$H_2{}^{17}O$, Ar-$H_2{}^{18}O$ and Ar-D_2O. Spectral searches for the mono-deuterated species are in progress. With the information at hand, the complex appears to have the Ar bonded nearly perpendicular to the plane of H_2O at an Ar-O distance of 3.7Å. Searches for the second state produced by the tunneling motion will be carried out first on the D_2O species. We have recently detected this state for the Ar-D_2S species and will look for the spectrum of the second state in Ar-H_2S in the near future.

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[1] R. C. Cohen, K. L. Busarow, K. B. Laughlin, G. A. Blake, M. Aaverth, Y. T. Lee, and R. J. Saykally, private communication.

3. Determination of the Structure of Ar-H_2CO

(S. E. Novick*, F. J. Lovas, R. D. Suenram, and G. T. Fraser)

The rotational spectrum of the weakly bound complex Ar-H_2CO has been measured using a pulsed beam Fourier transform microwave spectrometer. The rotational constants of the complex are A = 40059.961 MHz, B = 2174.589 MHz, and C = 2080.321 MHz. The argon atom sits almost directly above the carbon atom of the formaldehyde with an Ar - C distance of 3.614 Å and an Ar--C-O angle of 90°. It is likely that the hydrogen atoms of the formaldehyde execute hindered internal rotation about the C-O axis and thus their positions within the complex are not well specified.

Stark effect measurement on Ar-H_2CO yields electric dipole moment components μ_a=0.461(5) D and μ_b=2.209(10) D which are consistent with the "T-shaped" structure shown in Fig. 2.21.

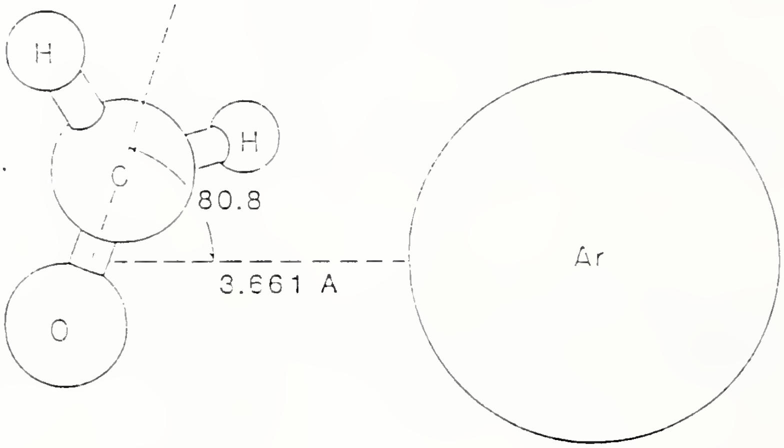

Fig. 2.21 The structure of Ar-H_2CO.

4. Rotational Spectra and Structure of Ar-CH_3OH and Kr-CH_3OH

(R. D. Suenram, G. T. Fraser, F. J. Lovas, J. Zozom*, and C. W. Gillies*)

Microwave spectra of Ar-CH_3OH, Ar-CD_3OH, and Kr-CH_3OH have been obtained using a pulsed nozzle Fourier transform microwave spectrometer. For each of these complexes two torsional states are observed at the ~1K rotational temperature of the expansion. These are the ground state and a metastable excited internal rotor state which correlates to the E internal rotor state of methanol. The a- and b-type ground state spectra are well characterized by the usual asymmetrical top formalism while the excited internal rotor states are complicated by the internal angular momentum. Attempts are presently underway to analyze the excited state spectra. Some preliminary spectroscopic constants for the ground internal rotor state of Ar-CH_3OH complex are (in MHz): A = 25468.82(13), B = 2084.42(2) and C = 1928.459(2).

In both complexes the rare gas atom is located approximately perpendicular to the C-O axis. For Ar-CH_3OH the distance between the centers of mass of the two subunits is 3.68 Å and the weak bond stretching force constant is 0.017 mdyn/Å (see Fig. 2.22). Similar results have been obtained for Kr-CH_3OH.

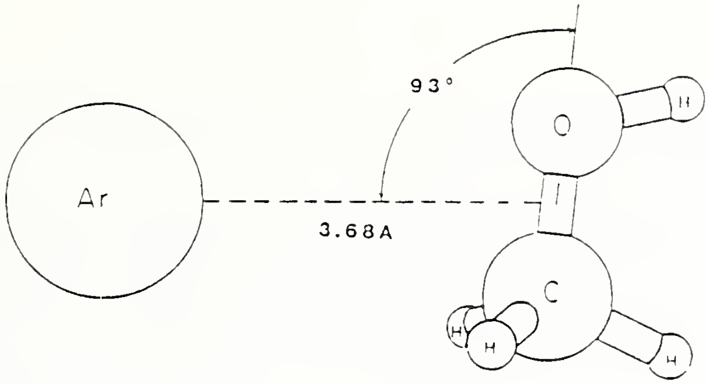

Fig. 2.22 The Structure of Ar Methanol.

5. Microwave Spectrum, Structure, and Electric Dipole Moment of the Ar-Formamide van der Waals Complex
(R. D. Suenram, G. T. Fraser, F. J. Lovas, C. W. Gillies*, and J. Zozom*)

The microwave spectrum of the Ar-formamide van der Waals complex has been obtained using a pulsed-nozzle Fourier-transform microwave spectrometer. The rotational constants of the complex are: A = 10725.7524(48) MHz, B = 1771.0738(22) MHz, and C = 1548.9974(16) MHz. The complex is shown to be non-planar with an inertial defect of -6.21 uÅ^2. The Ar atom is located 3.62Å from the center of mass of the formamide unit at Ar-O, Ar-N, and Ar-C distances of 3.55, 3.79, and 3.93Å, respectively. The shortest Ar-H distance is 3.25Å which is similar to that observed for Ar-vinyl cyanide (3.21Å). A view of the molecular structure is shown in Fig. 2.23 which indicates the out-of-plane angle. Stark effect and hyperfine analyses yield the following values for the electric dipole moment components and ^{14}N quadrupole coupling constants for the complex: $\mu_a = 0.922(1)$ D, $\mu_b = 3.407(5)$ D, $\chi_{aa} = -1.164(7)$ MHz, $\chi_{bb} = 1.906(5)$ MHz, and $\chi_{cc} = -0.742(6)$ MHz.

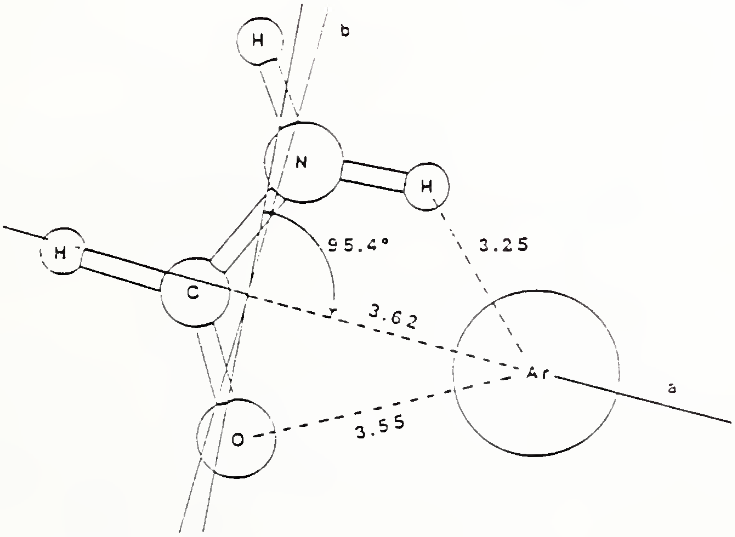

Fig. 2.23 Structure of Ar-formamide for the ground vibrational state.

6. Rotational Spectrum and Structure of Ar-CH_2CHCl

(F. J. Lovas and R. D. Suenram)

Our recent structural studies of Ar-CH_2CHCN and Ar-NH_2CHO illustrated a multicentered van der Waals interaction between Ar and these asymetric top binding partners. For the vinyl cyanide complex we also found two states which were interpreted as a double well potential produced by an inversion motion of the vinyl cyanide unit between two equivalent non-planar structural configurations. In order to determine if these structures are representative of a general configuration for rare gas complexes with asymmetric tops we have examined the rotational spectrum of Ar- vinylchloride. Indeed, we find two states for both ^{35}Cl and $^{37}C\ell$ isotopic species. The structure shown in Fig. 2.24 is similar to those reported earlier for the vinyl cyanide and formamide complexes.

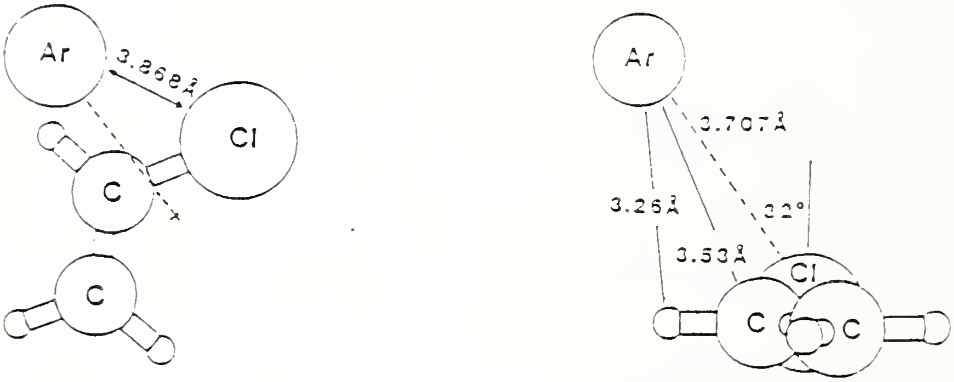

Fig. 2.24 Molecular structure of argon-vinylchloride

F. Matrix Isolation Spectra

1. Free Radical Stabilization and Spectra

(M. E. Jacox)

All of the experimental studies conducted during the past two years have benefitted from the use of the BOMEM Fourier transform instrument. In each of the systems studied, the enhanced sensitivity, resolution, or spectral range has been critical to the acquisition of data suitable for positive spectral assignments and for publication.

Studies of the reaction of H atoms with HCN were completed and published. No infrared data had previously been reported for the lowest energy reaction product, H_2CN. This study led to the assignment of five of the six ground-state vibrational fundamentals of this species, which is important in nitramine decomposition and in the combustion of nitrogen-containing molecules. Earlier gas-phase studies had yielded two bands attributed to H_2CN near 285nm and extended progressions for the two deuterium-substituted species. Because of predissociation, no rotational structure was resolved. The band separation of approximately 600 cm^{-1} observed for H_2CN could be explained either by the presence of a "hot band" or by the occurrence of two partially overlapping electronic transitions. The detection of both bands in the ultraviolet absorption studies or matrix-isolated H_2CN precluded the contribution of the lower frequency absorption by a "hot band." Weak absorptions were also observed beyond the second band in the matrix observations on H_2CN, permitting a tentative vibrational assignment for all of the electronic absorption bands which have been reported for $H_2CN\text{-}d_n$.

Studies of the infrared spectrum of t-HOCO, obtained both by the interaction of excited argon atoms with formic acid and by the reaction of H atoms with formic acid, were also completed and published. This species is intermediate in the OH + CO reaction, the principal source of CO_2 in hydrocarbon combustion. In 1970, studies of the vacuum ultraviolet photolysis of H_2O in a CO matrix conducted in this laboratory yielded the infrared spectra of both c- and t-HOCO. Although infrared absorptions of molecules isolated in an argon or neon matrix generally appear within about 1% of the gas-phase band center, the isomeric HOCO molecules can hydrogen-bond to CO, with potentially large shifts in the infrared absorptions associated with the hydrogen stretching and bending vibrations. No subsequent reports of the spectra of the HOCO isomers have appeared. Because diatomic reactants cannot diffuse through solid argon, the yield of products in the $Ar:CO:H_2O$ system--for which the hydrogen bonding would be avoided--would be undetectably small. The problem of hydrogen bonding was completely removed in the study in which the interaction of excited argon atoms with formic acid was the source for t-HOCO. Although only a 10 cm^{-1} shift in the C=O stretching fundamental was observed, the OH stretching fundamental of t-HOCO was found to be shifted by 150 cm^{-1} the torsion fundamental by 100 cm^{-1}, and the HOC in-plane deformation by 50 cm^{-1} as a result of hydrogen bonding with CO. In the experiments in which t-HOCO was stabilized as a product of the F + HCOOH reaction, a significant yield of t-HOCO•••HF was also observed. Thus, t-HOCO provides an interesting example of the participation of a single species in the formation of two different types of hydrogen bond. The determination of the infrared band centers for the isolated molecule provides a basis for the search for the gas-phase spectrum of this important combustion reaction intermediate. In turn, the gas-phase observation would constitute a second stage in the development of diagnostics for the detection of t-HOCO in combustion systems.

A review chapter entitled "The Stabilization and Spectroscopy of Free Radicals and Reactive Molecules in Inert Matrices" was prepared for publication in a book entitled, Chemistry and Physics of Matrix-Isolated Species, edited by L. Andrews and M. Moskovits, which is scheduled to appear early in 1989. This review is intended to serve as an in-depth guide to scientists who are beginning studies involving free radical stabilization in matrices or who need to know the conditions under which matrix isolation studies may provide data useful as a starting point for gas-phase free radical detection.

2. Molecular Ion Stabilization and Spectra

(M. E. Jacox and W. E. Thompson*)

A new series of experiments has begun in which the 16.6-16.8 eV energy of excited neon atoms is used as a photoionization source for matrix isolation studies of the spectra of molecular ions. This energy is above the photoionization threshold of virtually all molecules. Molecular cations play important roles in such diverse processes as those characteristic of the earth's ionosphere and of chemical vapor deposition and the plasma etching of microcircuits. While they are readily detected by mass spectrometers, frequently a mass probe cannot be introduced into a system and optical detection of ionic species would be desirable. Recently, high-resolution infrared spectra have been reported for a number of small molecular cations. However, for most such species the only spectral data available are those derived from low-resolution (> 50 cm^{-1}) photoelectron spectra. The development of matrix isolation studies as a survey tool for obtaining the infrared and ultraviolet spectra of molecular cations would provide an important first step in the establishment of optical diagnostics for these species.

The sampling configuration used for these experiments is shown in Fig. 2.25. A microwave discharge through a stream of neon flowing through a Vycor tube provides the neon-atom excitation. In approximately the plane of the coarse (approximately 1 mm^2) pinhole in the end of the discharge tube, a mixture of XY, the molecular ion precursor, with a several hundredfold excess of neon is introduced into the system. Approximately 2.5 cm downstream the interaction products are frozen onto a cryogenic surface maintained at 4K. Similar experiments using a beam of excited argon atoms, including those involved in the stabilization of t-HOCO, have previously been conducted at 14K. However, neon matrix experiments require the use of a cell which can be cooled to 4K, the temperature of liquid helium. Therefore, it was necessary to place in service a continuous-transfer liquid helium cell and to establish the conditions under which a stable discharge through neon could be maintained.

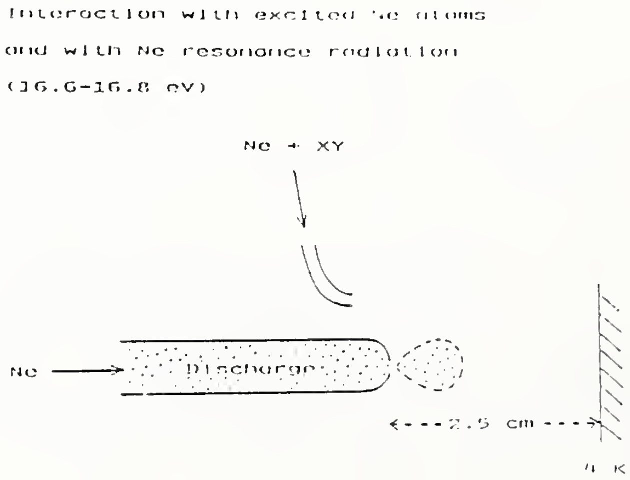

Fig. 2.25 Discharge configuration used for excited neon atom experiments.

The first molecule to be studied in this system was CO_2. High resolution infrared experiments have recently determined a gas-phase band center of 1423.1 cm^{-1} for the antisymmetric stretching fundamental, ν_3 of CO_2^+. As is shown in trace (a) of Figure 2.26 a weak to moderately intense, structured absorption appeared at 1421.7 cm^{-1} in the neon-matrix study. Isotopic substitution experiments confirmed the assignment of this absorption to CO_2^+; in trace (b) the counterpart of this peak appeared near 1380.4 cm^{-1} for a heavily carbon-12 enriched CO_2 sample, and in trace (c) the singly and doubly oxygen-18 substituted CO_2^+ species appeared at 1412.4 and 1399.8 cm^{-1}, respectively.

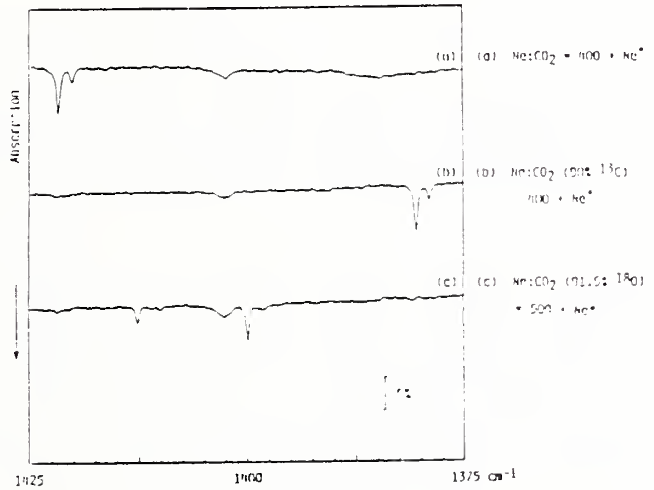

Fig. 2.26 Isotopically substituted CO_2^+ (ν_3) absorptions observed in solid neon.

In matrix isolation observations it is necessary for overall charge neutrality of the deposit to be maintained. Therefore, molecular anions must also be stabilized in these experiments. In the CO_2 experiments, an absorption appeared at 1658.2 cm^{-1} which had isotopic substitution behavior appropriate for assignment to ν_3 of CO_2^-. Earlier studies in this laboratory of charge-transfer interaction between alkali metal atoms and CO_2 in an argon matrix had led to the identification of this fundamental of CO_2^- at 1608 cm^{-1} when sodium was used and at 1596 cm^{-1} when cesium was present in the sample. Because alkali metal atoms can diffuse through rare-gas matrices and must be quite close to the CO_2 molecule before charge transfer can occur, in the earlier experiments the CO_2^- was stabilized primarily at $M^+ \cdots CO_2^-$. In the neon discharge experiments, the anion and cation concentrations are very small, and the molecular ions, which are trapped in random sites, cannot diffuse through the matrix. Therefore, it is believed that the position of the neon-matrix absorption of CO_2^-, 1658.2 cm^{-1}, most closely approximates the gas-phase band center.

A relatively broad absorption appears at 1402.4 cm^{-1} in all three of the traces of Fig. 2.26. This absorption, which is destroyed when photodetachment of electrons in the sample occurs, has tentatively been assigned to H_2O^+, formed from water desorbed from the walls of the sampling system. The ground-state bending fundamental of this important cation has been reported at 1408.4 cm^{-1} as a result of extrapolation of a long progression in this vibration in the optical emission spectrum. This value is consistent with that obtained in a study of the high resolution (ca. 2 cm^{-1}) photoelectron spectrum of H_2O. Observations on a $Ne:H_2O$ sample also yielded a product absorption near 3250 cm^{-1}, in the region in which the high resolution infrared absorptions of the two stretching absorptions of H_2O^+ were recently identified. Further experiments are planned in order to obtain a definitive assignment of the absorptions near 1402 and 3250 cm^{-1} and to establish the identity of the negatively charged species in the $Ne:H_2O$ system.

While new cation absorptions were not identified in these two experimental systems, the observation of peaks close to those of known cation absorptions demonstrates the utility of the sampling technique for producing molecular cations and supports the hypothesis that molecular vibrations of covalently bonded molecular cations, like those of free radicals, experience only small matrix shifts in solid neon.

Because O_3^+, O_4^+, O_3^-, and O_4^- are among the most important molecular ions in the D region of the ionosphere and because oxygen is frequently present as an impurity in samples used for cation formation, a series of experiments was conducted in which the excited neon was codeposited with a $Ne:O_2$ sample. As is shown in Fig. 2.27, several prominent absorptions were observed between 900 and 1400 cm^{-1} in this system. The peaks assigned to HO_2 and to NO_2^- are readily identified from previous studies of these species and are produced in the discharge because of the presence of trace impurities of water and nitrogen. The structured absorption near 1040 cm^{-1} is readily assigned to ozone, an expected product. Detailed isotopic substitution studies have provided further information on the identities of the carriers of the remaining absorptions. The prominent peak at 973 cm^{-1} can be assigned to O_4^-. Previous alkali metal codeposition experiments in this and other laboratories had determined values between 990 and 1000 cm^{-1} for this fundamental of O_4^-, stabilized as $M^+\cdots O_4^-$. Not shown in Fig. 2.27 is a moderately intense absorption at 976 cm^{-1}. This absorption lies very close to the peaks previously assigned in this laboratory to the antisymmetric stretching absorption of O_3^- in the various $M^+\cdots O_3^-$ species and has the isotopic substitution behavior appropriate for its assignment to this fundamental of O_3^-. The isotopic substitution experiments indicate that the prominent peaks at 1164 and 1320 cm^{-1} are contributed by a single isomer of O_4^+ which has two pairs of equivalent oxygen atoms. Weak absorptions between 2600 and 2950 cm^{-1} are also contributed by O_4^+. Prior to these experiments, mass spectrometric studies had established that O_4^+ is bound by approximately 10 kcal/mol with respect to $O_2 + O_2^+$, but no infrared or ultraviolet spectrum had been detected for this important molecular cation. The two most probable structures for O_4^+ are a trans-bent chain or a rectangle. Further analysis of the isotopic data may determine which of these two structures is most appropriate.

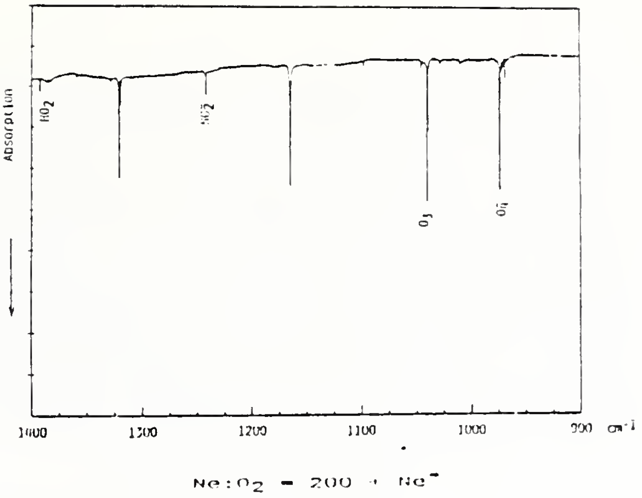

Fig. 2.27 Survey of major absorptions produced by the interaction of excited neon atoms with molecular oxygen.

3. Spectroscopy of Reaction Intermediates in Nitramine Decomposition and Combustion
(M. E. Jacox)

During the period from October 1, 1986 to June 15, 1987, this work was supported in part by the U.S. Army Research Office. The previously described studies on H_2CN and on t-HOCO were conducted as a part of this project. In addition, papers were prepared and published which present the first survey absorption spectrum for the near infrared electronic transition of HC_2 and a normal coordinate analysis for the CH_2NO_2 free radical.

4. Future Plans

a. Vibrational and Electronic Energy Levels of Transient Molecules
(M. E. Jacox)

During FY89 it is planned to complete the conversion of the vibrational frequency and electronic band center data to compiled dBase III+ files. The electronic spectral tables will continue to be updated, and a supplement to the 1984 ground-state vibrational energy level tables will be prepared for publication.

b. Free Radical and Molecular Ion Stabilization and Spectra
(M. E. Jacox and W. E. Thompson*)

Before moving on to a more general study of the spectra of molecular cations, it is important to complete the characterization of molecular ions which can be derived from atmospheric molecules. In addition to being likely contributors to the spectra obtained for other samples, these ions are inherently important in the chemistry of combustion and of the terrestrial ionosphere. Like O_4^+, N_4^+ is known to be relatively stable. A search will be made for its spectrum. A search will also be made for ions derived from the various nitrogen oxides, including N_2O, NO, and NO_2.

It is of considerable interest to search for simple protonated species, such as H_2Cl^+, for which the two stretching fundamentals have recently been detected in the gas phase. If this species is identified in the matrix, attempts will be made to use a discharge through a Ne:HCl mixture and photodetachment of the proton from H_2Cl^+ as proton sources and to search for H_3O^+, the vibrational spectrum of which is quite well established. Since most molecules have proton affinities greater than that of HCl (135 kcal/mol), the successful conduct of these experiments would point the way to further studies which could yield previously inaccessible spectroscopic data for a wide variety of protonated molecules.

Because O (^1D) forms an excimer with argon, even though this species is often the primary product in photochemical O-atom generation its reaction products have been difficult to observe in an argon matrix. Published studies have indicated that O (^1D) does not react with a neon matrix, in which it has a lifetime of approximately 32 sec. It is of interest to study the 122-nm photolysis of CO_2 in a neon matrix since O (^1D), but not O (^3P), reacts with CO_2 to form CO_3. If a good yield of CO_3 is stabilized, studies of other O (^1D) reactions will be pursued. One of the early systems to be investigated would be O (^1D) + N_2O, a possible source of a chain NNOO structure which recent ab initio calculations have indicated may have a ground-state potential minimum.

c. Spectroscopy of Reaction Intermediates in Nitramine Decomposition and Combustion

(M. E. Jacox)

Most of the experimental studies described in the section entitled, "Free Radical and Molecular Ion Stabilization and Spectra" are also important in relation to the later stages of nitramine decomposition and combustion. However, an important part of the overall project on nitramine decomposition is an attempt to obtain the previously unreported spectrum of the nitramine monomer, $CH_2{=}N{=}NO_2$. The most suitable source of this species is likely to be the photodetachment of H_2 from monomethyl nitramine, CH_3NHNO_2, or of CH_4 from dimethyl nitramine, $(CH_3)_2HHO_2$. It has recently been reported that CH_4 is photodetached from a variety of amines on isolation in an argon matrix and exposure to 193 nm radiation. Thus, the use of the 185-nm mercury emission line for photolysis of these precursor molecules appears to be an especially promising route to the stabilization of $CH_2{=}N{=}NO_2$.

G. General Spectroscopy and Theory

In addition to the previously described programmatic activities a variety of research problems were pursued in response to special opportunities, and special interests of the staff and outside guest scientisits. The following are descriptions of such projects of a general nature.

1. The Ozonolysis of Ethylene. Microwave Spectrum, Molecular Structure and Dipole Moment of Ethylene Primary Ozonide (1,2,3-Trioxolane)

(R. D. Suenram, F. J. Lovas, J. Z. Gillies*, and C. W. Gillies*)

The gas phase structure of ethylene primary ozonide (CH_2CH_2OOO) has been determined from millimeter wave spectra of five isotopic species. Partial substitution, r_s, parameters for the lowest energy oxygen envelope conformation (C_s symmetry) are r(CC)=1.546(3)Å, r(CO)=1.417(10)Å, r(OO)=1.453(10)Å, $r(CH_{endo})$=1.088(5)Å, $r(CH_{exo})$=1.095(5)Å, θ(CCO)=103.9(2)°, θ(COO)=102.1(4)°, θ(OCO)=100.1(12)°, and θ(HCH)=111.6(3)° (see Fig. 2.28). The electric dipole moment of the normal isotopic species is 3.43(4)D. Two vibrational states, 98(6) and 171(18) cm^{-1} above the ground state, have been assigned to successive excitations of the pseudorotational mode which corresponds to a ring-twisting vibration of the five membered ring. The barrier to pseudorotation is estimated to be high (greater than 300 to 400 cm^{-1}) in agreement with _ab_ _initio_ MO calculations. Ethylene primary ozonide, dioxirane (CH_2OO), formaldehyde and ethylene secondary ozonide (CH_2OCH_2OO) are observed as products of the ozone ethylene reaction in the low temperature microwave cell. A mechanism of the ozonolysis of ethylene has been developed which suggests that the reaction occurs primarily in the condensed phase on the surface of the cell. Microwave techniques utilizing _cis_- and _trans_-CHD=CHD show that ozone adds stereospecifically to ethylene in the formation of ethylene primary ozonide.

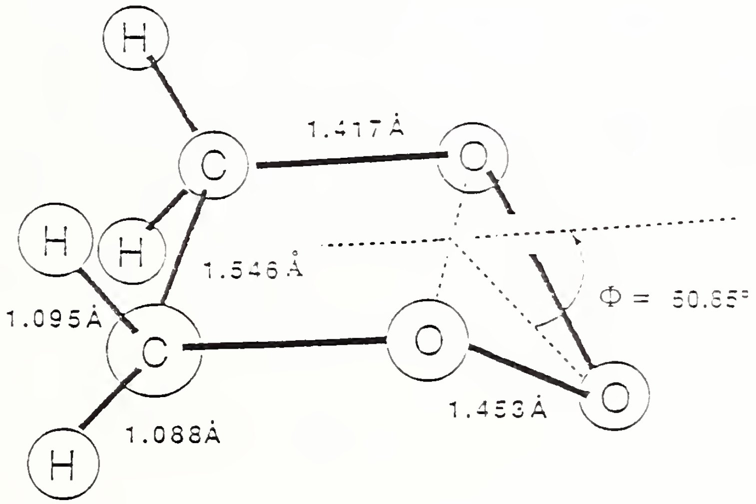

Fig. 2.28 Structure of ethylene primary ozonide.

2. Molecular Beam Studies of Larger Organic Species

(R. D. Suenram and F. J. Lovas)

In an effort to assess the feasibility of studying larger organic compounds with our pulsed molecular beam spectrometer we undertook the investigation of indole and carbazole. Both of these compounds are solids at room temperature and are fairly involatile. By placing samples of these compounds in our heated reservoir nozzle we were able to observe and assign the microwave spectra of both compounds. For indole, a nozzle temperature of 55°C with argon carrier gas proved to be adequate to produce intense rotational transitions. Carbazole was less volatile and required heating to 170°C to provide a sufficient quantity in the vapor phase to produce observable rotational transitions. For carbazole neon was used as the carrier gas instead of argon. Carbazole transitions were much weaker in argon presumably due to the formation of a significant fraction of higher polymers and complexes in the beam.

These studies, described below, have shown that the spectra of large organic molecules can be studied using a pusled beam microwave spectrometer to simplify the spectrum. The study of carbazole by conventional technqiues would not be possible due to the large number of rotational transitions in the spectrum.

3. Microwave Spectrum and ^{14}N Quadrupole Coupling Constants of Indole

(R. D. Suenram, F. J. Lovas, and G. T. Fraser)

The microwave spectrum of indole has been observed using a conventional Stark-modulated microwave spectrometer in conjunction with a heated absorption cell. Spectral transitions were also observed in a pulsed molecular beam Fabry-Perot microwave spectrometer using a heated nozzle source. The high resolution (20 kHz) available with the Fabry-Perot instrument allows the observation of the ^{14}N nuclear electric quadrupole hyperfine splittings. An analysis of the 44 measured transitions gives the following rotational constants: A = 3877.8366(64) MHz; B = 1636.0461(48) MHz; and C = 1150.0900(19) MHz. The ^{14}N quadrupole coupling constants that were determined from the hyperfine analysis are eQq_{aa} = 1.7263(43) MHz; eQq_{bb} = 1.6525(50) MHz; and eQq_{cc} = $^-$3.3788(48) MHz. The observed rotational constants are compared with those obtained from a recent optical study of indole and the ^{14}N quadrupole coupling constants are compared with those of pyrrole. The accompanying figure (Fig. 2.29) illustrates the resolution of ^{14}N hyperfine structure for one of the observed rotational transitions.

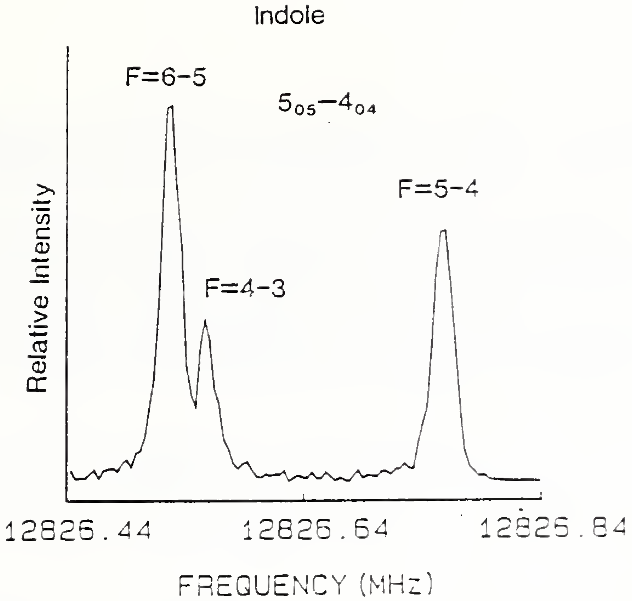

Fig. 2.29 A sample spectral window of indole in the adiabatic expansion showing the a-type 5_{05}-4_{04} rotational transition with its three most intense ^{14}N components. The F= 6-5 and F= 4-3 components are separated by ~30 kHz.

4. Microwave Spectrum and ^{14}N Quadrupole Coupling Constants of Carbazole

(R. D. Suenram, F. J. Lovas, G. T. Fraser, and P. S. Marfey*)

The microwave spectrum of carbazole was observed and analyzed in the 8-14 GHz region using a pulsed molecular-beam Fabry Perot microwave spectrometer. Carbazole was vaporized in a heated nozzle source and was entrained in neon carrier gas before expansion into the Fabry Perot cavity. The rotational transitions were fitted using a rigid rotor Hamiltonian without centrifugal distortion parameters. The rotational constants are A = 2253.1985(2) MHz, B = 594.1861(2) MHz, and C = 470.3503(1) MHz. The inertial defect is small (-0.36 μÅ) and consistent with a planar molecules shown in Fig. 29.

The high resolution available with the instrument (~10 kHz) allowed the determination of the ^{14}N nuclear quadrupole coupling constants as χ_{aa} = 2.0697(40) MHz, χ_{bb} = 1.8719(35) MHz, and χ_{cc} = -3.9416(35) MHz. A comparison of the electronic environment of the nitrogen atom was made for the series pyrrole, indole and carbazole.

5. Quadrupole Hyperfine Splitting in the J = 1 ← 0 Rotational Transition of CCl_3F

(M. D. Marshall*, H. O. Leung*, and R. D. Suenram)

The hyperfine structure of the J = 1 ← 0 stransition of CCl_3F has been completely resolved for both K = 0 and K = 1 using a pulsed molecular beam Fabry-Perot cavity microwave spectrometer. Using previously available rotational constants[1] for this molecule it is shown that the hyperfine splitting is qualitatively, but not quantitatively predicted using the classic method of Wolf, et al.[2] and the effective hyperfine constants,

eqQ_{zz} = 29.047 MHz and eqQ_{zz} - eqQ_{yy} = -110.95 MHz. To adequately describe the nuclear quadrupole coupling interaction in this heavy, oblate symmetrical top molecule it is necessary to consider in addition to those matrix elements off-diagonal in the quantum number J those off-diagonal in K. Such matrix elements include not only additional ones arising from the eqQ_{zz} - eqQ_{yy} term in the hyperfine Hamiltonian, but also those which find their origin in the usually ignored eqQ_{zy} term. The ability to measure this additional term will place more stringent limits on the assumption of cylindrical symmetry about the C-Cl bond.

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1. J. H. Carpenter, P. J. Seo, and D. H. Whiffen, J. Mol. Spectrosc. <u>123</u>, 187-196 (1987).
2. A. A. Wolf, Q. Williams, and T. L. Weatherly, J. Chem. Phys. <u>47</u>, 5101-5109 (1967).

6. Millimeter- and Submillimeter-wave Surveys of Orion A Emission Lines in the Ranges 200.7-202.3 GHz, 203.7-205.3 GHz, and 330-360 GHz

(P. R. Jewell*, J. M. Hollis*, F. J. Lovas, and L. E. Snyder*)

We have conducted a continuous spectral line survey of the Orion A position from 330.5 to 360.1 GHz. This survey covers nearly the entire 870 μm atmospheric window accessible from ground-based observations. Approximately 160 distinct spectral features composed of about 180 lines were detected, 30 of which could not be readily identified. In addition, we also surveyed Orion A from 200.7 to 202.3 GHz and from 203.7 to 205.3 GHz and detected 42 distinct, new spectral lines, including 4 that are unidentified at present. These data sets are the first thorough survey results in these spectral regions. Twenty of the known Orion A molecular species, including less abundent isotopic forms of several species, have been identified in the 870 μm survey. The largest percentage of transitions observed are attributed to SO_2 and CH_3OH. Previous surveys at 3mm and 1.2mm showed a high percentage of transitions from $HCOOCH_3$ for which only 6 transitions were identified in the present work. The data are being made available to the Astronomical Data Center at the Goddard Space Flight Center for distribution-by-request to the astronomical community.

7. Instrumental Studies for the BOMEM FTS

(W. B. Olson)

Considerable effort has been made to formulate a practical treatment of throughput or etendue in optical systems of cylindrical symmetry for the purpose of designing of optical systems of very high efficiency for the NIST BOMEM FTS. Ray transfer matrices can provide a first order solution to the problem of throughput matching of the optical subsystems required for sampling, but difficulties arise in precise interpretation when it comes to the execution of the design in practice. There are some areas of practical application where the ideal solution in terms of ray transfer matrices cannot be well translated into practice with quadric section type optical elements. These difficult areas lie in regions where the ideal solutions require a large solid angle subtended at some plane by the radiation. Non-imaging optical systems can provide a solution to this problem in principle, but in practice they are not perfect either, and it does not seem possible to derive analytical equations for actual efficiency.

Extensive three dimensional ray tracing has been done on White type multiple reflection absorption cells with two rows of images in the front mirror focal plane, and it has been found that there is a ratio of total width of the spots on the front focal plane to the separation of the two rows where optical aberrations nearly disappear.

A heat pipe of nickel has been devised and constructed for the heat pipe optical system of the BOMEM FTS. This should allow the use of high temperature fluorides in the heat pipe, which attack the current stainless steel heat pipes.

8. Analysis of the 3-μm Bands of Benzene

(J. Pliva* and A. S. Pine)

A comprehensive rovibrational analysis was performed for the 3-μm absorption bands of the benzene molecule measured on a difference-frequency laser spectrometer and deconvolved to an effective linewidth of 0.0010 - 0.0015 cm^{-1}. The four strong bands observed, centered at 3047.908, 3078.614, 3100.408, and 3101.854 cm^{-1}, are due to the E_{1u} fundamental ν_{12} sharing its intensity with the E_{1u} components of the combinations ν_{13} + ν_{16}, $\nu_2 + \nu_{13} + \nu_{18}$, and $\nu_3 + \nu_{10} + \nu_{18}$ via anharmonic resonances. The bands exhibit strong perturbations due to ℓ resonances with the inactive B_{1u}/B_{2u} components of the $\nu_{13} + \nu_{16}$ and $\nu_2 + \nu_{13} + \nu_{18}$ states, and numerous localized perturbations due to overtones and combinations of the 16 low-frequency vibrations of the molecule. Symmetry arguments and values of constants such as $C\zeta$ known for the fundamentals have been used to propose tentative assignments for many of the perturbing states. The Hamiltonian matrix used for the treatment of the 8384 assigned transitions, with all the components of the main interacting states plus 18 perturbing states, was of order 34 and contained 130 parameters of which 112 were eventually adjusted. A set of spectroscopic constants was obtained which reproduces all the data with a standard deviation of 0.0012 cm^{-1}. The analysis shows that the Fermi resonance between ν_{12} and $\nu_{13} + \nu_{16}$ combined with the other anharmonic interactions shifts the fundamental down by 16.46 cm^{-1} from its unperturbed position. It was found that x,y-Coriolis and anharmonic resonances of surprisingly high order have to be invoked to account for most of the localized perturbations observed in the spectrum.

9. Influence of an AC Stark Effect on Multiphoton Transitions

(W. L. Meerts*, I. Ozier*, and J. T. Hougen)

A multiphoton mechanism for molecular beam transitions was developed which relies on a large first-order AC Stark effect to modulate the energy separation of the initial and final states of the multiphoton transition, but which does not require the presence of any intermediate level(s). The theoretical formalism uses ideas from the laser multiphoton literature for a two-level system interacting with a monochromatic electromagnetic radiation field, together with a close analog of the rotating wave approximation. The diagonal matrix elements of the Hamiltonian operator corresponding to the large AC Stark effect are removed by a mathematical substitution which in effect transforms these diagonal elements into transition moments involving higher harmonics of the frequency of the monochromatic radiation field. The electric field strength of the true monochromatic radiation field is "distributed" among the higher harmonics of the effective field according to an expression involving Bessel functions. Because these Bessel functions are bounded, there exists a threshold for the magnitude of the transition dipole matrix element coupling the two levels. Below this threshold, the transition probability in a traditional one-photon molecular beam electric resonance experiment cannot be made unity simply by increasing the amplitude of the radiation field. In fact, if the coupling matrix element is small enough, the molecular beam electric resonance signal will become unobservable. The algebraic formalism described above was checked by computer solution of an initial value problem involving four real coupled linear differential equations. It was then used to explain the multiphoton transitions previously observed in molecular beam electric resonance studies on the two symmetric top molecules OPF_3 and CH_3CF_3 where the number of photons involved in a given transition varies from 2 to 40.

10. Far Infrared Spectrum of Methyl Amine. Assignment and Analysis of the First Torsional State

(N. Ohashi*, K. Takagi*, J. T. Hougen, W. B. Olson, and W. J. Lafferty)

The far-infrared spectrum of methyl amine has been studied in the 40 to 350 cm^{-1} region with a resolution of 0.005 cm^{-1} or better. The pure rotational spectrum in the first excited torsional state, as well as the fundamental torsional band, have been assigned. The data obtained have been combined with microwave data from the literature, and a global fit has been carried out, based on a group theoretical formalism developed previously. Over 650 transitions with $0 \leq K \leq 14$ and $K \leq J \leq 25$ were fit to 41 molecular parameters, with a standard deviation of $\pm 0.000\ 94\ cm^{-1}$. This standard deviation was achieved by including J and K dependent (centrifugal distortion) corrections to the structural parameter ρ. The goodness of the fit confirms the correctness of the theoretical formalism. Problems remaining presumably arise from the neglect of five tunneling and nontunneling terms with selection rules $\Delta K = \pm 1$. Some aspects of the torsional potential function and inversion potential function in this molecule were also considered.

11. Effect of Tunneling Motions on the Hyperfine Structure of Hydrazine

(L. H. Coudert*, J. T. Hougen, and R. D. Suenram)

In the present work, we attempt to describe the hyperfine structure in a molecule which exhibits significant tunneling splittings because of large amplitude inversion and internal rotation motions, but which still has a well defined equilibrium configuration. The approach involves setting up a complete quadrupole Hamiltonian for the two nitrogen atoms in hydrazine (NH_2-NH_2), which is made dependent upon the three large amplitude coordinates necessary to fully describe the various configurations of the molecule, and which contains all five elements of the electric field gradient tensor (i.e., $2q_{aa} - q_{bb} - q_{cc}$, $q_{bb} - q_{cc}$, q_{ab}, q_{ac}, and q_{bc}) at one nitrogen atom when the molecule is in one of its equilibrium configurations. The mean value of this quadrupole operator is calculated for each tunneling state. One interesting result is that for nondegenrate A or B-type levels only the sum of the two hyperfine Hamiltonians is involved, while for doubly degenrate E-type levels the sum as well as the difference appears. The difference contains the contribution of the nondiagonal term q_{bc}, and leads to large qualitative differences in the hyperfine pattern. These results are applied to the analysis of the hyperfine structure of selected transitions that have been recorded on the NIST Fourier transform microwave instrument. After a preliminary analysis of the hyperfine structure of each transition separately, a least square fit global analysis of the data was performed. This allowed us to determine the two diagonal quadrupole coupling constants as well as the bc nondiagonal one.

12. A Two Tunneling Path IAM-Like Treatment of the Microwave Spectrum of Divinyl Ether

(L. H. Coudert)

The microwave spectrum of the cis-trans conformer of divinyl ether, previously measured by Hirose and coworkers, has been fit using a two-dimensional IAM-like treatment which accounts for the 27 MHz tunneling splitting displayed by this molecule. This two-dimensional IAM-like treatment begins by first determining the various feasible tunneling path(s) connecting the two frameworks of the molecule. For the tunneling process corresponding to an antigeared rotation of each vinyl unit about axes coinciding with the respective CO bonds, two limiting cases are considered: if the molecule goes through a planar configuration during the tunneling, only one tunneling path arises; if the intermediate configuration is not planar, two equivalent tunneling paths occur. The consequences for the J and K dependence of the splitting are examined, and using this formalism the microwave data are fitted with an RMS deviation of 0.156 MHz. The parameters related to the J and K dependence of the splitting were also determined and their values are interpreted in a favor of a two tunneling path system. A comparison with the values obtained theoretically for those parameters was also carried out.

13. WKB Potential Well Ground States without Matching?

(C. Leubner* and J. T. Hougen)

Schmid[1] has recently conjectured that it might be possible in general to obtain semi-classical (WKB) ground state energies and wavefunctions for various potential surfaces without explicitly considering the problem of how wavefunctions obtained separately in the classically allowed and classically forbidden regions are to be matched across the boundary between those regions. We showed by formally expanding the energy as a power series in $\hbar$ in the usual WKB equations, that even in the one-dimensional case, Schmid's procedure yields an approximate ground state wavefunction only for potential wells which are nearly harmonic, and that the corresponding energy obtained is totally insensitive to any anharmonicity present. Furthermore, excited state wavefunctions cannot be obtained at all. Thus, despite its inherent simplicity, Schmid's method can only be of limited value in the analysis of the dynamics of real molecules on multi-dimensional potential surfaces.

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1. A. Schmid, Ann. Phys. (NY) 170, 333 (1986).

14. Measuring Transition Moments by Means of the Herman-Wallis Effect

(A. G. Maki and W. B. Olson)

In a recent study we made on using the Herman-Wallis effect to measure the transition moment of the fundamental band of $C\ell O$, it became apparent that this is a technique that has general applicability to diatomic molecules. It is not generally recognized that the theory has been well studied and the formulas for describing the Herman-Wallis effect take into account higher order terms both in the dipole moment function and also in the Dunham potential function. The Herman-Wallis effect relates the ratio of the transition moment divided by the dipole moment to the relative intensity of $\Delta J=+1$ and $\Delta J=-1$ transitions. To determine the transition moment it is necessary to know the dipole moment and a few other molecular parameters, but it is not necessary to know the number of molecules in the sample. In many cases it is extremely difficult to obtain an accurate measure of the partial pressure of the species of interest, but it is much easier to obtain the parameters needed to analyze the Herman-Wallis effect.

We are determining the Herman-Wallis effect from FTS infrared measurements on three different molecular species, LiH, NaH, and NaI. An example of this effect for NaH is shown in Fig. 2.30. Without the Herman-Wallis effect the two transitions shown would have the same intensity, to within 5%. In Table II we show the results found for NaH. A test of this technique on HF and HCl has shown that the transition moment obtained by application of this technique is within 1% of the value obtained by direct intensity and concentration measurements.

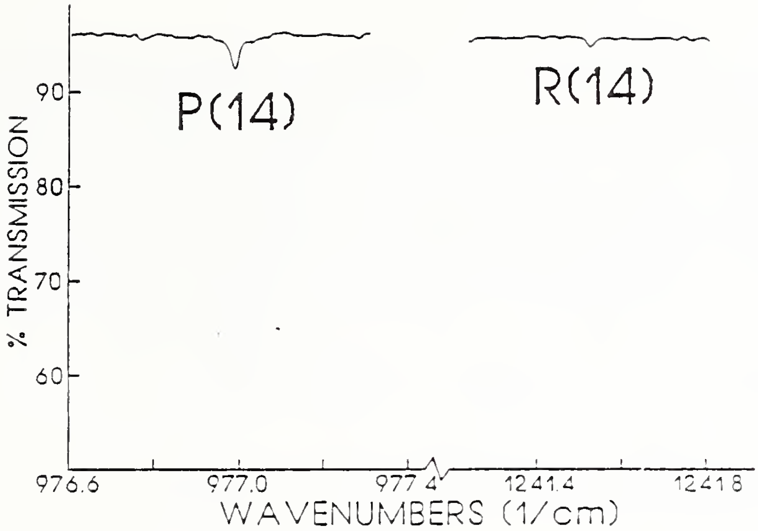


Fig. 2.30 Comparison of the relative intensities of the P(14) and R(14) lines the v=1←0 transition of NaH.

Table II. Relative Intensity Measurements and Estimated Transition Moment for the v=1-0 Transition of NaH

J	Obs. $\frac{S[R(J)]}{S[P(J)]}$	Obs.-Calc.
5	0.878	0.077
6	0.777	0.058
7	0.682	0.033
8	0.589	0.004
9	0.499	-0.028
10	0.405	-0.068
11	0.383	-0.039
12	0.323	-0.051
14	0.335	0.053

α = -0.046 ± 0.003[a]
β = 0.0[b]
μ_{10} = 0.31 ± 0.05 Debye
(assuming μ_0 = 6.6 D)

a) The uncertainty is three times the standard error.

15. The Vibrational Dependence of the Transition Moment
(A. G. Maki and W. B. Olson)

Simple harmonic oscillator theory says that the intensity of $\Delta v=1$ transitions should depend on $v''+1$ while $\Delta v=2$ transitions should have intensities that depend on $(v''+1)^2$. In a number of high temperature measurements we have qualitatively observed that this vibrational dependence is approximately correct, but conditions were never good enough to test this theory. In recent FTS measurements on the high temperature spectrum of NaI we have observed transitions from $v=1\leftarrow0$ up to $v=13\leftarrow12$. Since the Fourier transform spectrometer measures all wavelengths at the same time, it is particularly well suited for comparing the intensities of different transitions measured in the same interferogram. Our measurements verify the applicability of the harmonic oscillator treatment to within 5 or 10%, at least for this one case. We have good reason to believe this will be true for most other molecules.

16. An FTS Measurement of the Rotational Spectrum of LiH and LiD
(A. G. Maki and W. B. Olson)

For several years we have been measuring the high temperature infrared spectrum of diatomic molecules that are unstable in the gas phase at room temperature. Some of the species that we have studied have rather large dipole moments and small moments of inertia, making them good candidates for producing far-infrared pure rotational spectra. We have now measured the rotational spectra of LiH and LiD from 100 to 285 cm^{-1}. Transitions have been observed for both ^{6}LiD and ^{7}LiD in the v=0, v=1, and v=2 states. Fig. 2.31 shows a segment of the pure rotational spectrum of a mixture of ^{6}LiD and ^{7}LiD.

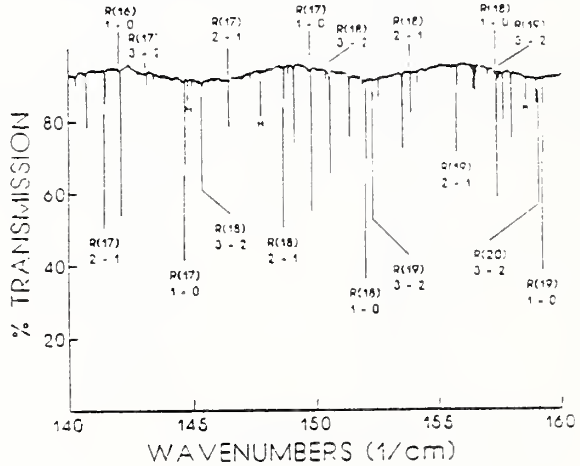


Fig. 2.31 Rotational transitions of a mixture of ^{6}LiD and ^{7}LiD from 140 to 160 cm^{-1}. Transitions labeled below the spectrum are due to ^{7}LiD and those labeled above the spectrum are due to ^{6}LiD. Lines due to LiH are indicated by an H. All other lines are due to H_2O.

17. High Temperature FTS Measurements

(A. G. Maki, W. B. Olson, G. Thompson*, and A. Weber)

We have extended to longer wavelengths our high temperature measurements of the infrared spectrum of molecules unstable in the gas phase at room temperature. The BOMEM Fourier transform spectrometer (FTS) has been used to record a number of high temperature spectra in the 100 to 400 cm^{-1} region. Aside from the pure rotational spectrum of LiH and LiD mentioned above, we have measured the following spectra: KI ($\nu_0 \approx 185$ cm^{-1}), NaI ($\nu_0 \approx 255$ cm^{-1}), and $T\ell C\ell$ ($\nu_0 \approx 280$ cm^{-1}). The analysis of the $T\ell C\ell$ spectrum was more difficult because of the two thallium isotopes and the two chlorine isotopes. High resolution was essential to the measurement and analysis of these spectra.

In addition, the spectrum of NaH was measured in the 900 to 1300 cm^{-1} region. This spectrum was used to determine the transition moment of NaH from the Herman-Wallis effect, as was described above.

18. Analysis of the Infrared Spectrum of the BO_2 Radical

(A. G. Maki, J. Burkholder*, C. J. Howard*, and A. Sinha*)

The absorption spectrum of BO_2 in the ground state, $X^2\Pi_g$, has been measured in the infrared with a high-resolution Fourier transform spectrometer. The 00^01-00^00 and 10^01-00^00 vibrational transitions have been measured for both the $^2\Pi_{1/2}$ and the $^2\Pi_{3/2}$ states. Because of the large number of vibronic levels arising from the Renner-Teller effect, there is a high likelihood of observing level crossings in this molecule and three examples of perturbations in these states are described. Improved ground state constants are reported.

19. Doppler Broadening of Raman Lines

(A. Weber)

For the purpose of determining molecular energy levels high resolution Raman spectroscopy is conducted on low pressure gases and vapors to avoid line shifts caused by velocity and phase changing collisions. Under these conditions Dicke narrowing is absent and the resolution is limited by Doppler broadening of the spectral lines, as well as instrumental effects such as the width of the exciting line and the characteristics of the spectrometer system. Conventional high resolution Raman spectroscopy of gases has reached a resolution limit of ca 0.05 cm^{-1}; this limit was, however, determined in the main by instrumental effects.

The use of currently available scanning Fourier transform spectrometers offers the possibility of achieving a nearly 10-fold improvement in the instrumental resolution capability. However, to realize such resolution in incoherent Raman scattering it is essential that line broadening effects due to the Doppler effect be minimized. A recalculation of the Doppler broadening using the laws of conservation of energy and linear momentum in their relativistic formulation gives, to a very high degree of approximation, the same result as that obtained non-relativistically. Thus, the Doppler broadened Raman linewidth (FWHM) is given by

$$\delta\nu_R = \sqrt{2\ell n2(kT/m_0c^2)}\ \sqrt{4(\nu_0^2 - \nu_0\nu_R)\sin^2(\theta/2) + \nu_R^2} \qquad (1)$$

where $\nu_R = \nu_0 - \nu_{scatt}$ is the Raman displacement ($\nu_R>0$ for Stokes scattering, $\nu_R<0$ for anti-Stokes scattering, ν_{scatt} = frequency of scattered photon) and θ is the scattering angle. The calculation also yields a term that describes a velocity dependent Raman line shift due to the recoil experienced by the molecule in the scattering process.

When combining Raman spectral data with those obtained by infrared absorption spectroscopy in a unified analysis of the molecular energy levels it is desirable to have a quantitative estimate of the quality of the Raman data relative to the data obtained by infrared spectroscopy. Figure 2.32 shows the ratio $\delta\nu_R/\delta\nu_{IR}$ as a function of scattering angle, where $\delta\nu_R$ is the Raman Doppler line width given by Eqn. (1) and $\delta\nu_{IR}$ is the Doppler line width for an infrared absorption line of the same frequency (wave number), for Stokes Raman displacements of 500, 1000, 2000, and 3000 cm^{-1} generated by the Ar 5145Å laser line. The Doppler widths of the Raman and infrared lines are seen to be equal only for the "forward" scattering configuration (θ=0°). When Raman frequencies obtained with scattering arrangements with θ>0 are to be combined with infrared data they should be weighted, for equal signal to noise ratios, at least by the inverse square of their relative Doppler widths. This weight would have to be augmented by additional factors which account for other causes of line broadening (e.g., pressure effects). Eqn. (1) gives the Doppler width of a Raman line for a static gas in thermodynamic equilibrium. It is equally applicable to incoherent as well as to coherent Raman scattering (but not CARS). In coherent Raman gain spectroscopy, however, the "forward" scattering geometry is automatically assured as part of the usual experimental configuration.

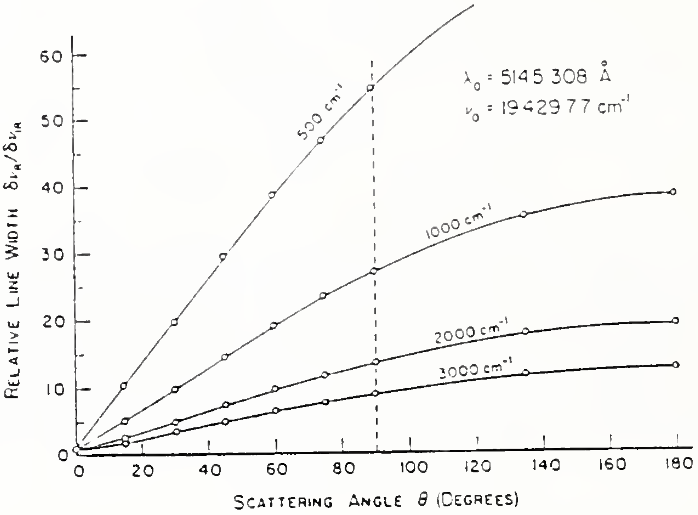


Fig. 2.32 Ratio of Raman to infrared Doppler line widths for Stokes Raman displacements of 500, 1000, 2000, and 3000 cm^{-1}.

20. High Resolution Spectroscopic Studies of CH_2F_2: The ν_8 Band at 1435 cm^{-1}

(R. D'Cunha*, P. K. Wahi*, V. B. Kartha*, and A. Weber)

Fourier transform infrared spectra of methylene fluoride were recorded with the NIST BOMEM DA3.002 spectrometer with an apodized resolution of 0.004 cm^{-1}. Detailed assignments up to $J_{max} = 25$ have been made for the ν_8 parallel A type band centered at 1435 cm^{-1}. Watson's A type reduced Hamiltonian in the I^r representation was used to obtain upper state molecular parameters. These reproduce the observed data to within the limits of the experimental accuracy.

however, exhibit only a single broad CO-particle absorption and give a similar limiting value for T_1.

The short time behavior of the CO-particle relaxation was further explored using IR pulses of 2 ps duration (FWHM). Fig. 3.1 shows a decay for one Pt sample; Rh gave a similar response. This initial decay indicates a lifetime of approximately 7.5 ps. The fast rise and immediate fall of the signal indicate T_1 contributions of less than 7 ps may still be present. Related measurements using much shorter IR pulses are needed to resolve the short time behavior.

This dramatic increase in relaxation rate, by about a factor of 15 compared to the Rh carbonyl compounds supported on SiO_2, can not be due to multiphonon relaxation to lower frequency vibrational states. The enhanced rate presumably arises from coupling to electronic degrees of freedom of the large metal particles, i. e., electron-hole pair damping. Short T_1 values (≈1 ps) have been estimated theoretically for adsorbates on metal single crystal surfaces due to this damping mechanism.

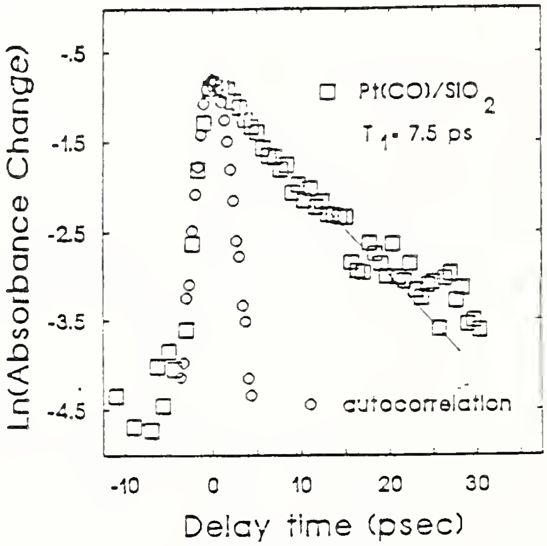


Fig. 3.1 Time dependence of the ir transient bleaching signal (ν_{laser}=2090 cm^{-1}) for CO chemisorbed on Pt particles (d ~ 30Å) supported on SiO_2 at T=20°C. Also shown is laser pulse autocorrelation, indicating experimental time resolution.

During the next year we plan to focus on two goals. We will try to directly measure where the vibrational energy goes when the initially excited CO(v=1) mode is deactivated. For metal carbonyl molecules in the gas phase, in solution, and on dielectric surfaces we intend to probe transient populations in other ir active modes by time-resolved two color ir absorption spectroscopy. There are several picosecond and femtosecond laser techniques that we are investigating in order to accomplish this goal, including direct ir absorption, and broadband ir absorption followed by up-conversion to the visible spectral region with multichannel detection. For strong Raman active modes such as M-C stretches, spontaneous anti-Stokes Raman scattering may also be useful for detecting transient low frequency vibrational populations.

The second goal is to measure T_1 for an ordered monolayer of CO on a metal single crystal prepared and characterized under UHV conditions. Interpretation of T_1 results on a single crystal are expected to be more straightforward and unambiguous than the interpretation of the transient bleaching signals for the polydisperse inhomogeneous supported metal particles discussed above.

This research is supported in part by the Air Force Office of Scientific Research.

B. Decomposition of Molecules from Metastable Vibrational States
(M.P. Casassa, B.R.Foy, D.S.King, and J.C. Stephenson)

1. Overtone Photodissociation of Molecules: HN_3

State-to-state photodissociation experiments provide an exceptionally detailed view of the dynamics of rovibrationally excited molecules, and have particular significance when complemented by high resolution photodissociation spectra and linewidth data. We have measured nascent distributions of kinetic, vibrational, and rotational energy, along with unimolecular decomposition rates and photodissociation spectra for the collision-free laser-induced reactions:

$$HN_3\ (X\ ^1A') \longrightarrow HN\ (X\ ^3\Sigma^-) + N_2\ (X) \qquad \Delta H = 15\ \text{kcal/mol},$$
$$\longrightarrow HN\ (a\ ^1\Delta) + N_2\ (X) \qquad \Delta H = 51\ \text{kcal/mol}.$$

An important feature of this system is that the minimum enthalpy channel is spin-forbidden, with a 36 kcal activation barrier to singlet-triplet crossing. The reactions were initiated in two different ways. Direct single-photon excitation of the 4th and 5th NH-stretching overtone transitions of HN_3 populated individual rovibrational states with sufficient energy to decompose via the triplet (spin-forbidden) channel. The second type of experiment used multiphoton pumping (IRMPD) of DN_3 by a CO_2 laser, which produced both singlet and triplet products.

The measurements were performed using low pressure HN_3 or DN_3 samples in a flow cell, and using HN_3 cooled in a supersonic expansion. The 10ns duration overtone pump laser operated at 575 ($v_1=6\leftarrow0$) or 662 nm ($v_1=5\leftarrow0$) with a spectral bandwidth $\approx0.4\ cm^{-1}$. In experiments with higher resolution, this laser produced a $\approx0.03\ cm^{-1}$ bandwidth. The IRMPD experiments employed a CO_2 laser with temporal "square wave" pulses of 50 ns duration focussed to $I=10GW/cm^2$. Most product state data were obtained with the CO_2 P(18) laser line at 946 cm^{-1}. The HN/DN fragments were probed by laser-induced fluorescence of the $A^3\Pi$ - $X^3\Sigma^-$ or $c^1\Pi$ - $a^1\Delta$ transitions using a frequency-doubled dye laser with a bandwidth of 0.7 cm^{-1} (etalon-narrowed to 0.05 cm^{-1} for the measurement of Doppler profiles). For lifetime measurements of the $v_1=5$ level, the time delay between pump and probe was stepped electronically in 1 ns increments. To measure the lifetime of the $v_1=6$ state, picosecond lasers were used, as in our earlier work on the vibrational predissociation lifetime of the NO dimer.

The experimental observations yield information about the distribution of energy in the reactant, the microscopic reaction rates, the location of barriers to dissociation, and the geometry of the transition states. Excitation of the NH-stretching overtone transitions of HN_3 to v_1 = 5 and 6 resulted in predissociation to $HN(X^3\Sigma^-)$ and $N_2(X)$ with lifetimes of 210 ± 110 and 1.0 ± .2 ns, respectively (see Fig. 3.2). Following excitation of either overtone under collisionless conditions, the HN $(X^3\Sigma^-)$ molecules were formed predominantly in the symmetric F_1 and F_3 spin-rotation states with no significant population (≤4%) in the anti-symmetric F_2 levels. Fragment Doppler profiles showed that most of the available energy (>96%) went into translational motion. The distribution of rotational population in the F_1, F_3 states was Boltzmann-like, characterized by a rotational "temperature" 280 ± 50 K for v_1 = 5 photodissociation, and 570 ± 60 K for v_1 = 6. There was no significant population (<5%) in excited HN $(^3\Sigma^-)$ vibrational levels.

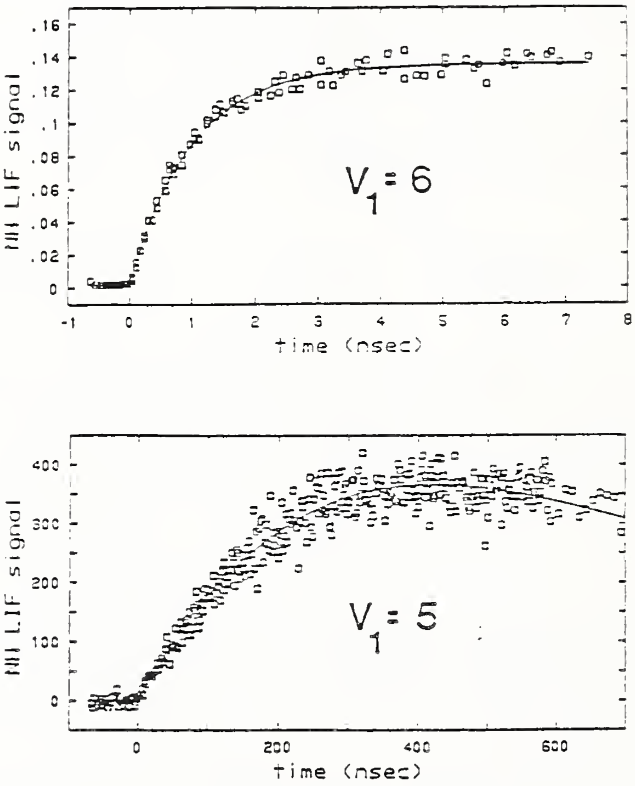


Fig. 3.2 Time-resolved appearance of X NH(v=0) product following excitation of $V_{NH}=5$ (lower) or $V_{NH}=6$ (upper) vibrational states of HN_3 in a molecular beam, giving lifetimes of 210 and 1.0ns, respectively.

Interestingly, the high resolution overtone photodissociation spectra revealed that the N-H stretching states are strongly mixed with background vibrational levels. Lines expected for a simple asymmetric top vibrational band are split into groups of 3 to 6 lines appearing with comparable intensity. We are working to analyze these spectra and exploring whether the dissociation dynamics depend upon the eigenstate excited within an overtone band.

Multiphoton vibrational excitation of DN_3 by a CO_2 laser led to dissociation forming DN in both $X^3\Sigma^-$ (spin forbidden) and $a^1\Delta$ (spin allowed) electronic states. The DN ($^1\Delta$) products were formed preferentially in the symmetric (A'), e-labeled lambda doublet levels: $\Delta(A')/\Delta(A") = 1.44$. The DN ($^1\Delta$) was formed with no vibrational excitation (<2%); the rotational state population distributions were Boltzmann-like with a rotational "temperature" of 425K. Doppler profiles gave a total kinetic energy of about 1500 cm^{-1} in the singlet channel. That the most probable value of fragment kinetic energy was not zero implies the presence of a small barrier in the singlet reaction. As in the overtone experiments, the DN ($X^3\Sigma^-$) molecules were formed predominantly in the F_1 and F_3 spin-rotation states with little population in the F_2 levels, and there was no significant population in excited DN ($X^3\Sigma^-$) vibrational levels. The distribution of rotational states was characterized by $T_R \approx 920K$ for the F_1 and F_3 states. Doppler profiles showed a large kinetic energy release of about 10,100 cm^{-1} total in the triplet channel.

Dramatic HN/DN spin selectivity, no fragment vibrational excitation, little rotational excitation and essentially total (>96%) kinetic energy release occurred in both the overtone pumping and IRMPD experiments. The large increase in unimolecular reaction rate with vibrational energy in the overtone experiments is inconsistent with the scaling of rate with state density ρ, $k_{uni}(E) \approx A\rho(E-E_a)/\rho(E)$, expected for statistical reactions, which predicts $k_{uni}(6\nu_1)/k_{uni}(5\nu_1) \approx 3$; the experimental ratio is 200. According to the calculations of Alexander and coworkers [J.Chem.Phys.89, 1388(1988)] F_1 and F_3 spin selectivity arises from the symmetry of the spin-orbit operator matrix elements for a planar transition state. A similar argument pertains to the population of Λ-doublets in the spin-allowed channel. Little product vibrational and rotational excitation occurs because the HN and NN bonds in the singlet-triplet crossing region have free-molecule lengths, the impact parameter is very small (linear NNN, $\Theta_{HNN} \approx 90°$), and there is little anisotropy in the exit channel of the potential surface.

During the next year we expect to complete many additional overtone chemistry experiments. Photodissociation spectra of the HN_3 overtone rotation-vibration levels will be obtained at high resolution using a cw ring dye laser pulse amplified at 20 Hz to produce very intense 10ns pulses with a bandwidth ≤ .002 cm^{-1} FWHM. For the $v_1=6$ state and combination bands like $5\nu_1 + \nu_3$ (ν_3 is the "reaction coordinate," i.e., the 1264 cm^{-1} N-N stretch) we will compare spectral linewidths, which give the dephasing decay times of the excited states, to the time-resolved dissociation rates of these states. This will show if rates of intramolecular vibrational relaxation (IVR) are faster than the reaction rates. Time- and state-resolved experiments will be done for the $v_1=7$ level, which is near the threshold for formation of NH($a^1\Delta$). Competition between the spin-allowed and spin-forbidden channels may be studied as a function of the HN_3 (V, J,

K) state initially excited. We will try to do similar experiments on other molecules such as $CH_3N_3 \rightarrow CH_3N_3(v_{CH}=5) \rightarrow CH_3N(X\ ^3A_2) + N_2$ or $CH_2N_2 \rightarrow CH_2N_2(v_{CH}=5) \rightarrow CH_2(a\ ^1A_1) + N_2$. The CH_3N may be probed via LIF of the $A\ ^3E \leftarrow X\ ^3A_2$ system and CH_2 via LIF of the $b\ ^1B_1 \leftarrow a\ ^1A_1$ system.

This research is supported in part by the Air Force Office of Scientific Research.

2. Dynamics of van der Waals Molecules: $(NO)_2$

Progress in our studies of vibrational predissociation of weakly bound molecular clusters has included a full characterization of the single quantum infrared photodissociation of the nitric oxide dimer. Excitation of either the symmetric (1869 cm^{-1}) or the antisymmetric (1790 cm^{-1}) NO stretching modes leads to fragmentation of the complex since the energy of either mode exceeds the 800 cm^{-1} dimer bond energy. The 1986 report described preliminary experiments which showed a dramatic mode specific effect, with the higher energy mode leading to a longer lifetime than the lower energy mode (880 ps vs 39 ps). Since 1986, picosecond experiments determined that the mode specific decay rates are independent of the NO fragment state which is probed, and product state distribution measurements showed no dependence on the initially excited mode. The latter effect was surprising, but may be understood if both modes dissociate via a channel involving a nonadiabatic transition. Infrared photodissociation spectra obtained using a pulsed difference frequency laser system gave the expected dimer band contours, and showed that such a technique is feasible for obtaining high resolution IR photodissociation spectra of clusters.

We hope to obtain higher resolution photodissociation spectra of the NO dimer and other vdW molecules by using a new infrared excitation source. Tunable ir pulses of about 10ns duration and ≤ .003 cm^{-1} spectral width will be generated as the difference frequency between a frequency doubled pulsed single mode Nd-YAG laser and the pulse amplified cw ring dye laser. Uncertainty principle broadening of the NO dimer lines due to the 880 ps and 39ps dissociation lifetimes is .006 and .13 cm^{-1}, respectively. Lifetime studies (by linewidth or timeresolved measurements) of different isotopes of the NO dimer may establish the mechanism responsible for the fast, mode specific dissociation i.e., anharmonic potential coupling vs. non-adiabatic curve crossing. For instance, if crossing to a repulsive triplet state occurred at an energy resonant with v_4 (but not v_1) for the normal isotope, this could account for the much faster v_4 dissociation rate. If so, a heavy isotope like $(^{15}N^{18}O)_2$ with different v_1, v_4 vibrational frequencies should give significantly different lifetimes. If instead anharmonic coupling caused the dissociation, then large lifetime changes upon isotopic substitution are not expected. Other vdW molecules which may be studied include the acetylene dimer and HF•NO. In both, mode specific dissociation rates, product energy states, and perhaps vibrational energy transfer across the vdW bond may be observed.

C. Molecular Desorption from Surfaces

(S. A. Buntin*, R. R. Cavanagh, D. S. King, and L. J. Richter*)

Recent experiments on the laser-induced desorption of nitric oxide (NO) from Pt(111) have shown that low energy photons can drive non-equilibrium electron-molecule chemistry on metal substrates. This was a surprising result since, unlike semiconductors, the lifetime of non-thermal conduction electrons in metals is very short (≤ 1 psec). The implication of hot electrons in driving molecular desorption was based on conflicting results from a series of state resolved experiments where laser induced desorption was compared to conventional thermal desorption.

The experiments were performed in an ultrahigh vacuum chamber equipped with surface diagnostics to assess the cleanliness and order of the Pt(111) sample. This substrate was saturated with NO at a temperature of 120 K. Experiments were performed on this sample, for which the NO coverage was about 0.4 monolayer, and for samples which had been annealed to 200 K, producing a coverage of 0.25 monolayer (predominantly in top sites). The heating laser was based on a 15 ns duration (FWHM) Q-switched YAG. The YAG output wavelength was varied either by harmonic generation or Raman shifting. The energy of the heating laser pulses was adjusted, at each wavelength to provide sample temperature jumps of about 100 K. The desorbed NO species were probed using laser induced fluorescence at a typical distance of 4 mm from the surface. The probe laser was a narrow-band frequency doubled dye laser. Two types of experiments were performed to obtain internal and kinetic energy distributions for the desorbing species from: 1) Velocity-selected rotational excitation spectra and 2) Internal-state selected time of flights (TOFs).

Results for time of flights (λ pump = 532nm) taken probing those NO species desorbing in a single quantum state - the J=8.5 rotational level of the vibrationless level of the F_1 spin-orbit state - are shown in Fig. 3.3 for three different sample preparations. The middle trace is for a sample with 0.25 monolayer coverage in top sites (200 K anneal). For this sample, there is a single component in the TOF. Although the peak surface temperature induced by the YAG laser did not exceed 300 K, this kinetic energy distribution was characterized by a temperature of 1200 K. The bottom trace was obtained for an unannealed sample, for which the TOFs showed contributions from two desorption channels - one similar to the energetic channel observed for the annealed sample and one of a thermal nature not observed for the annealed sample. The top trace was obtained for a sample annealed to 320 K. This annealing leaves a surface coverage of 0.1 monolayer (in a bridge-bonded site), with no top-site bound species. For this sample, there was no observable laser induced desorption despite the fact that the NO coverage is approximately half that which led to the signal in Fig. 3.3b. The observed desorption behavior following 100 K temperature jumps using visible and near-visible laser-induced desorption can be summarized as follows: no desorption takes place from the bridge sites, energetic species are desorbed from the top sites, and thermal desorption occurs from the low energy binding state. Most of our efforts to date have been spent in characterizing the energetic desorption channel which can be cleanly studied for samples annealed at 200 K.

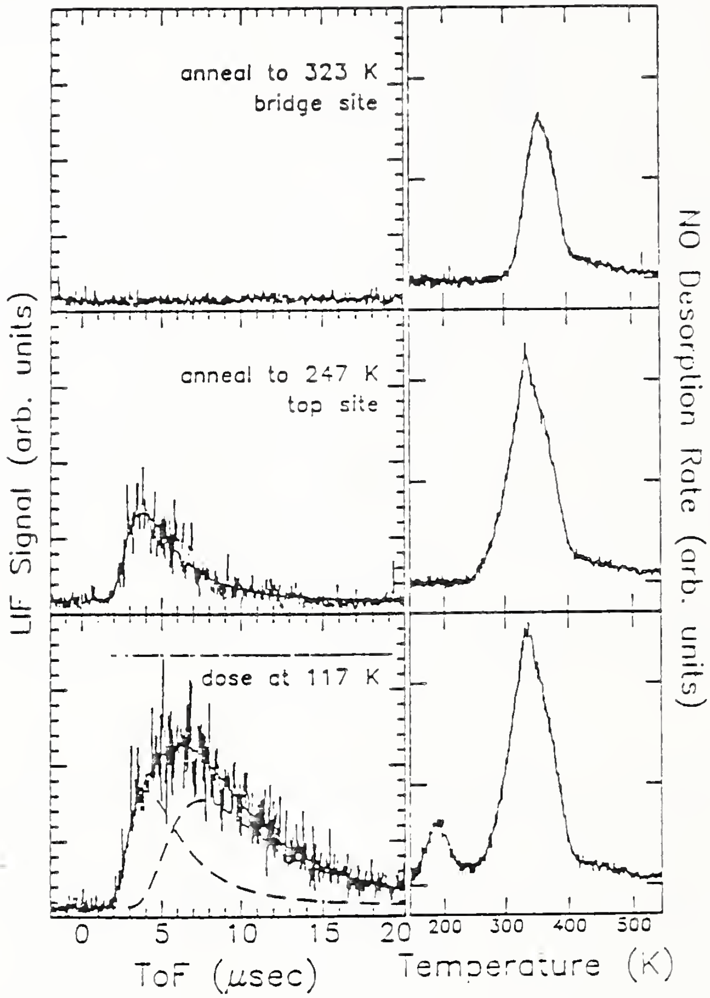


Fig. 3.3 Internal-state selected time of flights for the 532nm laser-induced desorption of NO(J=8.5; F_1) from Pt(111) for different initial surface coverages. The right-hand panels show thermal desorption results for the respective initial conditions.

The desorption mechanism responsible for these signals has to be consistent with a binding energy for the top sites of about 25 kcal/mole, 1.08 eV. When the heating laser wavelength was 532 or 355 nm, the desorbed NO had kinetic energies of 1200 to 2000 K, some 4 to 7 times the peak surface temperature with the measured value increasing with internal energy. Under these desorption conditions some 4% of the desorbed NO was in the v=1 vibrational level. For a heating laser wavelength of 1064 nm (1.17 eV) the kinetic energies were roughly 35% lower and there was no observable population in the v=1 level. The internal state population distributions were essentially the same for all heating wavelengths studied. Notably, there was an inversion in the spin-orbit state populations. The rotational population distribution at low J was independent of rotational energy, falling off rapidly with rotational energy above 300 cm^{-1}.

In the model we propose, the initial absorption of the incident photon is in the near-surface region of the metal. Some fraction of the nascent photogenerated electrons migrates to the surface layer and interacts with the adsorbed NO through its unoccupied $2^{\pi *}$ levels (shown by inverse photoemission to lie in the range from 1 to 2 eV above the Fermi level). Electron capture and neutralization drives the desorption process. In the case of the 1064 nm experiments, only electrons with the full 1.17 eV photon energy can participate in this desorption mechanism due to the energy requirements. For these electrons, desorption into the vibrationally excited v=1 level is not possible. In this model, the propensity for populating the higher energy F_2 spin-orbit state is due to symmetry constraints in the charge neutralization/desorption step.

There are a number of tests still to be performed to prove (or disprove) this mechanism. These include using heating laser photons of energy lower than the 1.08 eV binding energy, using heating pulses of varied time duration and examination of co-adsorbate systems such as NO/CO where the lowest unoccupied levels of the CO are near 3 eV. Experiments are currently underway using Raman shifting techniques to generate laser pulses at energies of 0.6 and 0.85 eV.

Hot carrier assisted desorption mechanisms have previously been proposed for semiconductor systems. One such system is NO/Si(111) where NO desorption has been observed following optical excitation above the Si band gap. We plan to study the desorption dynamics manifest by thermal and hot carrier assisted desorptions from such semiconductor systems.

The interactions of hydrogen at surfaces are believed to be phototypical for a broad range of gas-surface processes. Recombinative desorption of H_2 from hydrogen covered surfaces of metals and semiconductors are typical of such interactions, in that a surface reaction leads to the formation of a new chemical bond, the H-H bond. We are presently exploring four-wave mixing techniques inorder to generate vacuum ultraviolet wavelengths suitable for state-resolved studies of molecular hydrogen. In these desorption studies we plan to investigate both thermally driven H atom recombination, and recombinative desorption driven by optically excited carriers.

This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences.

4. QUANTUM CHEMISTRY GROUP

A. Introduction

The Quantum Chemistry Group is at a time of transition. The biotechnology competence has evolved into a new entity, the Center for Advanced Research in Biotechnology (CARB), while the scattering program is to be expanded to support a new NIST competence on the physics of very slow atoms. Dr. Walter Stevens will leave the group in October 1988 to become the Associate Director of CARB. He is already representing NIST interests in the administrative structure of CARB. Scientific projects initiated in the competence will continue as collaborative efforts between the Quantum Chemistry Group and Stevens. The slow atom competence extends support to an already successful collaboration between Dr. Fred Mies and Dr. Paul Julienne with experimental groups at both NIST and the University of Maryland. An additional scattering theorist will be hired in the next fiscal year. With a new postdoctoral fellow and an occasional foreign guest scientist, the effort can attain a necessary critical mass. The electronic structure group, on the other hand, is reduced to one permanent scientist but the collaborations with CARB and guest scientists will maintain a research program in this area. The scientific direction of the group will not change from the general directions indicated by the work of the last two years described below.

B. Electronic Structure

1. Ab Initio Reaction Field Program

(W. J. Stevens, D. Garmer, M. Krauss, and H. Basch*)

Final tests have been made of the first version of an ab initio reaction field computer program which will be used for quantum mechanical studies of complex systems. The reaction field approach divides a large molecular complex into an "active" region, which is to be characterized quantum mechanically, and a "spectator" region that may be modeled as an assembly of polarizable molecular fragments that are not directly involved in the chemistry. How the boundary between the active and spectator regions is chosen depends on the properties or chemistry one wishes to study. We are currently choosing the boundary so that the interactions between fragments in the two regions is of the nonbonded type. The Hamiltonian of the active region consists of the normal Hamiltonian for the active electrons and nuclei, plus an effective Hamiltonian that describes the electrostatic and exchange repulsion interactions between the active and spectator regions, and a perturbation Hamiltonian that accounts for the polarization of the spectator fragments. It is the polarization term that provides the "reaction" of the spectator region to molecular structure changes that occur in the active region.

Tremendous saving of computer time is possible through the reaction field approach, since only the electrons in the active region need to be considered explicitly, and the effective Hamiltonian between the active and spectator regions involves only one-electron integrals. We have developed methods for obtaining the parameters for the effective Hamiltonians from ab initio calculations on prototypical molecular fragments. These parameters appear to be transferable at the functional group level, so very complex spectator regions can be modeled by a collection of predetermined "fragment potentials."

The electrostatic potential due to a molecular fragment with a frozen electronic charge distribution can be represented by a collection of distributed multipolar expansions located at the atomic centers and bond midpoints [A. J. Stone, Chem. Phys. Lett. 83, 233 (1981)]. However, such expansions are convergent only at infinite distance from the expansion centers. At finite distances, one must account for penetration of the electronic charge distribution. We have used a functional form which gives the total electrostatic potential of a fragement as a sum of an exact nuclear part and an electronic part that includes a cutoff function to account for penetration.

$$\phi_{Tot} = \sum_{n} \frac{Zn}{r} + \sum_{k} \phi_{k}^{elec} \left[1 - Ae^{-\alpha r2}\right]$$

where ϕ_k^{elec} is the distributed multipolar expansion derived from the frozen electron density of the fragment, and A and α are parameters determined by a least squares fit to the quantum mechanical electrostatic potential in a volume surrounding the fragment. The electrostatic contribution to the active region energy is given by

$$E_{estat} = \langle \psi_{act} \mid V_k^{spec} \mid \psi_{act} \rangle$$

which is an easily evaluated one-electron integral.

Modeling the exchange repulsion (and orthogonality) interaction between the active and spectator regions requires some ad hoc assumptions about the localization of exchange operators. We initially tried a simple one-electron representation of the repulsive energy of the form

$$E_{rep} = \sum_{k} \langle \psi_{act} \mid V_k^{spec} \mid \psi_{act} \rangle$$

where V_k are exponential or gaussian functions centered at the atoms of the spectator fragment. The parameters defining V_k are determined by fitting ab initio calculations on prototypical fragments. While this functional form correctly mimics the repulsive interaction energy for a given pair of active and spectator fragments in a particular orientation, the V_k were found not to be transferable to different environments. We then tried a similar two-center energy term of the form

$$E_{rep} = \sum_{k} \langle \psi_{act} \mid V_k^{spec} \mid \psi_{act} \rangle + \sum_{\ell} \langle \psi_{spec} \mid V_k^{act} \mid \psi_{spec} \rangle$$

This is more complicated, since it requires the electron density of the spectator fragments, but it still involves only one-electron integrals. In this case, the potentials, V_k, are found to be transferrable between interacting systems. The transferability is good enough that one can generate the V_k by fitting the interaction between prototype fragments and a spherical "probe" atom (we use argon). Due to the short-range nature of the repulsive exchange interactions, in practical calculations the terms need to be evaluated only at the boundary between the active and spectator regions.

The polarization contribution to the active/spectator interaction energy is calculated perturbatively. The dipole polarizability of each spectator fragment is expanded in terms of electron-pair polarizabilities located at the centers of charge of the bond pairs and lone pairs that comprise the fragment. The electron-pair polarizabilities are obtained from ab initio calculations on prototypical fragments using a localized orbital formalism. These polarizabilities are found to be transferable at the functional group level. The energy contribution due to the polarization of the spectator fragments is given by

$$E_{pol} = \sum_k F_k \bar{\bar{\alpha}}_k F_k$$

where F_k represents the active region electric field evaluated at a polarizable point in the spectator region

$$F_k = < \psi_{act} \mid \frac{r}{r^3} \mid \psi_{act}>.$$

The induced moments in the spectator region can be added into the active region electrostatic interaction energy term, and the electronic wavefunction of the active region can be redetermined, iteratively, until a self-consistent polarization energy is achieved.

We have successfully tested this reaction field approach on a variety of hydrogen-bonded complexes consisting of water, formamide, and glycine. We find that the interaction energy surface for any pair of molecules can be reproduced to within 10-20% when either of the molecules is replaced by the reaction field Hamiltonian. The largest absolute errors are due to the representation of the electrostatic interaction, which is truncated at octupoles for each expansion center. We have also treated complexes of formamide hydrogen-bonded to two water molecules, and find the cooperativity in the hydrogen-bonding is predicted very accurately when both waters are replaced by reaction field Hamiltonians.

The next steps in the reaction field development include testing the transferability of the parameters in larger molecules such as proteins, testing the validity of the distributed dipole polarizability approximation in interactions of charged species (particularly anions), the addition of dispersion terms to the perturbation Hamiltonian, and the development of integral gradients that are needed for geometry optimization. Long range goals include the development of molecular mechanical methods for modifying the geometric structure in the spectator region in response to changes in the active region. Applications of the reaction field program in the coming year will include models of the active site of carbonic anhydrase with different metal substitutions, and a model of the active site in aspartyl proteases to determine the electrostatic potential and the relative energetics of proton transfers.

2. Theoretical Studies of Hydrogen Bonding

(W. J. Stevens and H. Basch*)

It is well established that ab initio SCF calculations using reasonable atomic basis sets can provide accurate data for the structure and stability of hydrogen-bonded complexes. It also is possible to analyze the theoretical calculations to determine the dominant contributions to hydrogen-bond energies and properties. We have studied a variety of hydrogen-bonded dimers during the past year, some of which have also been studied spectroscopically by the microwave group (see above, section 2).

2a. $CH_3OH + NH_3$ and $H_2O + NH_3$

The structure of the methanol-ammonia dimer was determined by the microwave group (see section 2). Stark measurements indicated a rather large dipole moment enhancement (0.96 D) upon complex formation. The analogous water-ammonia dimer has a smaller dipole enhancement (0.59 D) even though the dipole moment of water is 0.18 D larger than that of methanol. We carried out ab initio SCF calculations on both methanol-ammonia and water-ammonia at the experimental equilibrium conformations. The frozen fragment reduced variation space analysis developed in this laboratory by Dr. Stevens and Dr. Fink [Chem. Phys. Lett. 139, 15 (1987)], was used to isolate the factors which determine the dipole moment enhancement for each complex. The results indicated that methanol-ammonia should have a larger enhancement than water-ammonia by virture of the larger polarizability of methanol. The enhancement due to ammonia polarization was virtually identical for the two complexes, since the local electric field near the -OH group is the same in methanol and water.

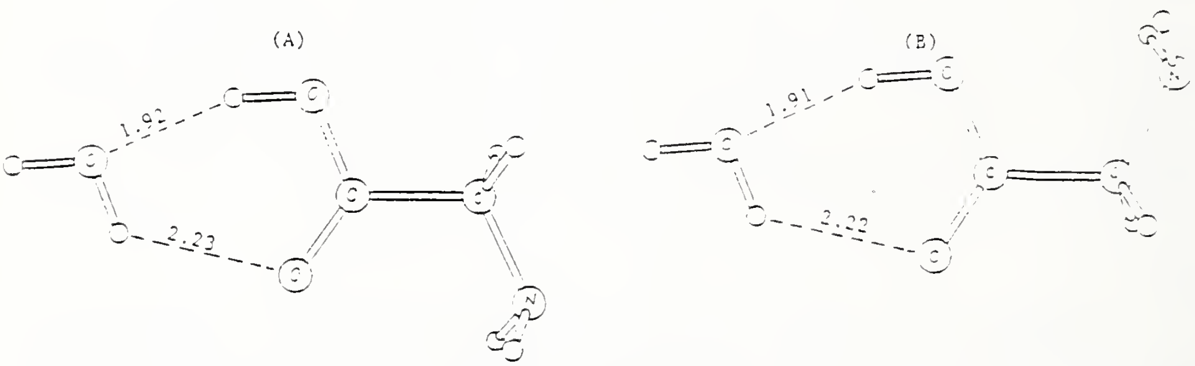
2b. $CO_2 + H_2O + H_2O$

Another study carried out in collaboration with the microwave group (see section 2) involved a cluster of CO_2 plus two waters. The positions of the heavy atoms in this complex were obtained from the analysis of the microwave spectrum. However, the proton positions could not be determined with any certainty because of the insensitivity of the moments of inertia to in-plane rotations of the waters about their centers of mass. The dipole moment of the complex was determined from Stark measurements. Ab initio calculations were carried out with the heavy atoms fixed in the positions predicted by the microwave analysis. The orientations of the two waters in the complex were varied until the calculations predicted a dipole moment that was compatible with the Stark measurements. A full quantum mechanical optimization of the structure was impossible due to the flatness of the potential energy surface and the large basis set required to correctly describe the electrostatic interactions and the polarization effects. The final predicted structure has one water bonded to the CO_2 in a nearly optimum orientation with the water oxygen pointing at the CO_2

carbon. A second water forms a bridge between the CO_2 and the first water by acting as a proton donor to the CO_2 oxygen and a proton acceptor from the first water. The water-water hydrogen bond is quite distorted, but the energy gained from the two water interactions with CO_2 more than compensates for the energy loss in the distorted hydrogen bond. The ab initio calculations find the complex to be planar, in agreement with the microwave analysis.

2c. $H_2NCOOH + H_2O$

We have carried out complete ab initio calculations, including geometry optimizations and electron correlation studies, on cyclic complexes of glycine with water. This work was stimulated by the discovery in this group of a highly stable, cyclic complex of formamide and water that was subsequently verified by microwave spectroscopy. The stability of such cyclic complexes is due to the formation of two hydrogen bonds. Each bond is distorted somewhat from an ideal linear configuration, but the binding energy obtained from the two distorted hydrogen bonds exceeds that of any single hydrogen bond that can be formed. Glycine-water complexes have not been observed experimentally, but our calculations predict two cyclic structures that are quite stable with binding energies of approximately 9 kcal/mol. The two structures are shown in Fig. 3.1. Both involve a cyclic, double hydrogen-bonded configuration between water and the carboxyl moiety. The difference in the two structures is a 180 degree rotation about the C-C bond in glycine, which also distinguishes two of the conformers of the glycine monomer. As expected, the monomer geometries are not distorted by the hydrogen bond formation. The energy separation between these two complexes is a little less than the separation in the glycine monomer conformers, presumably due to some cooperative polarization of the hydroxyl group by the water and the amine group. Other cyclic structures were examined that involve water binding between the carboxyl



Binding Energy = 8.6 kcal/mol
Relative Energy = 0.0 kcal/mol
Dipole Moment = 2.3 D

Binding Energy = 9.0 kcal/mol
Relative Energy = 1.4 kcal/mol
Dipole Moment = 2.2 D

Fig. 4.1 Structure of water-glycine complexes.

and amine groups, but these were found to be weakly bound and much less stable.

2d. $HCOOH + HCOO^-$

In the three dimensional structure of proteins, it is very common to find two carboxyl groups in close proximity to each other, particularly in metal binding sites or sites involved in hydrolysis reactions. We have begun a series of ab initio calculations aimed at characterizing these protein fragments in terms of structure, stability, proton mobility, and the influence of the protein environment. The first study involves the formate-formic acid complex, for which there is gas phase data on the stability but not the structure. We have carried out a full energy gradient optimization of the structure of the complex within the SCF approximation. The interaction energy surface is quite flat. We are currently investigating the proton-transfer reaction coordinate at both the SCF level and the MP2 correlated level. The next phase of the investigation involves the introduction of a water molecule, which will yield many new interesting structures as well as several proton transfer possibilities. Eventually, we will introduce a protein environment via the reaction field method and attempt to make predictions about stable structures and proton positions as a function of protein mutation.

3. Selectivity of Metal Cation Binding to Proteins

(M. Krauss and W. J. Stevens)

Ab initio molecular orbital calculations of the binding energy of metal cations to octahedral clusters of water, formamide, and formate ligands are used to model the enthalpies of metal substitution reactions at Ca binding sites in proteins. Since the binding of the cation to the first shell ligands substantially exceeds ligand-ligand binding energies, the conformation of the first shell in the bulk is essentially determined by the equilibrium geometry of the first shell cluster. A satisfactory model for calculating binding enthalpies is based on the first shell energetics and the Born model for determining the polarization interaction of the first shell with the environment. Cluster reaction enthalpies are calculated for transferring Mg^{+2}, Ca^{+2}, and Na^{+1} cations from a water cluster to the protein model cluster. The metal is bound to the lone pair electrons of the oxygen atoms in these ligands. Cluster size is determined by the metal to oxygen distance and is found to strongly affect cation binding selectivity between cations of the same and different charges. The selectivity is a function of both steric and electrostatic interactions. The selectivity between Mg and Ca is primarily dependent on steric factors which restrict the formation of optimal electrostatic bonds. However, there is also an electrostatic component independent of steric influences which is selective between cations of different charge.

The model is tested by a calculation of Na, Mg, and Ca cation enthalpies in water. Including dispersion and zero-point energies in the first shell cluster energetics, these enthalpies agree within 5% with the experimentally deduced values. Enthalpies are compared for clusters with different numbers of waters. It is evident that the W6 cluster is most stable for Mg and Na. However, for Ca, W6 and W9 yield comparable enthalpies reflecting the tendency for Ca to be found in variable first shell environments.

The model metal reaction enthalpies have been applied to an analysis of the binding sites in the protein, Subtilisin BPN'. For the A site, the energy of reaction is 20 kcal/mol favoring Ca binding over Mg. Desolvation energies determine the ion selectivity between Mg and Ca. Steric interaction between the protein ligands are larger than in water and prevent as optimal Mg-O bonds from forming in the protein cluster. For an optimal B site type cluster, Ca is bound by 13 kcal/mol over Mg. As the metal to oxygen bond distance is increased, Ca is even more strongly bound than Mg. Competition between Na and Ca is only possible if the protein site is substantially rigid. If the clusters around both the Ca and Na cations can achieve optimal bond distances, then the Ca cation will always be very energetically favored. When the cluster conformation is determined primarily by forces in the protein and not by the cation-ligand interaction, then several different conformations between the cations and ligands are possible and, for an appropriate cluster size, the enthalpy of reaction will approach zero. If the cluster containing one formate, one water, and four formamide ligands is fixed with the M-O bond distance 2.8Å or larger, the reaction enthalpy favors Na binding to the protein model cluster. Crystallographic analysis indicates the site is of comparable size for either Ca or Na binding, but each metal binds in a unique manner. The Ca ion binds to the carboxylate anion of an ASP residue, the carbonyl oxygen of a backbone residue, and four waters. It does not penetrate into the binding site but remains near the surface and bound to the ASP anion. The Na is found bound to three carbonyl oxygens of residues near the bottom of the site but still interacting at a longer distance with the residues at the surface containing the anionic moiety. The Na binding energy in the cluster varies slowly with the position in the cluster, but, because of the charge of Ca, the binding energy varies rapidly with position for Ca with the Ca more strongly bound in an optimal conformation with the formate anion. Binding energies of these different cluster conformations permit a rationalization of the experimental geometries. The relative rigidity of the B site in the protein is ascribed to ionic bonds in the second shell of residues around the site. Metal substitution and hydration enthalpies will be studied for other metal cations and the models extended to clusters with more than one formate or formic acid ligand.

4. Binding of Pt Ammines to DNA
(H. Basch*, M. Krauss, and K. Miller*)

Metal cation bonds to nucleic acid bases have large intrinsic bond energies. The binding of cis-diammineplatinum (DP) to single- or double-strand oligomers of DNA substantially alters the local helix geometry at the point of bonding. Experimental evidence suggests that DP binds preferentially to the N7 sites of the guanine (G) base in a GpG chelate, which can interfere with the physiological properties of DNA. Earlier we proposed a theoretical model for DP binding which showed a 'kinked' distortion of the DNA is feasible without seriously disturbing the duplex base-paired hydrogen binding. The details of the kinked structure have been examined with both quantum and classical mechanics modeling. Valence self-consistent-field (SCF) calculations of the energetics of clusters of DP, a phosphate anion, and water molecules indicate that the structure of the adduct depends on the hydrogen bonding of the polarized ammine ligand to nucleophillic sites in DNA. The possibility of water bridges significantly increases the number of types of structures. The cation can bind directly to the phosphate or it can bind to water which is in turn hydrogen bound to the phosphate. Direct or through-water binding of DP to phosphate is calculated to be competitive and the kinked conformations are dependent on the interaction with the environment and the extent to which the interacting species can be solvated. Detailed geometries obtained by molecular mechanics minimization are reported for the interaction of DP with the pentamer duplex, (AT, GC, CG, AT) and a number of water molecules. Binding of the DP to the carbonyl oxygen of the thymine (T) base is observed in the molecular mechanics conformations and the energetics of such a bond was also examined with SCF calculations. Binding of substituted DP was also investigated to determine the relative importance of steric and hydrogen binding on the adduct formation. Computer modeling of a series of cis- $Pt(NH_2R)_2^{+2}$, where R=H, CH_3, cyclopropane, cyclobutane, and cyclopentane, to the pentamer duplex of DNA shows that the receptor site geometry and the conformation of the DNA is changed little for binding all mono-substituted ammines. The binding energy decreases with the substituent size faster than the slight increase in van der Waals energy resulting from the increasing number of atoms. The reduction of binding is correlated with the decrease in physiological activity.

5. Electronic Structure of the P-O and P-S Bonds
(H. Basch*, M. Krauss, and W. J. Stevens)

The electronic structure of the P-O and P-S bonds is studied because of the importance of phosphates and phosphorothioates in biological systems. Although the study concentrated on these systems, the following molecules were examined to study the bonds in a variety of molecular environments: H_3PO, PO_3^-, $H_2PO_4^-$, and H_3PO_4, and their mono-substituted sulfur analogues. The analysis of the bonding was based on the gross atomic populations, plots of the charge density and appropriate difference-densities, and the electrostatic potential. For the phosphate anion and the thio analogue, the water binding energy was calculated to provide a more direct example of binding to the oxygen and sulfur sites to compare with the electrostatic potentials. The P-O and P-S bonds are found to be very polar in all the molecules. Population analysis shows an appreciable d population on P related to π back transfer. However, the strength of the bond and the short bond distance is related to the polar character of the bond and not the hypervalent or multiple bond character. The P-O and P-S bonds in the phosphorothioate anion show significant charge transfer from P to both O and S. The large negative potential near both atoms leads to ionic hydrogen bonding of water to both O and S. The bond energy to O is about 4 kcal/mol larger because of the closer approach of water to O. The electronic structure of the P-O bond is now being compared to the V-O bond.

Vanadate substrates have been suggested as a replacement for phosphates to create a stable transition state analogue. We will compare the electronic structure of the V-O and P-O bonds to determine the validity of the concept.

6. Anion Binding to Polar Molecules
(H. Basch*, M. Krauss, and W. J. Stevens)

The electrostatic interaction between an anion and a highly polar molecule is large and bound adducts are expected. However, adducts are possible for more than one set of reactants or channel that are accessible to one another by a substitution reaction. Whether the adducts are stable intermediates in channels other than the lowest energy one will depend on the magnitude of the binding energy and the barrier associated with reaction to a lower energy channel. A number of stable adducts or intermediates have been explored for phosphates with the general formula composition, $H_4PO_5^-$, or chlorine substituted phosphate anions, $H_3PO_4Cl^-$ and $H_2PO_3Cl_2^-$. Cl substitution for OH allows an exploration of the effect of the size and electronegativity of the interacting species. The polar nature of the P-O and O-H bonds suggests that the nucleophillic addition of an anion to both P and O sites would lead to stable adducts. Considering proton transfer between reactants, the following hydrogen-bonded adducts are possible:

1. $H_2PO_4^- \cdots H_2O$,
2. $H_3PO_4 \cdots OH^-$,
3. $HPO_3Cl \cdots H_2O$,
4. $H_2PO_4^- \cdots Cl^-$,
5. $PO_2Cl_2^- \cdots H_2O$,
6. $H_2PO_3Cl \cdots Cl^-$.

The stabilities of the OH^- and Cl^- adducts are interesting since we calculate binding energies of nearly 70 and 40 kcal/mol, respectively, which far exceed the binding energies observed for normal polar-anionic interactions. For example, the binding energy of water to the phosphate anion is of the order of 15 kcal/mol. Both electrostatic or hydrogen-bonded and five-coordinate adducts were studied. The electronic structure of the five-coordinate trigonal bipyramid adduct was examined as a function of Cl substitution in equatorial and apical positions. Both adducts 1 and 2 are stable, but the five-coordinate analogue structure is an intermediate local minimum. Adduct 1 is the lowest energy structure and the barrier to proton affinity exists to allow a stable adduct 2. The approach of OH^- to phosphoric acid induces a rotation of the all OH bonds around each P-O bond so that the acid adopts an umbrella conformation with three OH bonds pointed at the OH^-. The binding energy is comparable to three times the bond energy between OH^- and water. The Cl structures are not as strongly bound because of the larger size of Cl and the differences in the proton affinities of the anions. However, a reaction field analysis of the ionic hydrogen bonds reveals the electrostatic interaction is dominant as expected. The Cl substitution manifests itself by reducing the polarity of the neighboring P-O bonds and producing a concomitant reduction of the proton affinities of the substituted phosphate anions. This leads to the proton abstraction without a barrier by OH^- from the substituted molecules.

The apical OH ligands in the five-coordinate complexes are very polar and the central P atom of the equatorial moiety is quite positive with over one electron transferred to the surrounding ligands. For the Cl substituted five-coordinate structures, the stability and binding energy trends are related to the local polarity of the P-X bond and not the overall electronegativity of OH and Cl. Cl is more electronegative but still stable five-coordinate intermediates only have equatorial chlorines. When the chlorines are in apical positions, the structures are always found to be transition states and are dissociative for a chlorine ion. The local polarity influence on adduct formation for anions containing second row atoms will be examined more systematically for halide substitution and replacement of OH by SH. Reaction field methods will be used to analyze the interactions.

C. Scattering Program

We are actively involved in a variety of problems which can be classified as the spectroscopy of colliding molecular fragments. For example, a photon may be absorbed during a collision, or a photon may cause the dissociation of a molecule or the association of fragments to form a molecule. Such problems occur in a wide variety of areas in chemical physics, e.g., laser spectroscopy, development of new lasers, spectral line shapes, radiative redistribution and transport, excimer lasers, chemistry of planetary atmospheres, ultracold collision phenomena. We use two complementary approaches: (1) numerical state-of-the-art close coupled quantum scattering methods combined with ab initio calculations of interaction potentials and (2) powerful analytic tools based on the generalized form of the multichannel quantum defect theory (MCQDT). This combined numerical and analytic approach gives a comprehensive and unified ab initio quantum methodology for describing a variety of experimental observables. Our applications of this theory in FY87-88 are described below for the following topics:

C.1. Molecular photodissociation.
  a. Overlapping resonance effects on predissociation line shapes in O_2.
  b. Predissociation of the B and C states of CO.
  c. Intense laser photodissociation of H_2^+
C.2. Generalized MCQDT applications.
  a. Whole and half collision matrix methods for multichannel curve crossing problems.
  b. Factored frame transformation half collision analysis of collisions.
  c. Unified half collision analysis of photodissociation, collisional redistribution of light, and atomic collisions.
  d. Generalized MCQDT analysis of molecular bound states and collision cross sections involving molecular charge transfer states.
C.3. Theory of ultracold atomic collision phenomena.
  a. Molecular photoassociation spectroscopy.
  b. Associative ionization cross sections of Na(3p) + Na(3p) at 0.001K.
  c. Intense laser effects on cross section in optical traps.

d. Collision-induced optical trap loss processes.
e. Quantum threshold effects in ultracold collisions.
f. Ultracold collisions in magnetic fields.

C.1 Molecular photodissociation

a. Overlapping Resonance Effects on Predissociation Line Shapes in O_2
(P. S. Julienne, F. H. Mies, and L. Vahala*)

The Schumann-Runge bands of O_2 have long been known to be predissociated. These bands play an important role in upper stratospheric photochemistry, since they control the penetration of the solar flux in the 200-175 nm range. Numerous experimental studies of these bands have been carried out over several decades, and are still current today. Several years ago we (Drs. Julienne and Krauss) carried out an ab initio study of the predissociation line widths, and explained the basic mechanism of the predissociation in terms of 4 different molecular states which cross the bound $B^3\Sigma_u^+$ state. All experimental modelling of the widths, as well as our theory, assumed the standard Lorentzian model of the predissociation line shape. The blending of triplet fine structure components in the bands has made the extraction of lineshapes from experimental data difficult. Theory predicts different widths and level shifts for each fine structure component. Theory also predicts that two of the fine structure components of the same J but different N can interfere and give rise to non-Lorentzian line shapes. Such interfering resonances are called overlapping resonances (predissociating bound states are scattering resonances).

We have applied our two-fold approach to the question of the photodissociation line shapes of the Schumann-Runge bands. We have calculated line shapes using both a multichannel close coupled scattering calculation and an analytic theory based on the generalized MCQDT which uses parameters obtained by perturbation theory. We find the two methods to be in excellent agreement. The calculation gives an excellent illustration of the power of the MCQDT formalism to introduce the effect of multistate couplings into molecular spectroscopy problems involving both bound states and continua.

We have used our numerical close coupling code to calculate the spectral line shape for transitions from specific O_2 $X^3\Sigma_g^-$ ground state fine structure levels to the upper multichannel continuum which represents the two closed fine structure bound state channels interacting with multiple continua. The bound closed channels represent the F_1 and F_3 triplet fine structure components of the same J and respective N = J-1 and J+1. We have carried out model studies including both single and multiple continuum interactions. Fig. 4.2 illustrates a typical profile for the two interfering ${}^NP_{13}(3)$ and $P_3(3)$ lines predissociated by interaction with the ${}^3\Sigma_u^+$ state. The non-Lorentzian character of the lines in this model calculation is evident in comparison with the correct line shape obtained by close coupling.

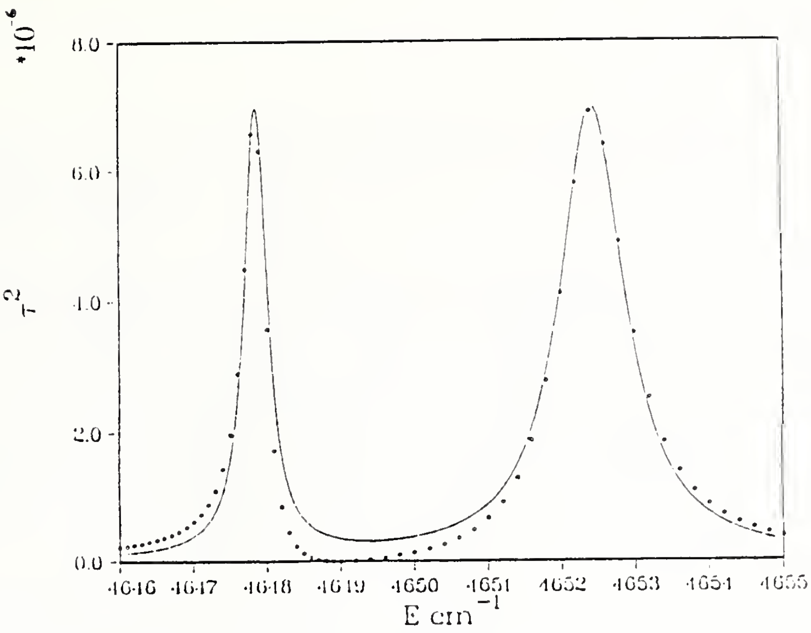


Fig. 4.2 Lorentzian fit to two interfering fine-structure lines in predissociating O_2. Solid points indicate exact numerical results of close-coupling codes.

The MCQDT analysis of the line shape uses the analytic structure of the excited state multichannel wavefunction to give an analytic representation of the line shape. The expression is:

$$|\tau(E)|^2 = D\ L(E)\ D,$$

where D is a 2 component vector containing the product of Franck-Condon and Hönl-London amplitudes for the two interfering lines and L(E) is a 2 x 2 matrix line shape function which can be expressed in terms of ordinary molecular spectroscopic perturbation matrix elements. It contains both the effects of the spin-spin and spin-rotation interactions and the predissociation by one or more continua including the effects of width and level shift. The MCQDT theory allows for interference between the two bound levels. In Fig. 4.3 the MCQDT profile is in excellent agreement with the numerical close coupled profile. The MCQDT formalism is expected to have much utility in molecular spectroscopy, since it can treat bound and continuum interactions equally well in a consistent way.

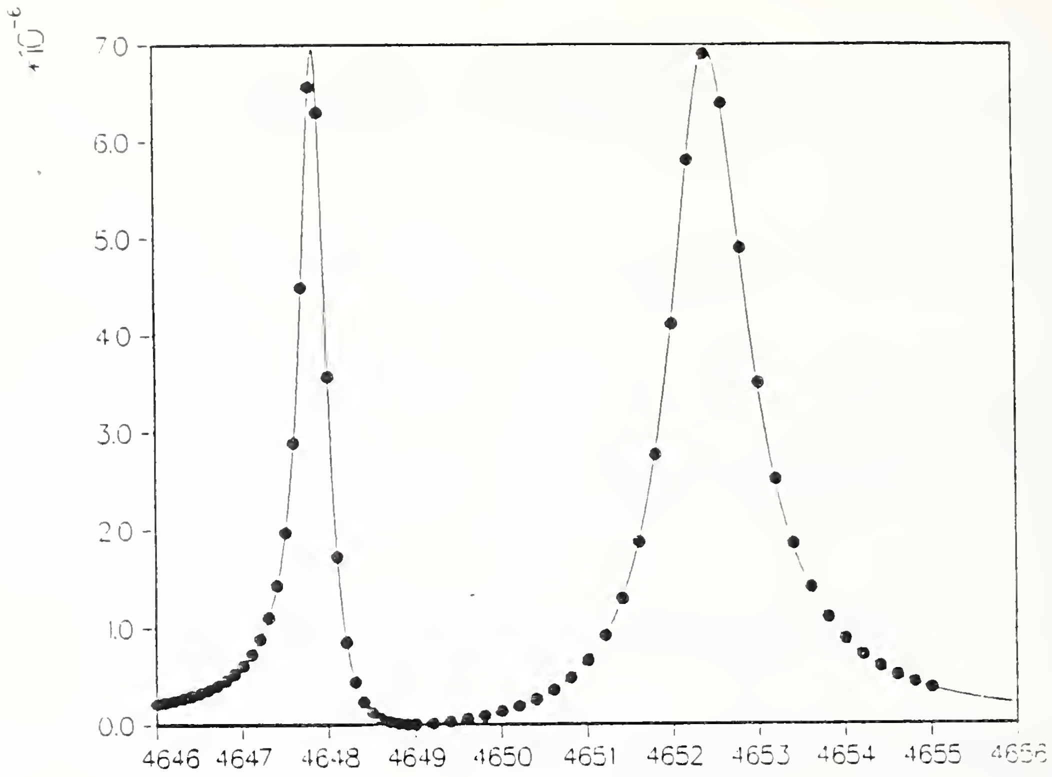


Fig. 4.3 Resultant exact fit to interferring predissociating lineshapes in O_2 using analytic expressions predicted by MCDQT.

b. Predissociation of the B and C states of CO

(P. S. Julienne and F. Rostas*)

CO is an astrophysically important molecule which can be photodissociated by light with wavelength shorter than 112 nm. The photodissociation between 112 and 90 nm only occurs in discrete bands which are predissociated. New high resolution absorption and emission spectra for a number of bands in this region have recently been obtained by F. Rostas and coworkers at the Observatory of Paris, Meudon, France. We have been analyzing these data in collaboration of the group at Meudon in order to interpret the predissociations and obtain a predictive model of the predissociations in the ns and np $^1\Sigma$ Rydberg series perturbed by the $D'^1\Sigma$ valence perturber.

The positions and intensities of the vibrational and rotational levels of the B 3sσ $^1\Sigma$ and C 3pσ $^1\Sigma$ Rydberg states are perturbed due to strong interactions with the nearby D $^1\Sigma$ valence state. These are especially evident in the B state, where the vibrational spacings depart significantly from the spacings in the CO^+ molecular ion. An anomalous rotational constant is found for B v=2, and the rotational levels become diffuse and break off with increasing J. Although the C state is higher in energy than the B state and also crossed by the D' state, vibrational levels to v=4 are observed, and v=0, 1, and 2 are seen in emission. Level shift perturbations are also seen for the C levels, but these are much smaller than for the B state.

We have constructed a model to explain these data. The model uses deperturbed spectroscopic constants to construct model diabatic potentials for the B, C, and D′ states. The D′ state is known in its R_e region from 4 observed vibrational levels. It is necessary to extrapolate the left limb to small R in the region of crossing with the B and C states, for which the R_e is the same as for the molecular ion. Diabatic coupling matrix elements are assumed by the model, and curves and couplings are adjusted to account for the level positions, predissociation widths, and absorption intensities, assuming diabatic transition dipoles.

The coupling matrix element between diabatic B and D′ states is so large, 3000 cm^{-1}, that a strong coupling model is necessary to treat the problem. Our numerical close coupling code is set up as a three channel scattering problem to calculate the predissociation line shapes for the B and C bound levels which are strongly coupled to the D′ continuum. Perturbation theory based on either a diabatic or adiabatic weak coupling model predicts the wrong results. It is necessary to calculate the predissociation widths and shifts in a strong coupling model which solves the coupled equations which treat the strong coupling between the B and D′ states. One important consequence of this calculation is that the C state predissociation, which is much weaker than that of the B state, can be calculated using Fermi Golden Rule perturbation theory, but only if the golden rule matrix element is calculated between the unperturbed C state and the strongly coupled two channel B-D′ mixed state. The correct C state widths can not be calculated by either a diabatic or adiabatic model of the D′ state alone.

This work is still in progress to fine tune the parameters of the model. The model is capable of accounting for the magnitudes of the width and level shift perturbations, as well as the band oscillator strengths of the various B-X and C-X bands. The model is expected to predict the predissociation behavior of the higher members of the Rydberg series.

c. Intense Laser Photodissociation of H_2^+
(F. H. Mies and A. Giusti*)

We are performing a joint theoretical study of the influence of intense laser fields on the photodissociation of diatomic molecules. This is motivated by experimental studies in Saclay, France [see C. Cornaggia, et al., Phys. Rev. A34, 207 (1986)] where non-linear contributions to the photodissociation of H_2^+ in a strong laser field has been observed in a multiphoton experiment involving the H_2 molecule. A four photon process leads to the production of the $H_2^+(1s\sigma_g)$ in a variety of vibrational rotational states depending on the laser frequency. (The ion is produced by photoionization of the $H_2(E^1\Sigma_g^+)$ excited state which is accessed by a three photon process). At field intensities in excess of $I = 10^{11} W/cm^2$ the observed photodissociation rate

$$H_2^+(1s\sigma_g, v^+) + h\nu \rightarrow H_2^+(2p\sigma_u; \epsilon) \rightarrow H(1s) + H^+ + \epsilon$$

exceeds the predictions of conventional weak-field theory, which ignores any field-induced distortions of the molecular states, and yields a linear dependence on I.

A photodissociation process may be viewed as a laser-induced predissociation of field-dressed molecular bound state imbedded in a field-dressed dissociation continuum with a radiative coupling strength $V_{rad}=eE\cdot d$ which is proportional to $|E| = (2I/c)^{½}$. In the weak-field limit the resultant predisociation rate is equivalent to the photodissociation rate and is proportional to I. In the strong-field limit the width and position of the field-dressed resonance state exhibits non-linear effects, and eventually adjacent vibrational states begin to overlap and lead to profound saturation effects.

Preliminary calculations using rigorous closed-coupled scattering codes and algorithms which solve driven equations needed to describe a bound-continuum transition yield results which are consistant with experimental observations. Our collaboration involves a number of interesting theoretical studies concerned with the proper gauge that is needed to describe the H_2^+ transition dipole; the comparison of complex variable methods versus multichannel close-coupled scattering codes applied to the laser-induced predissociation; and the proper description of a three-particle continuum that is needed to rigorously describe the simultaneous ionization-dissociation of the H_2 molecule.

Future experiments will be conducted at Saclay using two lasers of different frequency and intensity. This will provide a much more thorough analysis of the intense laser field modifications associated with the final photodissociation process and our theoretical calculations will be directed toward a rigorous description of such two-color experiments.

C.2 Generalized MCQDT applications.

a. Whole and Half Collision Matrix Methods for Multichannel Curve Crossing Problems

(F. H. Mies and Y. Band*)

We have developed two new numerical methods of solving coupled quantum scattering equations which are most convenient for treating the dynamics of conventional atom collisions, which can be called a "full collision" process, as well as processes that proceed from an initial bound state, such as photodissociation, which can be viewed as a "half collision" process. In both cases we can also describe the scattering under the influence of intense laser fields. To describe any scattering process we begin by choosing a set of channel states sufficient to describe all the dynamic observables. For a given set of channels we must then construct an associated interaction matrix U(r) which contains all the physics of the collision process of interest. The dynamics is then completely defined by the resultant scattering matrix S which is obtained by solving the usual multichannel second-order Schrödinger equation.

Our new methods consist of replacing the multichannel second-order Schrödinger equation by an equally exact set of first order equations which allow us to numerically propagate a specially designed Half Collision Matrix X(r) which asymptotically defines the usual scattering matrix

$$S = e^{i\xi}X(X^*)^{-1}e^{i\xi}.$$

The method requires us to <u>choose</u> a set of diagonal reference potentials V(r) which then define a diagonal set of reference phase shifts ξ. Given our choice of V(r), which is completely at our disposal and can be chosen for our convenience in propagating the coupled equations, the resultant half collision amplitude X(r), which now incorporates all the non-adiabatic couplings between our reference channel states, is rigorously defined.

The matrix X(r) can only be propagated in classically open regions of configuration space. However, we can always derive a stable first-order algorithm for propagating the associated Full Collision Matrix $\Sigma(r) = X(X^*)^{-1}$ which is valid throughout all configuration space, and also asymptotically yields the required scattering matrix $S = e^{i\xi}\Sigma e^{i\xi}$. The numerical methods were applied to a multichannel curve crossing in atom diatom vibrational energy transfer collisions. Exact results (i.e., agreement with conventional close-coupled results for S were obtained using the Full Collision Matrix Method throughout all space, or applying the Half Collision Matrix Method in classically allowed regions. Many improvements, elaborations and applications of these numerical techniques will be developed in future collaborations.

In addition to these rigorously defined Matrices, a Classical Half Collision Matrix $Z(r) = e^{+\beta}X(r)e^{-i\beta}$ can be defined by introducing a WKB-like phase function $\beta(r)$ for each channel and then neglecting rapidly oscillating terms in the propagation of the first-order equations for Z(r) that are associated with the sum of such phases $\exp(\beta_i+\beta_f)$ and only retaining terms multiplied by phase differences $\exp(\beta_i-\beta_f)$. Although this random phase approximation is only valid if the non-adiabatic coupling is restricted to classically accessible regions of coordinate space, it is quite a useful and generally valid approximation for most molecular dynamics. It has the important consequence that Z(r) and hence the half collision amplitude is unitary, such that $X(r)X^\dagger(r)=1$ for all r. In this case, since we are no longer solving the coupled equations exactly, the choice of reference potentials V(r) is much more critical. Fortunately, the best choice is generally made quite obvious simply by examining the exact interaction matrix U(r) which defines the dynamics. This multichannel semiclassical approximation has many powerful applications in scattering theory and molecular spectroscopy. It is presently being applied to multichannel curve crossings, lineshape theory, and final state distributions of fine-structure states in photodissociation.

b. Factored Frame Transformation Half Collision Analysis of Collisions
(F. H. Mies)

Often is would appear that the complete dynamics of a multichannel scattering process can be physically separated into two or more distinct regions of space with uniquely different interactions and distinctly different combinations of channels which are strongly coupled. Such a situation is especially evident in atom-atom scattering and diatomic dissociation where strong chemical and electronic interactions, often represented in Hund's case (a) or (b), are prevalent at short distances, while weaker spin-orbit interactions dictate a predominately case (c) coupling only at intermediate distances, and ultimately, as $r \to \infty$, and nuclear angular momentum becomes dominant, we approach a pure case (e) representation. Further refinements are required if atomic hyperfine splittings are present, and of course external Stark and Zeeman fields will introduce further separate regions of dynamic couplings on the way to the asymptotic set of fragment internal states which define the scattering cross-sections. Let us choose to designate say i=1,N distinct regions of internuclear separation r

Region(1) $0 \le r < r_1$

Region(i) $r_{i-1} < r < r_i$

Region(N) $r_{N-1} < r \le \infty$

based on the assumption that each region has some dynamically distinct feature which we choose to isolate for special consideration. In general, we can imagine that region N is where the hyperfine dynamics is dominant and all other couplings, such are couplings between any fine-structure states of the atoms have become negligible. The simple criterion for such a separation is that the fine-structure splittings of the atomic fragments are large compared to any residual molecular state interactions, but which, in turn, may be large or comparable to any hyperfine splittings. We can always include a complete set of channels that carry us from region 1 to region N and solve the complete dynamics exactly. However we choose these separate regions for our numerical convenience in blocking the complete interaction matrix U(r) into dynamically uncoupled sub-sets of channels at various ranges of the internuclear coordinate r. Our intention is to solve the close-coupled dynamics separately in each region using these substantially smaller subsets, and obtain an appropriately blocked half collision amplitude $X_i(r)$ at $r=r_i$ derived with the initial boundary condition $X_i=1$ at $r=r_{1-1}$. These can always be combined to obtain the exact asymptotic amplitude.

$$X(\infty) = X_1(r_1) \cdot X_2(r_2) \cdots X_i(r_i) \cdots X_N(\infty)$$

which then yields the complete scattering matrix $S = e^{i\xi} X(X^*)^{-1} e^{i\xi}$.

In general this separation is not especially useful since the form of the coupled equations for the amplitude $X_i(r)$ beginning at $r=r_{i-1}$, even with the initial boundary condition $X_i=1$, depends on the resultant amplitude $X_{i-1}(r_{i-1})$ obtained from the preceeding region. Fortunately, one very simplifying feature of most atomic collision processes, is that, excect for the smallest region i=1 where curve crossings and predissociations are assumed to occur, all couplings between the atomic fragments generally occur in classically accessible regions. This implies that

$$X_i(r)X_i^\dagger(r) = 1 \text{ for all } r \text{ and } i>1$$

In this case the propagation of $X_i(r)$ for $i>1$ is independent of the preceeding amplitude, and we can perform the scattering calculations separately in each region. The final structure of the scattering matrix takes the very useful form

$$S = [e^{i\xi}X_N\cdots X_2e^{-i\xi}]\ S_1\ [e^{-i\xi}X_2\cdots X_Ne^{i\xi}]$$

where S_1 is the scattering matrix defined by the short range interactions in the absence of the final state interactions contained in the product of amplitudes $X_N\cdots X_2$.

The structure of this factorized scattering matrix offers a multitude of powerful applications in spectroscopy and atom dynamics. The most immediate applications are being made in atomic lineshapes theory and in developing criterion for the use of frame transformation theory especially for product state distributions in photodissociation and predissociation.

c. Unified Half Collision Analysis of Photodissociation, Collisional Redistribution of Light, and Atomic Collisions

(P. S. Julienne)

The half collision methods which we have developed can be used to give a unified picture of a variety of collisional processes. In particular we have shown how the half collision factorization of the T matrix elements can be used to analyze and give a unified description of several kinds of processes which superficially seem to be different. Specifically the analysis is applied to collisional redistribution of light, molecular photodissociation, and atomic energy transfer collisions. In particular, we analyze recent experiments which involve the collision of two atoms, one of which is aligned or oriented. In one type of experiment, an atom is aligned in one frame prior to a collision in a beam frame, and the production of products measured as a function of angle between the two frames. In other experiments, a polarized photon is absorbed during a collision or used to photodissociate a molecule, and the alignment of a product atom is detected. The underlying theme in the unified picture is a common half collision description of the collision dynamics.

We first obtain a separation of the cross sections into geometric factors which define the various experiments and reduced dynamical factors which are independent of experimental geometric parameters such as laser polarization direction or angle between laser and beam frames. The reduced dynamical factors depend on the angular momentum quantum numbers, but not space projection quantum numbers, and on T matrix elements calculated for a given total angular momentum J. These T matrix elements are the ones that would be found by a standard close coupling calculation for the coupled equations for the given J.

At this point approximations are introduced into the theory. We make the usual MCQDT separation into different zones of internuclear separation R characterized by distinct physics. There will always be a long range or asymptotic zone which describes the noninteracting separated atoms. There will also be one or more short range zones characterized by one or more molecular Born-Oppenheimer potentials and some Hund's coupling case. The collision dynamics describes the transitions between these different molecular zones and the asymptotic zones. We introduce the assumption that the transition in question between some initial and final molecular Born-Oppenheimer states occurs in a short range clasically allowed molecular zone where the reference states can be chosen so the interaction is described by weak coupling. The connection between the short range and asymptotic zones can be characterized by strong coupling in either the initial or final states. With these assumptions the half collision factored form of the T matrix can be used:

$$T(f \leftarrow i) = N_f t N_i ,$$

where N_i and N_f describe the respective initial and final state half collision dynamics which connect the asymptotic and short range transition zones and t describes the weak coupling Franck-Condon type transition at short range.

When the above factorization is used in the reduced dynamical cross section expressions, much physical insight about the collision dynamics can be obtained from constructing models of the N matrices. One such model is a sudden or recoil limit model which has been used widely in photodissociation experiments. We have also worked out the limiting expressions of this model for several different types of redistribution and aligned atom collision cases. The usual recoil limit model does not explain alignment experiments well because it neglects axis rotation dynamics. We have introduced a more accurate model of the N matrix, obtained by solving coupled semiclassical equations, to account for axis rotation dynamics. The model gives a satisfactory account of collisional redistribution experiments, and corresponds to a picture where the orbital alignment follows the rotating molecular axis over the short range part of its trajectory. The same N matrix model predicts that an aligned atom collision is described by an asymmetry parameter whose magnitude depends on the long range part of the trajectory wher the alignment is <u>not</u> coupled to the rotating axis.

d. Generalized MCQDT Analysis of Molecular Bound States and Collision Cross Sections Involving Molecular Charge Transfer States

(F. H. Mies and S.-H. Pan*)

Fully quantal calculations for the vibrational bound levels and adjoining continuum of alkali-halide charge transfer states have been made using new algorithms derived from the Milne quantum number function for the radial motion of the diatom. Because of the asymptotic coulombic interaction, the molecular potential actually supports an <u>infinite</u> number of bound vibrational states which conform to a Rydberg-like spectrum and can be characterized by a vibrational quantum defect. As predicted by conventional quantum defect theory for perturbed Rydberg series, we also observe that the vibrational quantum defect extrapolates across the dissociation limit to yield the threshold elastic scattering phase shift for the dissociative continuum state. The implicit dependence of the defect on the rotational state of the molecule yields a complete description of the rotational-vibrational spectrum. Because the system is heavy, the mass and rotational dependence of the computed quantum defects generally conform to appropriate WKB-like predictions. These numerical results are critical ingredients that are needed to describe the photodissociation spectra and predissociation of the alkali-halides.

Since the so called ionic or charge-transfer state of the alkali-halide molecule XM dissociates into a positively charged alkali metal $M^+(^1S)$ and a negatively charged halide ion $X^-(^1S)$, it must correspond to a non-degenerate $^1\Sigma^+$ state of the molecule. Asymptotically, this state lies just above the lowest $^1\Sigma^+$ state which correlates with the neutral ground state fragments $M(^2S) + X(^2P)$. Together these two $^1\Sigma^+$ states can be expected to dominate the two body collisional charge transfer processes. For example, the asymptotic splitting of the LiI system that we will be studying

$$Li(^2S) + I(^2P) \rightleftarrows Li^+(^1S) + I^-(^1S)$$

is just 2.329 eV. We use the prevalent diabatic representation of these states and designate $1^1\Sigma^+$ as the predominantly ionic state which describes the ground electronic state at r_{eq}, "diabatically" crosses the neutral $2^1\Sigma^+$ state at larger r_c, and asymptotically dissociates into ionic fragments.

Between the ionic and neutral thresholds the bound rotational-vibrational levels of the ionic $1^1\Sigma^+$ state will be predissociated by diabatic coupling to the dissociating covalent $2^1\Sigma^+$ state. Our calculations of the unperturbed bound and continuum states of the isolated ionic state are needed as preliminary data to our subsequent multichannel quantum defect analysis (MCQDA) of the predissociation and photodissociation of these molecules. The bound state phase $\nu_J(E)$ required in the MCQDA, $\nu_J(E) = \pi N_J(E)$ is simply the modular-π equivalent of the vibrational number function $N_J(E)$ for an isolated charge-transfer state. This analytic function defines the bound states by the condition $\tan \nu_J(E) = 0$ as $E \rightarrow E_{J,v}$ and is precursor to a more thorough and systematic analysis of the complete spectroscopy and dynamics of charge transfer systems. In particular the energy dependence of $\nu_J(E)$ is required to give exact analytic representations of the predissociation lineshapes and level shifts.

In previous studies of the charge-transfer dynamics only the diabatic coupling between the neutral and charge-transfer $^1\Sigma^+$ electronic states were included. Although the $1^1\Sigma^+ \rightarrow 2^1\Sigma^+$ coupling certainly dominates the dynamics, there are a total of 12 covalent electronic states ($^1\Sigma^+$, $^1\Pi$, $^3\Sigma$, $^3\Pi$) which correlate with the neutral ground state fragments and cross the ionic state. When combined with the angular momentum states of the rotating collision complex, six of the electronic states form channel states of the same parity and total angular momentum state J as the ionic collision complex, and a completely rigorous description of the scattering requires solving a seven channel close-coupling problem. However, our preliminary analysis of the predissociation suggests it is adequate to merely include additional coupling to the neutral $^3\Pi_0^+$ state and simply develop a three channel model. Using these three channels from pure case(c) molecular states, with appropriate radial, rotational and spin-orbit couplings, we have evaluated the partial widths for predissociation into the specific j=½ and j=3/2 fine-structure states of the X(^{2}P). We have utilized a rigorous analytic multichannel quantum defect representation of this resonance scattering in order to isolate the effect of varying fine-structure splitting on the charge-transfer spectra for different alkali-halogen systems.

C.3. Theory of Ultracold Atom Collision Phenomena

Experimental methods for cooling and trapping atoms at ultracold temperatures have matured to the point that collisions of such atoms can now be observed. The collision cross section for associative ionization of two excited Na atoms has now been measured at NIST in an optical trap with $T < 1$ mK. Collisional processes are believed to limit the densities which are possible in neutral atom traps. Experimental studies of cooling and trapping of several other atomic ground and excited metastable species is currently in progress in various laboratories. We therefore expect that collisional and spectroscopic studies of ultracold collisions will become increasingly important in the future. The very low collision energy, long deBroglie wavelength, and long time scale associated with ultracold collisions result in many novel features of such collisions. We are beginning a program to develop the theory of ultracold collisions. The theoretical tools we have been developing for collisions in a radiation field and for MCQDT analysis of collisions can be naturally and readily applied to ultracold collisions. Some of our applications are described below.

a. Molecular Photoassociation Spectroscopy
(P. S. Julienne, H. Thorsheim*, and J. Weiner*)

The availability of ultracold atom sources offers the possibility of doing a new kind of high resolution molecular spectroscopy which can be used both as a probe of the collision and as way to access new Franck-Condon regions of the molecular spectrum. This is photoassociation spectroscopy, which can be represented by the equations,

$$A + A + \hbar\omega \rightarrow A_2^*$$

$$A_2^* \rightarrow \text{fluorescence} + A_2 .$$

The process is very similar to the familiar laser induced fluorescence (LIF). The main difference is that the <u>initial</u> state in photoassociation is a continuum or scattering state instead of a bound state. During a collision of A with another A atom, the absorption of a photon excites a bound vibrational rotational level of an excited molecular state, which is then detected by its fluorescence. Having an ultracold source offers a great advantage over a normal or room temperature source. First, the excitation spectrum (fluorescence signal versus ω) will be very sharp, since thermal broadening due to the kT spread of collision energies is very small, e.g., kT/h = 21 MHz for T = 1 mK. Second, the cross section for the process near threshold will be much larger than at higher temperatures. A simple semiclassical reason for this is that the very slow moving atoms have much longer time to interact with the photon. Our theoretical calculations suggest that it should be possible to generate high enough photoassociation fluorescence signals to be measured.

We have carried out specific calculations for the magnitude of the photodissociation rate coefficient and spectrum for the case of collision of two ground state Na atoms. We treated the case of both the $^1\Sigma_u \leftarrow {}^1\Sigma_g$ and $^3\Sigma_g \leftarrow {}^3\Sigma_u$ absorptions. Note that in a collision the latter is just as likely as the former, so that the triplet spectrum is readily accessible. We used the well known molecular Born-Oppenheimer potentials and transition dipoles to calculate the spectra. A typical example is shown in Fig. 4.4, for absorption to $v' = 130$ of $^1\Sigma_u$ at a collision temperature of 10 mK. The spectrum shows well resolved rotational structure, with a rapid drop off to high N due to inability to penetrate the ground state centrifugal barrier. The transitions to $N' = 3$ and 5, and to a lesser extent, $N' = 4$ and 6, show enhancements due to shape resonances in the respective lower $N'' = 4$ and 5 levels. Note that photoassociation Franck-Condon factors will favor high v' in the excited state, where the transition takes place at long range. Also note that the spectrum not only contains information about the excited state energy levels, but also about the lower state scattering resonances. A study of spectral intensities will give information about collision dynamics, and possibly can be used to improve the ground state potentials.

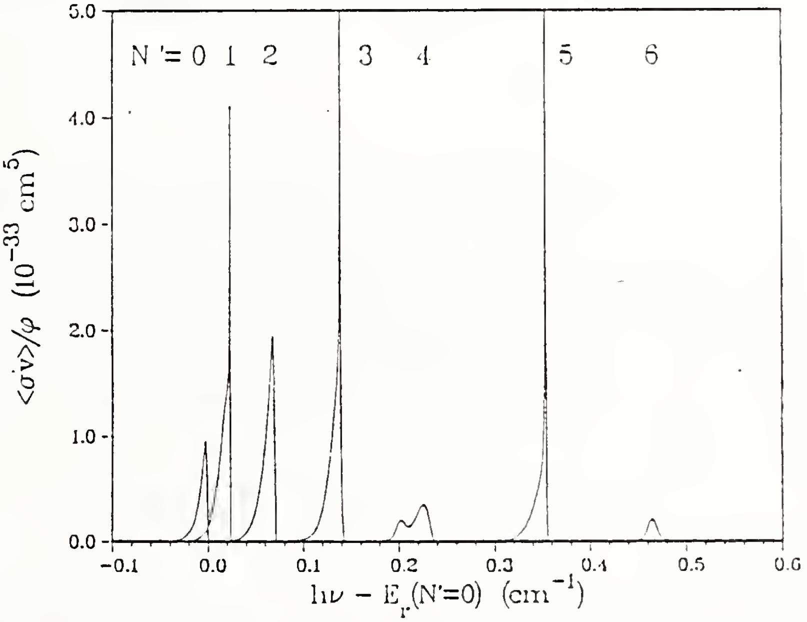


Fig. 4.4 Model photoassociation spectra at T = 0.01K for Na_2. The broadening of the lines is due to the thermal spread of collision energy in the ground state.

Our calculation suggests the feasibility of photoassociation experiments. The theory used was very simple and needs to be improved for realistic conditions. It is necessary to take into account the small relativistic electron and nuclear spin terms which affect the collision and especially the spectroscopy of the $^3\Sigma \rightarrow {}^3\Sigma$ transition. It is also necessary to take into account the true quantum threshold behavior of the cross section and the linewidth of the excited state due to spontaneous emission. We will continue to study the ultracold photoassociation process.

b. Associative Ionization Cross Sections of Na(3) + Na(3p) at 0.001 K.

(P. S. Julienne, W. D. Phillips*, H. Thorsheim*, and J. Weiner*)

The NIST experimental laser cooling and trapping group of Dr. W. D. Phillips has succeeding in constructing an optical trap in which Na atoms are trapped at a density of 10^{10} cm^3 and temperature of 0.75 mK. Due to the strong laser tuned near the Na $^2P_{3/2} \leftarrow {}^2S_{1/2}$ resonant transition, there is a large fraction of excited atoms present in the trap. By measuring the current of Na_2^+ ions formed in the trap, the group measured the cross section for the associative ionization of two excited Na atoms to make molecular ions:

$$Na^* + Na^* \rightarrow Na_2^+ + e^- .$$

The cross section, 9×10^{-14} cm^2, is quite large and is about three orders of magnitude larger than the measured cross section at room temperature.

We have begun theoretical studies of such threshold cross sections. These are described more fully below. However, the plausibility of a large cross section can be readily established. The cross section can be written in the form,

$$\sigma = \pi(\lambda/2\pi)^2 \ (\ell_{max}+1)^2 \ P,$$

where ℓ_{max} partial waves are assumed to contribute and P is the probability of association ionization averaged over partial waves. P is a complicated dynamical quantity which depends on the molecular potentials, nonadiabatic mixings, spin-orbit and hyperfine interactions, and all other quantities which control the dynamics. Even if only a single s-wave is assumed to contribute to the cross section, an upper limit to the cross section can be found by assuming that P = 1. The upper limit is 6×10^{-13} cm^2, which is nearly an order of magnitude larger than the measured value. This shows that P is actually much less than unity, as we would expect. At room temperature P is known to be around 0.1.

c. Intense Laser Effects on Cross Sections in Optical Traps

(P. S. Julienne)

The laser intensity in the optical trap described in the previous section in which the associative ionization cross section was measured is very large, corresponding to a Rabi frequency of about 1400 MHz and an AC Stark shift in molecular potential energy which is about 50 times kT when the two excited Na atoms are far apart. Since the Na_2 molecule detunes from and becomes decoupled from the laser field during the course of a collision because of the R-dependent molecular potentials, the nature of the molecule-field interaction changes dramatically during the course of the collision. We have therefore set up a simple model to describe the interaction of two like atoms which interact with each other and also with the laser field. We only consider interactions through the first order dipole-dipole multipole interaction term. It is necessary to introduce a 4-state model with treats the case of two ground state atoms, the degenerate case of one ground, one excited atom, and the case of two excited atoms. The model describes the separated atoms as two field-dressed atoms which interact with each other at long range with $1/R^3$ potentials in all 4 states. The atoms when close together form a molecule which is decoupled from the laser field. The adiabatic potentials which are found by diagonalizing the 4 x 4 interaction matrix give effective potentials on which the atoms move.

There are two important features of the model. First, the R-dependent decoupling of the molecule from the field at small R causes the asymptotic AC Stark shift to vanish at small R, thereby providing an R-dependent drop in the effective potential which accelerates the atoms towards one another and increases their collision velocity while the atoms are still far apart, $R > 100\ a_0$. Second, the long collision time makes it possible for spontaneous emission to be a significant loss process for collision processes involving excited states. In a strong field, strong coupling to the excitation laser occurs to short enough distance that the long range acceleration ensures a short enough collision time that spontaneous emission is not significant. However, in a weak field, there is little field induced acceleration and the decoupling from the exciting field occurs at such long distance that spontaneous emission prevents the excited state collision from continuing. The simple model therefore predicts that the associative ionization cross section at low collision energy will behave dramatically differently in strong and weak laser fields.

When the above simple model is applied to the conditions in the NIST optical trap, the model predicts about a 4 order of magnitude decrease in associative ionization cross section in optical molasses as compared to the optical trap. Since the NIST experiment is a time-alternating experiment between molasses and trap conditions, this prediction can be tested by time-resolving the ion and excited state fluorescence signals between the two conditions. In a recent experiment at NIST by Phillip's group, the qualitative theoretical prediction was dramatically confirmed! The ratio of ion signal in the trap to that in molasses was found to be about 50 with the present signal to noise, in spite of the fact that the fluorescence (excited state density) varied by less than a factor of 2. Thus, we have theoretical prediction and experimental confirmation that the nature of the collision dynamics is strongly influenced by the strength of the laser field. A reaction can be turned off or on by field-induced modification of collision dynamics.

d. Collision-induced Optical Trap Loss Processes

(P. S. Julienne, S.-H. Pan*, H. Thorsheim*, and J. Weiner*)

Collisions between the species in an atom trap can lead to loss of atoms from the trap, and thereby limit the density of atoms which can be trapped. One example is the associative ionization process discussed above, which destroys two atoms in the trap. Other collisional trap destruction processes of an unknown nature have been observed by other groups. We have examined the following collisional loss process:

$$\text{Na}(3p) + \text{Na}(3s) \rightarrow \text{Na}(3s) + \text{Na}(3s) + \hbar\omega.$$

If the emitted photon is red shifted by $\Delta = \hbar\omega - \hbar\omega_0$ from the resonance transition frequency ω_0, an atom will escape from the trap if its kinetic energy $\Delta/2$ is greater than the trap depth D. This process is just the far red wing emission from the pressure broadened Na resonance line. Therefore, we need to calculate the spectrum and calculate the rate of emitting a photon with red shift greater than 2D. Since we have shown that a strong radiation field can have a large effect on collision dynamics, we will first consider only the case of a weak optical field in the trap.

We have calculated the emission spectrum by using the known long range form of the Na_2 potentials and transition dipoles. There are several possible transitions which contribute to the emission when a $\text{Na}\,^2P_{3/2}$ atom collides with a rare gas atom, namely, $0_u^+ \rightarrow 0_g^+$, $1_g \rightarrow 0_u^-$ or 1_u, $0_g^- \rightarrow 0_u^-$ or 1_u, and $1_u \rightarrow 0_g^+$. We have carried out fully quantum mechanical calculation of the spectrum for the $0_u^+ \rightarrow 0_g^+$ transition. We have also carried out a semiclassical calculation using the usual stationary phase and random phase approximations which give the quasistatic expression for the spectrum. Other than quantum oscillations about the envelope of the smooth semiclassical spectrum, the two are in quite good agreement even for a collision energy of 0.001 mK. It might at first glance seem surprising that semiclassical theory should work so well at large R where the interaction potential is only a few mK, but we find that the criterion for applicability of the WKB approximation, $d\lambda(R)/dR \ll 1$, is well satisfied here for the long range C_3/R^3 potential of the excited state. Therefore, the semiclassical theory can be used for all transitions. The semiclassical theory is analytically very simple, and for each transition only depends on the long range C_3 coefficient and transition dipole. The final expression for the rate coefficient for trap loss due to collisions with temperature T for a trap of depth T_D (both in Kelvin) takes on the simple form,

$$K(T,T_D) = F_s \times 1.3 \times 10^{-11}/(T^{1/6}T_D^{5/6})\ \text{cm}^3\ \text{sec}^{-1},$$

where F_s is a factor which takes into account the probability of survival versus spontaneous emission in the long range approach of the two atoms. The survival factor F_s is difficult to calculate accurately, but can be estimated from classical trajectory calculations. It is a sensitive function of T, but is between 0.1 and 0.01 for T on the order of 1 mK. The loss rate is comparable in magnitude to that due to associative ionization.

e. Quantum Threshold Effects in Ultracold Collisions

(P. S. Julienne)

The very low collision energy, and large deBroglie wavelength, in ultracold collisions raises the question of the nature of quantum threshold effects which might affect the cross section. The threshold laws for inelastic scattering processes are well known as a function of partial wave quantum number for different kinds of long range potentials. What is needed in this case is a study of actual cases using realistic potentials and masses of colliding atoms. The basic ideas can be readily stated in terms of the MCQDT formulation of the threshold behavior, although the ideas can be traced back at least as far a H. Bethe's 1935 study of threshold neutron scattering from atomic nuclei. The range of internuclear separation is divided into two zones. In the inner zone the wavefunction is approximated by the WKB wavefunction $\sin\beta(R)/k(R)^{1/2}$. In the long range zone the wavefunction is a linear combination of the regular and irregular Bessel functions, but the irregular function can not contribute as $E \to 0$ and the phase shift vanishes. The long range function is determined by energy normalization, and the short range WKB component must be matched to the long range form. The matching requires that the short range part be multiplied by a R-independent factor C(E) which depends on collision energy. When E is sufficiently large the WKB and long range Bessel function can always be matched by a WKB connection between large and small R, and C(E) = 1. As $E \to 0$ the small R decaying tail of the long range Bessel function can not be matched to the short range WKB function except by a function $C(E)\ \alpha\ k_{\infty}^{1/2}$ in the case of an s-wave.

The T matrix element for a process which only occurs in the short range molecular zone will be proportional to the short range wavefunction, and therefore has the form,

$$T(E) = C(E)\ T_{short},$$

where T_{short} represents the amplitude for the short range process and is relatively insensitive to total energy. It is nearly constant as $E \to 0$. Therefore, the threshold behavior can be estimated by examining the C(E) function. This assumes the approximation that only a single potential is important. In reality, the asymptotic states are usually not nondegenerate, especially if hyperfine interactions are included, and several potentials can contribute. A full theory will require that we treat the long range multichannel interactions. However, a single channel theory is useful for estimating qualitative effects.

Therefore, we have calculated the C(E) function for a variety of cases. We have treated model cases involving collisions of Na atoms and collisions of two He ^3S metastable atoms. The latter are the subject of laser cooling efforts at the Ecole Normal Superieure in Paris, are likely to be cooled to $T \approx 30\ \mu K$ in a atom trap, and are known to Penning ionize in collisions at 20 K. Two s state atoms interact at long range with a potential which varies as $1/R^6$. The C(E) function shows the expected power law behavior at low enough collision energy. The critical energy where C(E) changes from its high energy value of unity depends on the potential and mass of colliding atoms. In particular the threshold shape is quite sensitive to the proximity of the last bound state of the potential to threshold. C(E) can manifest structure due to shape resonances for angular momentum quantum number $\ell \geq 1$. Even an s-wave, $\ell = 0$, can exhibit "resonance" like structure if a bound state exists sufficiently close to threshold. For two ground state Na atoms, C(E) shows departure from unity for collision energies on the order of 1 mK and less, with power law threshold behavior evident below 100 μK. It is possible for s, p, and perhaps also d waves to contribute to Na scattering at 1 mK. However, He ^3S meta-stable collisions show departure from unity for collision energies on the order of 10 mK. Only s waves are likely to contribute at 30 μK. The detailed shape of C(E) is very sensitive to the whole potential, since it depends on the position of the last bound state. Ultracold collisions are likely to sample the range of collision energies where quantum threshold effects are important, but the extreme sensitivity of the threshold behavior to the details of the potential will make predicitive calculations difficult. Perhaps experimental studies can be used to refine experimental or theoretical potential models.

Collisions of ground and excited states of like atoms with $1/R^3$ potentials will be much less sensitive to the potentials. The C(E) function remains unity even to temperatures below 1 μK, and semiclassical theory can be used just as at higher temperatures. This was discussed above in the discussion on collision-induced trap loss processes.

The near threshold magnitude of the cross section for an inelastic exothermic process is likely to be very large. In fact, the cross section diverges as 1/v as the collision velocity $v \to 0$ at threshold. This was pointed out long ago by Bethe (1935) in connection with threshold neutron scattering. The collision rate coefficient, $T\sigma$, remains finite, however. The observed large value of near threshold cross section for Na^* associative ionization is consistent with this general expectation of large threshold cross section for such processes.

f. Ultracold Collisions in Magnetic Fields

(F. H. Mies, P. S. Julienne, and C. J. Williams*)

Since some varieties of neutral atom traps use a magnetic field in the trapping process, it is necessary to develop the theory needed to describe collisions in a magnetic field. Collisions in a magnetic field may result in trap loss processes, just as for collisions in an optical field. Since Zeeman shifts, just like AC Stark shifts, can be many times kT, the magnetic field can cause large perturbations on the collision just as a laser field can. In many ways it is simpler to formulate the problem of collisions in a static magnetic field than in an oscillating electromagnetic field, since the problem of spontaneous emission during the collision need not be considered for the former if only ground state collisions are treated.

We have begun to develop the Hamiltonian matrix necessary to set up a close coupled calculation of the cross sections which describe scattering of two like atoms in ^2S ground states with nuclear spin I. We consider the ordinary molecular electronic-rotational Hamiltonian, the various spin-dependent interactions (electron-electron, electron-nuclear, and nuclear-nuclear), and the magnetic field interaction. We have formulated the frame transformation between the Hund's case (a) basis in the molecular frame and the asymptoptic basis in the laboratory frame in which the Zeeman sublevels are quantized along the magnetic field axis. The molecular $^1\Sigma_g^+$ and $^3\Sigma_u^+$ potentials are defined in the former frame, and the asymptotic scattering states are defined in the latter. We intend to treat the cases of H (I=1/2) and Na (I=3/2). We have written a computer code to calculate the S-matrix for these cases. Detailed calculations will be carried out in the future.

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6. INVITED TALKS

Casassa, M. P., "Time- and State Resolved Measurements of Vibrational Predissociation of van der Waals Molecules," ILS-III Conference, Atlantic City, NJ, November 1987.

Fraser, G. T., "High Resolution Spectroscopy of Weakly-Bound Complexes," Harvard-MIT Physical Chemistry Seminar, Cambridge, MA, October 1987.

Fraser, G. T., "Sub-Doppler Infrared Spectra of CO_2 Complexes," 3rd Laser Science Conference, Atlantic City, NJ, November 1987.

Fraser, G. T., "Sub-Doppler Infrared Spectra of CO_2 Complexes in the Region of the $2\nu_2{}^0+\nu_3/\nu_1+\nu_3$ Fermi Diad of CO_2," Naval Research Laboratory, Washington, D.C., November 1987.

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Heilweil, E. J., "Vibrational Relaxation Measurements of Carbon Monoxide on Metal Clusters," Sixth International Conference on Ultrafast Phenomena, Kyoto, Japan, July 1988.

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Julienne, P. S., "Calculation of Collision-Induced Emission Loss Rate Coefficient," American Physical Society Division of Atomic, Molecular, and Optical Physics, Baltimore, MD, April 1988.

Julienne, P. S., "Nonlorentzian Line Shapes in O_2 Schumann-Runge Predissociation," American Physical Society Division of Atomic, Molecular, and Optical Physics, Baltimore, MD, April 1988.

Julienne, P. S., "Collision-Induced Spectral Phenomena at Ultracold Temperatures," 9th International Conference on Spectral Line Shapes, Torun, Poland, July 1988.

Julienne, P. S., "Na Resonance Line Broadening in Ultracold Collision," 9th International Conference on Spectral Line Shapes, Torun, Poland, July 1988.

Julienne, P. S., "The Strange World of Ultracold Atomic Collisions," Laser Science and Engineering Seminar, University of Iowa, Iowa, September 1988.

King, D. S., "Energy Flow and Decomposition of Energetic Molecules from Metastable Vibrational States," High Energy Density Matter Conference, Newport Beach, CA, March 1988.

King, D. S., "Dynamics of Highly Excited Molecules," Department of Chemistry, University of Pennsylvania, Philadelphia, PA, May 1988.

Krauss, M., "Use of Pseudo Potentials in Quantum Chemistry," University of New Orleans, Department of Chemistry, New Orleans, IL, October 1987.

Krauss, M., "Calculations of Metal Binding of Biomolecules," University of New Orleans, New Orleans, IL, October 1987.

Krauss, M., "Theoretical Model of Metal Binding Sites in Proteins," OHOLO Conference, Eilat, Israel, May 1988.

Lafferty, W. J., "IR Spectra of Loosely Bound Molecules," University de Paris, Paris, France, June 1988.

Lovas, F. J., "Rotational Spectra and Structures of the Molecular Complexes $(H_2O)_2$, H_2S-H_2O and $(H_2S)_2$," 12th Austin Symposium on Molecular Structure, University of Texas, Austin, TX, March 1988.

Mies, F. H., "Unified Analysis of Atomic Scattering and Diatomic Spectroscopy," Laboratoire de Photohysique Moleculaire, Paris, France, March 1988.

Mies, F. H., "A Half Collision Analysis of Photodissociation," Laboratoire de Photohysique Moleculaire, Paris, France, March 1988.

Mies, F. H., "Ultracold Collisions in Strong Laser Fields," Institute of Physics, Academia Sinica, Beijing, Peoples Republic of China, August 1988.

Pine, A. S., "Difference-Frequency and Color-Center Laser Spectroscopy of van der Waals Complexes," Adriatico Research Conference on "Coherent Sources for Frontier Spectroscopy," International Center for Theoretical Physics, Trieste, Italy, August 1988.

Stephenson, J. C., "Picosecond Studies of Molecular Energy Transfer," Chemistry Department, Columbia University, New York, NY, February 1988.

Suenram, R. D., "Structure Studies of Hydrogen Bonded Water Complexes using Pulsed-Molecular Beam Microwave Spectroscopy," Penn State University, State College, PA, February 1988.

Suenram, R. D., "Structure Study of $H_2O\cdots H_2O\cdots CO_2$ Trimer," 12th Austin Symposium on Molecular Structure, Austin, TX, March 1988.

Suenram, R. D., "Microwave Spectrum of Carbazole," 12th Austin Symposium on Molecular Structure, Austin, TX, March 1988.

Suenram, R. D., "Microwave Spectrum Structure, and Dipole Moment of the $H_2CO\cdots CO_2$ Complex," 12th Austin Symposium of Molecular Structure, Austin, TX, March 1988.

Suenram, R. D., "Structural Studies of CO_2-H_2O Hydrogen Bonded Complexes," University of Kansas, Lawrence, Kansas, April 1988.

Weber, A., "High Resolution Spectroscopy of van der Waals and Hydrogen Bonded Complexes at NBS-Gaithersburg," University of California - Berkeley, Berkeley, CA, January 1988.

Weber, A., "High Resolution Spectroscopy of van der Waals and Hydrogen Bonded Complexes at NBS-Gaithersburg," Jet Propulsion Laboratory, Pasadena, CA, January 1988.

Weber, A., "High Resolution Spectroscopy of van der Waals and Hydrogen Bonded Complexes at NBS-Gaithersburg," UCLA, Los Angeles, CA, January 1988.

Weber, A., "Gas Phase Fourier Transform Raman Spectroscopy," Pittsburgh Conference, New Orleans, LA, February 1988.

7. MOLECULAR SPECTROSCOPY DIVISION SEMINARS

Brocks, G. Phillips Research Laboratories, Eindhoven, The Netherlands, "Large Amplitude Motions and Calculated Spectra of Molecular Dimers" May 1988.

Butcher, R. J. Cavendish Laboratory, Cambridge University, England, "CO_2 Laser Saturation Spectroscopy of SF_6 and CH_3I at kHz Linewidths" March 1988.

Coalson, R., Department of Chemistry, University of Pittsburgh, Pittsburgh, PA, "Time Domain Approaches to Excited State Spectroscopy" January 1988.

Dykstra, C. E., Chemistry Department, University of Illinois, Urbana, IL, "Theoretical Studies of Hydrogen Bonding" May 1988.

Field, R. W., Department of Chemistry, MIT, Cambridge, MA, "Acetylene: Isomerization, Dissociation, and Chaos" December 1987.

Hovde, D. C., Department of Chemistry, University of California - Berkeley, Berkeley, CA, "Laser Magnetic Resonance Studies of Ions" January 1988.

Janda, K., University of Pittsburgh, Pittsburgh, PA, "Rotational Rainbows, Quantum Diffraction and Intermolecular Vibrational Relaxation, All in a Triatomic Molecule" December 1987.

Kleiner, I., Laboratoire de Chimie Physique Moleculaire, Universite Libre de Bruxelles, Belgium, "Work at the University of Brussels: HNO_3, CH_3CHO, etc." July 1988.

Meerts, W. L., Physics Department, University of Nijmegen, The Netherlands, "Order and Chaos in the S_1 State of Pyrazine ($C_4N_2H_4$)" June 1988.

Miller, R. E., Department of Chemistry, University of North Carolina, Chapel Hill, NC, "Infrared Spectroscopy and Vibrational Predissociation of Several Binary and Tertiary Complexes" October 1987.

Muenter, J., University of Rochester, Rochester, NY, "Microwave and Infrared Spectroscopy of Acetylene Containing Complexes" April 1988.

O'Brien, S., Department of Chemistry, Rice University, Houston, TX, "The Photophysics of Buckminsterfullerene" January 1988.

Pascale, J., Service de Physique des Atomes et des Surfaces, Saclay, France, "Quantum Mechanical Study of Non-reactive Collisions Between Rb(5p) and H_2 or D_2" October 1987.

Phillips, L., Department of Chemistry, Cornell University, Ithaca, NY, "High Resolution Spectroscopy of Tryptophan and Tryptophan Analogs in a Supersonic Jet" October 1987.

Povilly, B., University of Lille, Lille, France, "Theoretical Study of Energy Transfer in Collisions of Aligned Calcium 4s5p ^1P Atoms with Noble Gases" October 1987.

Pulay, P., Department of Chemistry and Biochemistry, University of Arkansas, Favetteville, AR, "Local Treatment of Electron Correlation in Large Molecules" November 1987.

Rice, J., Naval Research Laboratory, Washington, D.C., "The Study of Oriented Biomolecular Reactions Using van der Waals Pre-cursors" April 1988.

Rothberg, L., AT&T Bell Laboratories, Murray Hill, NJ, "Charged Solition Dynamics in Trans-Polyacetylene" February 1988.

Stahl, W., Institute for Physical Chemistry, Kiel University, Germany, "Current MW Experiments at Kiel University" July 1988.

Synder, L. E., Department of Astronomy, University of Illinois, Urbana-Champaign, IL, "Molecular Radio Spectroscopy of Comets" April 1988.

Tyuterev, V. G., Institute of Atmospheric Optics, USSR Academy of Science, Tomsk, USSR, "Processing and Extrapolation of Vibration-Rotation Energies of Non-Rigid Molecules Based on Non-Polynomical Rotational Hamiltonians" June 1988.

Weinstein, H., Department of Biophysics, Mt. Sinai Medical School, New York City, NY, "Theoretical Analysis of Biological Specificity and Activity: Recognition of Neurotransmitters and Calcium Binding Structures" November 1987.

Whetten, R. L., Department of Chemistry, University of California, Los Angeles, CA, "Optical Spectroscopy of Large Clusters" April 1988.

Williams, C., Department of Chemistry, North Western University, Evanston, IL, "Vibrational Predissociation of the Hydrogen-bonded HCN Dimers" May 1988.

Wilson, T., Max Planck Institute, Bonn, Germany, "Hot NH_3 and CH_3OH in the Galaxy" March 1988.

Zimmerman, G., Department of Chemistry, Bryn Mawr College, Bryn Mawr, PA, "Spectroscopy and Photochemistry of Ruthenum Oxides" October 1987.

8. TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Hougen, J. T.

Member, Editorial Advisory Board, Journal of Molecular Spectroscopy.

Member, Editorial Board, Journal of Chemical Physics.

Member of the subcommittee on Notations and Conventions for Molecular Spectroscopy for the "IUPAC" Commission on Molecular Structure and Spectroscopy.

Jacox, M. E.

Member, Editorial Advisory Board, Review of Chemical Intermediates.

Member of National Science Foundation panel for the review of proposals for Engineering Research Equipment Grants and Research Initiation Grants.

Member, Editoral Board, Reviews of Chemical Intermediates.

Member, Air Force Office of Scientific Research High Energy Density Materials Panel.

Member, U. S. Army Research Office Study Group on Nitramine Propellant Ignition and Combustion Research.

President-Elect, NBS Chapter, Sigma Xi, 1987-88; President, 1988-89.

Lovas, F. J.

Member, International Astronomical Union Commision 14: Fundamental Spectroscopic Data.

Maki, A. G.

Member, Editorial Advisory Board, Journal of Molecular Spectroscopy.

Weber, A.

Editorial Advisory Board, Journal of Raman Spectroscopy.

Editorial Advisory Board, Journal of Physical and Chemical Reference Data.

Member, Program Committee, International Conference on Infrared and Fourier Transform Spectroscopy, Washington, 1989.

Member, International Advisory Committee, International Conference on Raman Spectroscopy, Calcutta, November 1988.

Member, Program Committee, QELS - Quantum Electronics and Laser Science Conference, Baltimore, MD, April 1989.

Councillor, American Physical Society (for the Division of Chemical Physics) 1988.

American Physical Society representative to the Chemistry Division of the AAAS, 1988.

9. PROFESSIONAL INTERACTIONS, CONSULTING AND ADVISORY SERVICES

Casassa, M. P.

Collaborated with Dr. R. R. Cavanagh, Surface Science Division, on picosecond infrared laser studies of vibrational relaxation of adsorbed molecules.

Collaborated with Dr. W. L. Hase, Wayne State University, on classical trajectory calculations of NO dimer vibrational predissociation.

Consulted with Dr. K. C. Janda, University of Pittsburgh, on studies of the photodissociation of van der Waals.

Fraser, G. T.

Collaborated with Professor Roger Miller, University of North Carolina, on infrared studies of van der Waals complexes.

Collaborated with Professor John Muenter, University of Rochester, an infrared studies of van der Waals complexes.

Heilweil, E. J.

Collaborated with Dr. C. Sandroff, AT&T Bell Communications Laboratories, on Picosecond Streak Camera Studies of Colloidal Lead-Halide Semiconductor Luminescence.

Collaborated with Dr. R. R. Cavanagh, Surface Science Division, on picosecond transient infrared measurements of vibrational dynamics in transition metal-carbonyl systems.

Consulted with Dr. E. Zink of Princeton University, Department of Biochemistry, to obtain transmission electron micrographs of transition-metal particles supported on silica.

Hougen, J. T.

Collaborated with Dr. W. Fawzy of Emory University on a theoretical formalism for fitting the spectrum of ArOH.

Collaborated with Professor W. L. Meerts and Professor J. J.ter Meulen and students of Katholieke Universiteit Nijmegen on the interpretation of the spectra of $SiCl_2$ and 1,4 dimethylnaphthalene.

Consulted with students of Professor R. Saykally and Professor Y. T. Lee of the University of California at Berkeley on the spectra of various ions.

Consulted with Isabelle Kleiner of the Universite Libre de Bruxelles on theoretical discussions of the spectrum of acetaldehyde and other internal rotor molecules.

Jacox, M. E.

Dr. V. A. Apkarian, Department of Chemistry, University of California, Irvine. Mechanisms for explaining thermoluminescence in matrix isolation systems.

Dr. Jeffrey Hudgens, Chemical Kinetics Division. Vibrational assignment of Rydberg transitions of H_2CF.

Dr. N. Yabumoto, Electrical Communications Laboratories, Nippon Telegraph and Telephone Corporation, Tokyo, Japan. Spectra of free radicals derived from the silanes and halosilanes.

Dr. Ventakesh PaiVerneker, Martin Marietta Laboratories, Catonsville, MD. Spectra of reaction intermediates in the decomposition of energetic materials.

Dr. David Gutman, Department of Chemistry, Illinois Institute of Technology. Structure of HF complexes with free radicals.

Dr. H. Harvey Michels, United Technologies Research Center, E. Hartford, CT. Infrared spectrum of fluorine azide; chemical bonding and infrared spectra of CO_3 and N_2O_2 species.

Dr. Henry Helvajian, Aerospace Corporation, Los Angeles, CA. Principles and practice of matrix isolation spectroscopy.

Dr. K. Kawaguchi, Institute for Molecular Science, Okazaki, Japan. Infrared spectrum of products of the vacuum ultraviolet photolysis ofdiacetylene in solid argon--a potential low-lying electronic transition of C_4H.

Dr. Arthur Fontijn, Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY. Chemical reactivity of small high-temperature molecules.

Dr. C. Wittig, Department of Chemistry, University of Southern California, Los Angeles, CA. Spectrum of t-HOCO.

Drs. N. Presser and A. T. Pritt, Aerospace Corporation, Los Angeles, CA. Principles and practice of matrix isolation spectroscopy.

Dr. W. R. M. Graham, Department of Physics, Texas Christian University, Fort Worth, TX. Infrared spectrum of $(C_2H_2)_2$.

Dr. A. F. Tuck, NOAA, Boulder, CO. Strength of HF hydrogen bond to water aggregates.

Julienne, P. S.

Collaborated with Dr. L. Vahala, Old Dominion University, Norfold, VA, on collaboration of photodissociation line shapes.

Collaborated with Dr. W. Phillips, NIST, on interpretation of ultracold associative ionization collisions.

Collaborated with Dr. F. Rostas, Observatory of Paris, on interpretation of strong perturbations in the Rydberg spectra of CO.

Collaborated with Dr. J. Weiner, University of Maryland, on theory of collisions of supercold atoms.

Collaborated with Dr. R. Bieniek, University of Missouri at Rolla, on application of the Lewis-Cooper model to the collisional redistribution of light for Sr + Ar.

Consulted with Dr. K. Burnett, Oxford University, England, on the development of time dependent collision theory of ultracold collisions.

Consulted with Drs. P. Kleiber and K. Sando, University of Iowa, on interpreting atomic alignment following molecular photodissociation.

Collaborated with Dr. H. Hotop, University of Kaiserslautern, West Germany, on interpreting strong predissociations observed in photoelectron spectra of HBr^+.

King, D. S.

Collaborated with Dr. R. Bodanness, NIH, potential applications of photophysics, photochemistry, and non-linear optics in medical research.

Krauss, M.

Collaborated with Dr. K. J. Miller, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, on reaction field analysis of binding in DNA.

Collaborated with Dr. H. Basch, Bar Ilan University, Israel, on molecular orbital calculations of biomolecules.

Collaborated with Dr. B. Grillott, University Pierre et Marie Currie, Paris, on calculations of the dipole moment functions of multimers of rare gase atoms.

Lovas, F. J.

Collaborates with Professor L. E. Snyder, University of Illinois, and Dr. J. M. Hollis, NASA/Goddard Space Flight Center, on interstellar molecular searches.

Collaborates with Drs. C. W. Gillies and J. Zozom, Rensselaer Polytechnic Institute, Troy, NY, on microwave spectral studies of ozone complexes.

Collaborates with Drs. S. E. Novick and T. Blake, Wesleyan University, on structures of weakly bound complexes of CO_2 and H_2CO.

Collaborates with Drs. J. Rice, Naval Research Laboratory, and W. Stahl, University of Kiel, on the rotational and structural study of CO_2-H_2S.

Collaborates with Drs. M. D. Marshall, Amherst College, and H. O. Leung, Harvard University, on the rotational spectrum of N_2-H_2O.

Collaborates with Dr. K. Matsumura, Seinan Gakuin University, on rotational and structural studies of complexes containing H_2O and SO_2.

Collaborated with Dr. P. S. Marfey, SUNY at Albany, on the rotational study of the carbazole.

Maki, A. G.

Collaboration with Drs. Carlton Howard and James Burkholder, NOAA, Boulder, CO, on the high resolution spectrum of nitric acid and chlorine dioxide (OClO).

Collaboration with Dr. Rafael Escribano, Instituto de Estructura de la Materia, Madrid, Spain, on the infrared spectrum of SO_3, ClO_2, and HNO_3.

Pine, A. S.

Collaborated with Dr. J. M. Pliva, Department of Physics, Penn State University, University Park, PA, on the analysis of the perturbed spectrum of fluoroform.

Collaborated with Dr. A. G. Robiette, Oxford University Computing Service, Oxford, England, on the analysis of the local mode spectrum of the overtones of germane.

Collaborated with Dr. L. L. Strow, Department of Physics, University of Maryland, Baltimore, MD, on line coupling and rotational collapse of Q-branches of N_2O.

Stephenson, J. C.

Collaborated with Professor Millard Alexander, University of Maryland, College Park, MD, on dissociation of HN_3.

Collaborated with Professor Paul Dagdigian, John Hopkins, Baltimore, MD, on dissociation of HN_3.

Stevens, W. J.

Collaborated with Dr. R. Osman, Mt. Sinai Medical School, on quantum chemistry modeling of mechanisms of metallo-enzymes.

Collaborated with Dr. D. Beveridge, Wesleyan University, on Monte Carlo simulation of the aqueous solvation of biomolecules.
Consulted with Dr. H. Basch, Bar Ilan University, Israel, on research field Hamiltonians for molecular calculations.

Consulted with Dr. B. Lengsfield, Ballistics Research Laboratory, on accurate calculations of structures and properties of small molecules.

Collaborated with Dr. James Jensen, Edgewood Arsenal, on effective core potentials and effective fragment potentials.

Suenram, R. D.

Collaborated with Professor K. I. Peterson, University of Rhode Island, on the microwave investigations of $(CO_2)_2$ H_2O and $(H_2O)_2$-CO_2 trimer species.

Collaborated with Professor S. E. Novick, Wesyleyn University, on spectroscopic studies of several van der Waals complexes.

Collaborated with Professor M. A. Marshall, Amherst College, on spectroscopic studies of the water-nitrogen van der Waals complex.

Collaborated with Dr. H. O. Lenny, Harvard University, on spectroscopic studies of the water-nitrogen complex.

Collaborated with Professor C. W. Gillies and J. Gillies, Rensselaer Polytechnic Institute, on microwave investigations of numerous van der Waals and hydrogen bonded species.

Collaborated with Professor Marfey of SUNY, Albany, NY, on the microwave investigation of carbazole.

Consulted with Professor M. Onda, Sophia University, Tokyo, Japan, on the construction of a pulsed Fourier transform spectrometer.

Consulted with Dr. W. Stahl, University of Kiel, on the construction of a pulsed fourier Transform spectrometer.

Collaborated with Professor W. Klemperer, Harvard University, and Dr. K. I. Peterson, University of Rhode Island, on the microwave investigation of the water-carbon monoxide van der Waals complex.

Collaborated with Professor R. Saykally, University of California, Berkeley, on spectroscopic measurements of the Ar-H_2O complex.

Weber, A.

Collaborated with Dr. K. Narahari Rao, Ohio State University, Columbus, OH, on discussions of the organization of the 1987 and 1988 Columbus Symposia.

Collaborated with Drs. W. C. Harris, National Science Foundation and I. W. Levin, National Institutes of Health on the planning for the 7th International Conference on Fourier Transform Spectroscopy, to be held in Washington 1989.

Collaborated with Drs. R. D'Cunha and V. B. Kartha, Bhabha Atomic Research Center, Bombay, India, on the IR spectrum of CH_2F_2.

Collaborated with Dr. V. B. Kartha, Bhabha Atomic Research Center, Bombay, India, on the IR spectra of CD_3CCH and CH_3CCD.

Quantum Metrology Division
Technical Activities FY 1988

Overview

Research in this division emphasizes problems of more or less fundamental significance whose resolution entails advances in the state of the art of measurement. At the present time areas of emphasis include:

1. X-ray inner shell physics and optics pursued primarily with a dedicated beamline facility at the Brookhaven National Synchrotron Light Source.

2. Gamma ray spectroscopy as applied to determination of fundamental constants and the study of nuclear recoil processes pursued at the High Flux Reactor in Grenoble.

3. Neutron Physics centered on elementary particle aspects and fundamental tests to be centered at the Gaithersburg cold neutron facility but already underway at a pilot level in Grenoble.

4. Optical and x-ray metrology of crystal lattices as required in the determination of elementary particle masses, fundamental constants and QED tests primarily in Gaithersburg with sojourns at various heavy ion accelerators.

In addition to these larger efforts several smaller activities are being pursued at the Gaithersburg site. These include an effort to provide an all Z wavelength tabulation using a sparse set of accurate measurements and relativistic SCF calculations, ground support for high resolution spectroscopy of active regions on the sun and a collection of technology development exercises concerning crystals, imaging detectors and spectrometers.

As will be evident in the more detailed sections below, some of these activities have been reasonably productive over the past year or so while others have been in a state of intense development or needed renewal. In addition, two of them, synchrotron radiation and gamma-rays, have encountered surprisingly exciting branch paths whose delineation cannot be evaded in any responsibly managed program. The synchrotron radiation case has already attracted significantly enhanced support from the NIST Director while the gamma ray case has only very recently been given any exposure at all. Past history and current austerity make any resource augmentation extremely unlikely in this case.

More broadly speaking, the division's diversity and delocalization have made it a relatively costly operation which is unfortunate in the present climate. With much more difficult situations evident at all organizational levels, our external activities have been largely sustained by systematic cannibalization of our internal programs. Efforts in the areas of laser metrology and gravity were stopped several years ago, while in the present year it was necessary to eliminate an in-house x-ray program and initiate an additional internal program reduction as well. To a great extent, it was on the strength of in-house efforts that most external activities were undertaken. One approach to this problem has been to formally constitute Groups in the Quantum Metrology Division (QMD)in the areas of Synchrotron Radiation, Neutron Physics, and other Gaithersburg operations. It is hoped that it may bring the problem into better focus and encourage cultivation of outside funding wherever this can be pursued in an appropriate manner.

1. X-Ray Physics - Brookhaven

The 1988 Fiscal Year has been a "dark" period for the QMD's beamline X-24A at the National Synchrotron Light Source (NSLS). The NSLS x-ray ring was shut down during most of the year, with some beam time available for testing and alignment during the last four months of FY88. Full operations returned at the beginning of FY89. What beam time has been available was used primarily to observe the alignment of three beam-defining apertures in the beamline with respect to the electron orbit in the storage ring. The sensitivity of beamline X-24A to orbit position has been confirmed by these studies, leading to realignment of one of the beam apertures, and to plans for careful beam-position monitoring in the beamline itself. Also, NSLS has acknowledged the need for a special beam-orbit adjustment for beamline X-24, with this procedure scheduled to take place in FY89.

The remainder of FY88 has been devoted to analysis and publication of measurements performed earlier, and to making improvements to the beamline. One emphasis on previous results has been in the area of polarized x-ray fluorescence from molecules. During FY88, insight has been gained in the applicability of this phenomenon to other systems by analyzing data on several chlorine-containing molecules, and in the interpretation of polarized x-ray emission data using a classical theoretical model. This work has led to publication in Physical Review Letters, and invitations for presentations at national and international meetings. It was selected for supplementary support by the Director. This support will be directed toward further understanding of alignment processes (as studied with polarized x-ray emission) in molecules and other systems. This support begins in FY89 and is expected to continue for three years.

A second area of emphasis is the on-going analysis of sub-threshold x-ray inelastic scattering. This process bears directly on the polarization of molecular fluorescence, and also has intrinsic importance in that x-ray emission features can be observed free of lifetime broadening effects. Significant advances were made in the theoretical modeling of this effect as observed in argon gas, and the improvements in this model have already influenced the analysis of satellite free molecular x-ray fluorescence.

A third area of analytical activity has been in studies of exotic cases of x-ray diffraction. The conventional Ewald-Laue formulation of the dynamical theory of x-ray diffraction breaks down in a number of cases such as at very high photon energy, when Bragg angles are near 90°, and when diffraction occurs simultaneously with strong specular reflection from the surface. These special cases are beginning to attract interest because they exhibit characteristics that are useful for such things as high energy x-ray spectroscopy, analysis of the atomic structure of material surfaces and interfaces, production of intense x-ray beams with sub-micron size, and new x-ray monochromators for the next generation of synchrotron radiation facilities. Our group has studied experimentally a number of these cases and Cowan is modifying the orthodox theory to permit the needed analysis.

We have continued to make improvements to beamline X-24A during FY88. Most of the changes are intended to enhance the efficiency of the beamline both with respect to its output characteristics, and with regard to mechanical aspects such as alignment, vacuum, etc. For example, the second x-ray mirror in the beamline, used to focus the monochromatic beam, has been repolished and recoated to a measured surface roughness of less than 10Å rms. Preliminary investigations have shown qualitative improvement in this mirror's focussing and light scattering properties. We also improved the support mechanism for the first x-ray mirror, resulting in better stability and positioning accuracy.

2. Gamma-Ray Measurements - Grenoble

High energy gamma-ray wavelengths ($E_\gamma < 6$ MeV) are measured at the Institut Laue-Langevin (ILL) using a two-crystal diffraction spectrometer developed at NIST. This spectrometer uses crystals whose lattice spacings have been compared to the NIST x-ray/optical interferometer crystal using the delta D spectrometer. The diffraction angles are measured with polarization sensitive Michelson interferometers which are calibrated using an optical polygon. The measurements are performed at ILL because of the unique source handling capability of this facility.

During the past year we have made precision wavelength measurements on gamma-rays produced in the reactions H(n,γ)D, ^{48}Ti(n,γ) ^{49}Ti, and from the decay of ^{192}Ir. The 2.2 MeV gamma produced in the H(n,γ)D reaction had been previously measured by us with an uncertainty of approximately 1 ppm. Improvements in the crystals and a doubling of the source strength suggested that this uncertainty should be reduced to $\approx$ 0.5 ppm, the new measurements differed from the previous results by a few ppm. In order to understand this discrepancy, measurements of the 340 and 1381 keV lines from the ^{48}Ti(n,γ) ^{49}Ti reaction and the 295, 316, and 612 keV lines from the decay of ^{192}Ir were recorded. Measurements were taken with different crystals and in different orders. The Ir source has a 72 day half-life which permits diagnostic measurements to proceed when the reactor is non-critical. We stopped using a controlled atmosphere for the angle interferometers and improved the measurement of spectrometer and crystal temperatures. Instabilities at the 0.5 ppm level seem still to persist and need further tests.

One of the goals of our work at the ILL is measurement of a value for $N_A h/c$. This combination of constants which (the wavelength to atomic mass unit conversion factor) follows from measuring an energy interval in both the atomic mass unit and wavelength. One of the possible intervals includes the ^{15}N binding energy (10.8 MeV) available in the reaction

$^{14}N(n,\gamma)\ ^{15}N$. Fortunately this energy interval can be obtained by measuring several lower energy gamma-rays (≈5 MeV) whose sum equals 10.8 MeV in a redundant manner. A first attempt to record the 5 MeV gamma-rays failed because the silicon nitride source was very weak. A second attempt to record these lines was made in October 1988, with a factor of ten increase in source strength.

In addition to precision wavelength measurements, the NIST-ILL flat crystal spectrometer has been used extensively during the past year for measurements of nuclear lifetimes in the range 10^{-12} to 10^{-16} seconds. A nucleus in an excited state emits a high energy gamma-ray (1-5 MeV). A secondary gamma-ray emitted by the recoiling nucleus is Doppler broadened if the gamma-ray is emitted before the recoiling nucleus comes to rest. The high resolution of the NIST flat crystal spectrometer permits one to extract nuclear level lifetimes from the broadened profiles. Precise lifetime measurements have been made on gamma-rays emitted in the decay of ^{49}Ti, ^{84}Cr, and ^{57}Fe.

The interest in the NIST-ILL flat crystal spectrometer continues to increase. The scientific proposals submitted in September 1988, included two new types of measurements: 1) the measurement of crystal structure factors at high energy in order to look for higher order Q.E.D. contributions, and 2) measurement of the helicity of the neutrino. Both of these experiments require the high resolution of the flat crystal spectrometer.

3. Neutron Physics

The QMD effort in neutron physics has diversified this year with activities having a variety of scientific, geographical and administrative directions. The long-term thrust of the neutron program is aimed at the establishment of a major user facility at the National Cold Neutron Facility at the NIST research reactor. During the last year, while construction on the National Cold Neutron Facility was underway, members of the division have been involved in experimental work at the existing NIST reactor and at neutron sources elsewhere, as well as being engaged in planning for the new facility.

Our experiment designed to measure the lifetime of the free neutron achieved a major milestone by accepting first beam at the Institut Laue-Langevin in July of 1988. This represents a culmination of three years work. This project, supported in part by the Department of Energy, NATO and the Science and Engineering Research Board (U.K.) is a collaboration between personnel from NIST, the University of Sussex (U.K.), the E.E.C. Central Bureau for Nuclear Measurements (Belgium) and the Institut Laue-Langevin (France). It is our expectation that this project will resolve outstanding discrepancies among various measurements of this important fundamental constant. Data collection at ILL will continue through December 1988. In 1989 the apparatus will be moved to Gaithersburg in preparation for the anticipated startup of the Cold Neutron Facility in late summer 1989.

Another project which began data collection at the ILL is an experiment to measure the radiative capture cross-section for low energy neutrons on ^{3}He. This cross section is an important input for the theories which predict the production rate of high energy neutrinos in the solar interior. An accurate knowledge of this cross-section will be required to interpret data from the upcoming generation of solar neutrino detectors. Data collection from this experiment was completed in October 1988. Analysis is currently underway. We expect this measurement to provide the definitive determination of this cross section.

A joint program to develop new techniques for the absolute determination of neutron fluxes has also progressed during the last year. This is a collaborative effort with personnel from NIST, Los Alamos National Laboratory and Harvard University. Within NIST this work involves personnel from CAMOP and CRR. Design and development work on several new flux monitors has progressed and we expect to carry out a major series of intercomparisons of these techniques in early 1989 at the NBS reactor.

With considerable support from the Cold Neutron Facility Project (IMSE) we have been carrying out conceptual design work for the new user facility. A major proposal to NSF and DOE to provide support for a national participating research team in fundamental neutron physics based at the new cold neutron facility has been submitted. Matching funds from ISME have been assured. We expect to begin detailed design work for this project in late 1988.

To help stimulate research in this area we are providing partial sponsorship of an international Workshop on Fundamental Physics to be held at the Institut Laue Langevin in March 89. This workshop follows in the spirit of the highly successful workshop held in Gaithersburg three years ago.

4. Crystal Lattice Measurement

The utility of x-ray and γ-ray wavelength measurements in determining fundamental constants, testing basic theory and establishing elementary particle masses depends entirely on the robustness of the bootstrap by which local scales in these regions are linked to visible secondary standards. We have pioneered a three-step process which today provides the only known hope that such measurements are of non-trivial significance. The three steps are: 1) Optical measurement of a (Si) lattice spacing, the XROI measurement; 2) Sensitive intercomparison of other crystals with surrogates of the sample calibrated in (1) using a highly sensitive lattice comparator, the Δd machine; and, 3) utilization of these calibrated crystals in accurate angle-measuring diffraction spectrometers as described above for the case of γ-rays.

Although this entire chain has been realized in no other laboratory, in 1980 a group from the PTB reported results for the first step (XROI) differing very significantly (1.8 ppm) from what we had reported earlier (1974-76). This discrepancy led a complete re-build of the NBS experiment (1983-85) with many improvements and to discovery in 1986 of a significant systematic error in the original NBS measurement. Work since that time has aimed toward obtaining a new result with about a ten-fold accuracy gain that would approach the limit of available crystal uniformity, ca 0.01 ppm.

This has been a rather arduous exercise for many reasons among which two might be mentioned: To preserve the historical thread, work has proceeded using as much as possible the early NBS apparatus whose characteristics were very well matched to the original (1968) goal of 0.3 ppm but are somewhat overmatched at the 0.01 ppm level. Dominant corrections required arise from trajectory characterization, nowadays measured on-line during data taking. Unfortunately, although the needed level of angular sensitivity (10^{-11} radians) is rather easily reached, the "platform" from which these curvatures are measured is, itself, subject to drifts many times larger.

Most recent progress has resulted from progressive improvement of instrumental stability and from development of data analysis algorithms which provide for distinguishing between instrumental drift and trajectory curvature. Although the needed data reduction protocols have not as yet been stabilized for production, exploratory work using the concepts of principal factor analysis and self-modelling non-linear regression appear to offer stable and convergent procedures for dealing with trajectory data. Preliminary indications are that procedures to date are consistent and that significantly improved accuracy is also at hand.

The "absolute" measurement procedure, XROI, is too difficult and time consuming to be repeated for each crystal sample which is used for x-ray and gamma-ray diffraction. Thus a technique which allows rapid and accurate comparison of crystal lattice spacings is needed. The comparisons are made with a two crystal transmission spectrometer used in the non-dispersive mode. An elongated first crystal (5 cm long), two x-ray sources, and two detectors permit left and right reflex to be recorded simultaneously. Crystals with known and unknown lattice spacings are alternately and automatically placed in the second crystal position for comparison. By carefully matching the thickness (within a few microns) of the first and second crystals, the x-ray profiles are provided with fine structure which is a significant aid for determining the angular separation of the left and right reflexes.

The targeted accuracy of the comparison measurements is 0.01 ppm and most of the activities of the past year have been directed to the attainment of this goal. In order to obtain uniform and matched crystals, a mechanical/chemical polishing technique was developed. By careful and repeated polishing and measuring, crystals of the desired thickness were obtained. In addition the crystals were mounted in a more strain free manner which is mechanically more stable. The temperature stability of the spectrometer was improved by using a closed circuit cooling system for the x-ray tubes. A more sensitive temperature measuring system was also installed.

A large volume of data was recorded with 0.75 mm thick crystals. In addition to establishing the performance of the spectrometer, these measurements provide preliminary results for the lattice spacing difference between the crystals used in the NIST and PTB absolute lattice measurements (a few parts in 10^8) and for the compressibility of the lattice spacing due to atmospheric pressure.

Dynamical diffraction theory predicts a maximum transmitted intensity for a crystal thickness around 0.45 mm. The gain in intensity as the thickness is changed from 0.75 mm to 0.45 mm is more than a factor of two. A new set of 0.45 mm crystals has recently been prepared by the above described polishing technique and definitive comparisons of the NIST and PTB crystals have begun. Following this very important comparison, a number of crystals which have been or will be used for x-ray and gamma-ray diffraction will be compared to the absolutely measured NIST sample.

This work was materially enhanced by the participation of two visiting scientists during this year. Dr. Weiben Gao (PRC) contributed to the development of strain-free polishing techniques while Dr. Lars Nielsen was active in the experimental measurement program.

5. Miscellaneous

Two visiting scientists are currently engaged in theoretical and semi-empirical calculations of inner shell transition energies. Dr. P. Indelicato (CNRS) has made significant progress in certain aspects of the relativistic many-body problem. He summarizes the current situation as follows:

"In FY88 studies of the relativistic many-body problems were started. Using a set of Multi-Configuration Dirac-Fock programs developed in collaboration with Y.K Kim and J.P. Desclaux (CENG-Grenoble), the agreement between MCDF calculations of transition energies in two electron ions and experiment has been improved by one or even two orders of magnitude. At the same time we have been able to get very accurate results for the three electron system, although the accuracy of the latter calculation is somewhat less than in the two electron case because of huge numerical difficulties. This breakthrough in precision has been produced by several means. We have been able to use existing high precision non-relativistic results on electron-electron correlations to correct our relativistic energies. We then showed that relativistic contributions to electrostatic correlations and magnetic correlations are for high Z elements the major contribution to correlation energy. We have improved the calculation of QED corrections for very heavy elements by taking into account higher orders in the vacuum polarization, as well as finite nuclear size effects on the self-energy. Finally we have been able to show, by comparing 2p-2s experimental energies in two electron systems, that calculations made with the Coulomb gauge for the electron-electron interaction are giving better results than calculations made with the Lorentz gauge. This was known in the case of two body systems like positronium, but had never been demonstrated in the case of several particles in an external field. As a by-product of the improvement of the code, we have been able to perform the most precise calculation of K alpha transitions in heavy atoms (up to fermium). The agreement with experimental data is astonishingly good for Z=<83, but for higher Z there is a disagreement about three times bigger than combined theoretical and experimental uncertainty. It is not to be excluded that further progress in this direction will lead to very interesting results."

A second visitor, Dr. Nissan Spector (Israel Atomic Energy Commission) has begun work aimed toward systematic application of these powerful methods to those elements for which high accuracy experimental data are available. As preliminary exercises he has explored both the Desclaux code and that due to I.P. Grant under several extreme conditions: neutral to highly charged ions, for both light and heavy elements. He reports that:

"The calculations revealed important characteristics of the programs, i.e., their success in giving highly accurate predictions, both of energies and relative intensities, of the recently observed Te XXVI [N. Spector, Nuclear Instruments and Methods B31, 211-213 (1988)], hitherto untreated theoretically by either of them, versus the non-convergence of their eigen functions in the case of neutral sodium successfully treated elsewhere [N. Spector, M.H. Tiulier, C. Bonnelle, Phys. Rev. A 27, 944-946 (1983)]. They also indicate the difficulties that might be encountered in the middle-of-the-shell configurations, in particular for the rare-earths.

Altogether both programs seem complementary and an insight into their intricacies might turn out to be profitable in future theoretical predictions. Therefore more calculations, for a variety of cases, seem to be still needed, in order to benefit better from these two important and heavy codes."

Other theoretical results have emerged from the work of J.W. Cooper who reports that:

"Work on argon K shell photoionization described in the last annual report was completed and a paper describing the results has been accepted by Phys. Rev. A and is scheduled for publication in Oct. 1988.

Work on modeling the $K\alpha$ and $K\beta$ argon near threshold emission spectra obtained at Brookhaven was initiated in collaboration with P. Cowan. Although this work is incomplete, preliminary results indicate that it should be possible to successfully model the observed shifts in the emission spectra due to resonant Raman effects. A preliminary report of this work was given at the April APS meeting.

New experimental results on the 3p sub-shell absorption spectra of atomic Mn, Mn^+ and Cr were obtained in the fall of 1987 by T. Lucatorto and co-workers. The new results confirmed earlier work and provided detailed spectra in the near threshold region. In order to explain these results a series of calculations were performed which provided identifications of some of the new structure observed and lead to an explanation of the radical differences in the absorption spectra of the isoelectronic species Cr and Mn^+. A paper describing the new experimental results and their theoretical interpretation has been written and submitted to Phys. Rev. Lttrs.

In April, 1988 a paper by T. Carlson et. al. reported an unexpected anisotropy in the angular distributions of Auger electrons observed following atomic near threshold resonant inner shell excitation and indicated that new theoretical developments were needed to explain the experimental results. Analysis of resonant Auger process indicated that the process could be treated in much the same way as single electron photoionization and a formalism was developed to calculate the angular distributions. Calculations for a typical case, 2p-4s excitation in argon, were made and compared with the experimental results. A brief paper describing this method and the calculations has been written and will be submitted to Phys. Rev. A, Rapid Communications.

Collaboration with H.P. Kelly and his group at UVA has been initiated. In particular, a proposal to study relaxation effects in atomic photoionization with J. W. Cooper and H.P. Kelly as principal investigators has been submitted to DOE. Regardless of the outcome of this proposal, we intend to continue the collaboration, since our work is closely related and uses alternative theoretical methods.

An effective halt to U.S. satellite-based solar studies in the x-ray region has led to strong U.S. and U.K. participation in a 1991 Japanese mission. The joint effort on high resolution spectroscopy of active regions is coordinated by L. Cuhane, Univ. College, London and includes contributions from Rutherford Lab., the U.S. Naval Research Laboratory and NIST. A 4-spectrometer assembly has been designed to concentrate on He-like spectra of S, Ca and Fe together with the hydrogen-like spectrum of Fe. Both prototype and flight models are in late assembly. Following the design phase, our work now concentrates on production and characterization of the large radius germanium crystals. This effort is supported by funds transferred from NRL. It is on schedule at this time with flight hardware completion expected in 1989.

Outlook - Future Plans

Several of the areas described are in late phases of development or re-development. This is rather obvious in the case of x-ray physics at Brookhaven where work should be re-started by the time the panel meets after more than 18 months of darkness. This work is materially enhanced by the new funding which will permit development of electron spectroscopy from oriented molecules under near-threshold excitation. Similarly, the Gaithersburg component of neutron physics work focusses on developments for use at the cold neutron facility. The new guide hall will open early in 1989 with the lifetime experiment returning from Grenoble in the spring, and it should accept first beam during the summer. Meanwhile planning for the massive stable platform for neutron interferometry will proceed. It is reasonable to expect γ-ray work to proceed through the coming year while lattice interferometry winds down and inter-crystal comparisons proceed at the level needed to sustain the spectroscopy programs.

Two future activity directions are not evident in the previous narrative. The first is in the area of high Z few-electron spectroscopy. This will involve only a few experimental periods per year using heavy ion accelerators at Argonne and the GSI in Germany. These experiments while limited by the characteristics of the accel-strip-decel-capture excitation process provide useful preliminary experience for future work with decelerated cooled beams of heavy ions. At the GSI in particular beginning around 1992-3 it should be possible to accumulate totally stripped cooled beams of all stable elements up to uranium. We have already an approved experimental program and should begin planning over the next 1-2 years. No support for this work is at hand and a prior attempt at external support failed.

There is also a potentially fruitful domain associated with the Race-Track Microtron currently under construction at the Gaithersburg site. As required for its originally planned operation as a driver for a free-electron laser, the RTM will produce quasi-cw electron beams having exceptionally high quality. Such beams interacting with periodic structures whose spatial scales are smaller than that of the currently planned wiggler magnet produce radiation having progressively shorter wavelengths. Although the mechanisms involved do not as yet offer the general possibility of lasing, a wide class exists in which the production process is coherent, ie., in which N individual interactions yield fluxes which vary a N**2. The structures, their scale, mechanism and wavelength domain for the 100-200 MeV beams to be available are as follow: Micro-undulators having space periods below 1mm make radiation up to 500 ev. Coherent transition radiation arrays with scale lengths in the range 10-30 microns make 1-3 kev x-rays. Channelling radiation from crystals such as diamond and silicon make radiation in the range of 20-40 keV. In the first two cases, the radiation is spectrally concentrated by a factor of the order of 1/N on axis while channeling radiation spectra are likely determined by de-channeling processes. In one other mechanism, namely parametric x-ray generation, much narrower spectral bandwidths are available with correspondingly higher flux densities. It would appear that the systematic exploration of these alternative mechanisms for x-ray production should be interesting to outside communities in view of their potential applications in the areas of micro-lithography, x-ray microscopy and medical imaging.

Invited Talks

Quantum Metrology Division (575)

John W. Cooper

"Autoionizing Resonances in Mn, $Mn^{\pm}$ and Cr 3p Subshell Absorption," Seminar at U. Virginia, May 11, 1988

Paul L. Cowan

"New Directions in Atomic Physics with X-Rays Using Synchrotron Radiation," CBS Colloquium, NBS, March 9, 1988

"Diffraction of Evanescent X-rays," March Meeting of the American Physical Society in New Orleans, March 22, 1988.

"Diffraction of Evanescent X-Rays," Tokyo Institute of Technology, Nagatsuta, Japan, August 23, 1988.

"Diffraction of X-Rays at Glancing Angles and Back-Reflection for X-Ray Standing Wave Studies," University of Tokyo, Tokyo, Japan, August 24, 1988.

"Self-Filtering Crystal Monochromators for Synchrotron X-Radiation," with S. Brennan, Third International Conference on Synchrotron Radiation Instrumentation, Tsukuba, Japan, August 30, 1988.

"Performance of a Tunable Secondary X-Ray Spectrometer," with S. Brennan, R.D. Deslattes, A. Henins, D.W. Lindle, B.A. Karlin, Third International Conference on Synchrotron Radiation Instrumentation, Tsukuba, Japan, August 31, 1988.

"Data Acquisition and Beamline Control Software," with S. Brennan, Third International Conference on Synchrotron Radiation Instrumentation, Tsukuba, Japan, August 31, 1988.

"Performance of a High Energy Resolution, Tender X-Ray Synchrotron Radiation Beamline," Third International Conference on Synchrotron Radiation Instrumentation, Tsukuba, Japan, September 1, 1988.

Richard D. Deslattes

"Electromagnetic Spectroscopy of Practically Everything: DC to Daylight and Gamma-Rays Too," Physics Department Colloquium, Texas A & M University, March 10, 1988

"Accurate Spectroscopy at High Photon Energies," March Meeting of the American Physical Society, New Orleans, March 22, 1988; Invited Paper 19th Annual Meeting of the American Physical Society, Baltimore, MD April 18, 1988

"Naked Ions for High-Z Atomic Spectra," Physics Colloquium at Texas A & M University, April 25, 1988

"Experimental Status of High-Z One and Two Electron and One Vacancy Systems," Institute for Theoretical Physics, University of California, Santa Barbara, April 28, 1988

Maynard S. Dewey

"A New Precision Measurement of the Halflife of the Neutron," Princeton University, June 2, 1988

Geoffrey L. Greene

Physics Colloquium, Yale University, January 21, 1988

Paul Indelicato

"Recent Progress in the Theory of Relativistic Effects and QED Connections in 2 and 3 Electron Ions," International Conference on the Physics of Multiply Charged Ions, Grenoble, France, September 14, 1988

Robert E. LaVilla

"The Anomalous Th M X-Ray Emission Spectrum," for the 19th Annual Meeting of the American Physical Society, Baltimore, MD, April 18, 1988

Dennis W. Lindle

"Atomic and Molecular Physics Using Intense Synchrotron-Radiation Sources," Seminar at the University of California-Riverside, December 4, 1987

"Near-Threshold X-Ray Fluorescence Spectroscopy of Molecules," SPIE Symposium on X-Ray and VUV Interaction Data Bases, Calculations, and Measurements, Los Angeles, January 14, 1988

"Near-Threshold X-Ray Fluorescence Spectroscopy of Molecules," University of Maryland, January 29, 1988

"Polarization Effects in Molecular X-Ray Fluorescence," CBS Colloquium, NBS, March 16, 1988

"Polarization of Molecular X-ray Fluorescence," March Meeting of the American Physical Society," New Orleans, March 22, 1988

"Near-Threshold X-Ray Fluorescence Spectroscopy of Molecules," Physics Colloquium at Louisiana State University, April 12, 1988

"X-Ray Polarized Fluorescence Spectroscopy of Chlorine-Containing Small Molecules," D.W. Lindle, P.L. Cowan, T. Jach, R.E. LaVilla, R.D. Deslattes, Poster at the 19th Annual Meeting of the American Physical Society, Baltimore, MD, April 18, 1988.

"Soft X-Ray Polarized Fluorescence from Molecules," Advanced Light Source Users' Meeting, Berkeley, CA, June 2, 1988

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*T.A. Carlson, D.R. Mullins, C.E. Beall, B.W. Yates, J.W. Taylor, D.W. Lindle, and F.A. Grimm, "Angular Distribution of Ejected Electrons in Resonant Auger Processes of Ar, Kr and Xe," submitted to Phy. Rev. A.

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H.P. Layer and G.L. Greene, "The Elastic Deformation of a Monolithic Perfect Crystal Interferometer: Implications for Gravitational Phase Shift Experiments," submitted to Phy. Rev. Lett.

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D.W. Lindle, "Photoionization Studies of Atoms and Molecules Using Synchrotron Radiation," submitted to Nucl. Instrum. Meth.

D.W. Lindle, P.L. Cowan, T. Jach, R.E. LaVilla, and R.D. Deslattes, "Polarized X-Ray Emission Spectroscopy," submitted to Nucl. Instrum. Meth.

D.W. Lindle, P.L. Cowan, T. Jach, R.E. LaVilla, R.D. Deslattes, and R.C.C. Perera, "Polarized X-Ray Emission Studies of Small Molecules," (in preparation).

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*Based on work performed prior to joining QMG.

TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Quantum Metrology Division (575)

John W. Cooper - Board of Editors, Atomic and Nuclear Data

John W. Cooper - Physics Editor, NBS Journal of Research

John W. Cooper - Member, NBS Washington Editorial Review Board

Paul L. Cowan - General User Oversight Committee, National Synchrotron Light Source

Richard D. Deslattes - Member, Program Committee of the Ninth International Conference on Vacuum Ultraviolet Radiation Physics (VUV-9) 1989

Richard D. Deslattes - Member, The University of Chicago Review Committee for the Physics Division at Argonne National Laboratory

Richard D. Deslattes - Member, Executive Committee of the PRT/IDT Council for the National Synchrotron Light Source

Richard D. Deslattes - Member, Program Committee for the International Conference on X-Ray Physics, X-89

Geoffrey L. Greene - Member, National Steering Committee for the Advanced Neutron Source (1986 -)

Geoffrey L. Greene - Member, National Academy of Sciences/National Research Council Committee on University Research Reactors (1986-)

Dennis W. Lindle - Advanced Light Source User's Organization Executive Committee

COLLABORATIONS

Quantum Metrology Division (575)

Paul Cowan

AT&T Bell Labs, Murray Hill

Development of total reflection standing waves for studies of organic monolayers

Collaborator	Michael Seuls

Glancing incidence x-ray diffraction studies

Collaborator	Paul Fuoss

Surface Studies with x-ray standing waves

Collaborator	J. Rowe F. Sette J. Patel

EXXON Research Labs

Glancing incidence x-ray diffraction studies of surface and interface structure

Collaborator	Ken Liang

Deutsches Elektronen Synchrotron (DESY)

Glancing incidence x-ray diffraction studies

Collaborator	G. Materlik R. Frahm M. Clausaitzer

X-ray standing wave studies

Collaborator	G. Materlik R. Frahm B. Dev

RISO National Laboratory, Denmark

Glancing incidence x-ray diffraction studies

Collaborator	R. Fiedenhansl

Max-Plank Institute fur Festkörperforschung

Glancing incidence x-ray diffraction studies

Collaborator	Robert Johnson Francois Grey

X-Ray standing wave studies of electrochemical systems

Collaborator	Kohl

University of California, Lawrence Berkeley Laboratory

Studies of molecules by x-ray spectroscopy

Collaborator	R.C.C. Perera

Development of synthetic multilayers for x-ray filters

Collaborator	J. Kortright, R.C.C. Perera

Stanford University, Stanford Synchrotron Radiation Laboratory

Novel instrumentation development for synchrotron radiation

Collaborator	S. Brennan

Total reflection x-ray standing wave studies

Collaborator	S. Brennan

Glancing incidence x-ray diffraction studies

Collaborator	S. Brennan

Vanderbilt University, Department of Chemistry

XPS studies of multivacancy processes in gases and vapors

Collaborator	S. Banna

Paul Cowan and Dennis W. Lindle

AT&T Bell Labs

Structure studies of adsorbates on crystal surfaces, development of a new experimental technique (normal incidence x-ray standing wave analysis), and studies of post-collisional interactions of Auger electrons

Collaborators	Jack Rowe Francesco Sette

Lawrence Berkeley Laboratory

Multi-layer mirrors as power filters in synchrotron-radiation beamlines

Collaborators	J. Kortright P. Plag R.C.C. Perera

Paul Cowan, Robert E. LaVilla and Dennis W. Lindle

Brookhaven National Synchrotron Light Source

Participating research teams (PRT) conduct research at the National Synchrotron Light Source on beam lines that were constructed in a collaborative effort.

Lawrence Berkeley Laboratory

X-ray fluorescence of freons

Collaborator	R.C.C. Perera

R.D. Deslattes

Argonne National Laboratory

Collaborator	Robert Dunford

University College, London

High resolution Bragg crystal spectrometer for the HESPP Mission (also with the Rutherford Appleton Laboratory)

Gesellschaft für Schwerionenforschung (GSI) Darmstadt, FRG

Spectra of heavy ions

Collaborator	H. Beyer

U.S Naval Research Lab

NBS & NRL joint project to construct, commission and operate five beamlines at the brookhaven national light Source.

Collaborators	Many other researchers

R.D. Deslattes, E.G. Kessler, G.L. Greene, and M.S. Dewey

Institut Laue Langevin

Absolute gamma-ray spectroscopy at high energies

Collaborators
H. Borner
S. Robinson

Geoffrey L. Greene

Sussex University & McGill University

Measurement of the neutron half life

Collaborators
J. Byrne
P. Dawber

Los Alamos, Drexel University and Harvard University

Measurement of the fundamental characteristics of neutron β-decay

Collaborators
J. Wilkerson
T. Bowles (LAHL)
H. Robertson
T. Chupp (Harvard)
R. Steinberg (Drexel)

Center for Radiation Research, NBS and European Center for Nuclear Measurements, Geel, Belgium

Absolute neutron dosimetry

Collaborators
David Gilliam (NBS)
J. Pauwels (ECNM)

Investigations into new techniques of absolute neutron flux determination

Collaborator

University of Missouri

Neutron Interferometry

Collaborators
S. Werner
H. Kaiser
R. Berliner

Investigations employing neutron interferometry

University of Washington, Department of Physics

Studies on nucleon-nucleon weak interactions

Collaborator B. Heckel

D.W. Lindle

Indiana University

Polarization of molecular x-ray fluorescence

Collaborator Peter W. Langhoff

University of California, Lawrence Berkeley Laboratory

Threshold photoelectron spectroscopy of gases

Collaborator David A. Shirley

Martin-Marietta, Oak Ridge National Laboratory

Resonant photoelectron spectroscopy of atoms

Collaborator Thomas A. Carlson

Georgia State University, Department of Physics and Astronomy

Angle-resolved photoemission from atoms

Collaborator Steven T. Manson

TIME AND FREQUENCY DIVISION
FISCAL YEAR 1988

I. INTRODUCTION

The principal functions of the Time and Frequency Division, located in Boulder, are: to produce and maintain the standards of time and frequency and coordinate them internationally, to provide time and frequency services for the United States, and to perform research and development on new standards and measurement methods. There is a secondary responsibility for the realization of the meter, since, by international agreement, the standard of length is now based on the frequency standard, the speed of light being a defined constant. The Division has played a major role in the measurement of the speed of light and the new realization of the meter.

This report describes the work of the Division along organizational lines as shown below.

Each of these sections begins with a short description of the general program and goals of the Group along with a list of staff and guests in the Group. In an effort to relate the Division's work to it's mission, a set of objectives have been used. The work of each group is described with these objectives as headings. Individual objectives are often supported by more than one group, and, because there is collaboration between some of the groups, some tasks are referenced in more than one place. Accomplishments and plans are listed under each objective heading.

Objectives

- Generate NIST time scales UTC(NBS) and TA(NBS).
- Maintain international time and frequency coordination.
- Provide radio and satellite broadcast services.

- Provide seminars and measurement services on a reimbursable basis.
- Develop advanced methods for time transfer.
- Establish the second and the meter for the International System.
- Perform research and development on new primary frequency standards.
- Perform basic studies in areas related to future frequency standards.
- Develop methods for precise time, frequency and length measurements.
- Provide reference frequencies from the microwave to visible regions.
- Measure spectral frequencies of atoms and molecules.
- Advise industry and government agencies on time and frequency metrology.

Section II of this report provides a general discussion of a few of the key programmatic issues in the Division as well as an outline of some of the significant research opportunities (basic and applied) for the future. This discussion is not meant to be comprehensive, but rather to convey a general sense of the programmatic and research directions.

II. OVERVIEW OF TIME AND FREQUENCY DIVISION ISSUES

A. SOME KEY PROGRAMMATIC ISSUES

Primary Frequency Standards

Radiatively cooled, trapped ions may be the best choice for future frequency standards. The first demonstration within the Division of a beryllium standard operating at an accuracy of one part in 10^{13} has bolstered that view. The Division should demonstrate a prototype beryllium ion standard at an accuracy level of one part in 10^{14} in the near future. The recent success in isolating and probing single mercury ions provides even more opportunity. Work on this system indicates that systematic uncertainties in a narrow-linewidth, ultraviolet transition can be understood at a level approaching one part in 10^{18}. There is rising interest in the study of slowed neutral beams, but work on these is in an embryonic stage and no one has yet proposed a specific scheme for using them to produce a frequency standard. While there are many other motivations for continuing this research, we view the long-term potential of the slowed-neutral concepts as providing a performance which is intermediate between that of the optically pumped technology of NIST-7 and the higher-accuracy performance expected from trapped ions.

The very highest accuracy primary standards will most likely operate at frequencies in the optical region. This is due to the fact that, regardless of the clock frequency, the observation time most often determines the minimum linewidth and thus, for a given observation time, the Q of the resonance increases directly with frequency. For this reason, the Ion Storage Group has been investigating an optical frequency standard based on single mercury ions and it seems likely that they will demonstrate such a device in the very near future. Although an optical frequency standard could be used directly in the optical region, it poses another challenge if it is to be used as a reference for microwave frequencies where it could then be used as a time standard. The challenge is that of accurately and routinely relating an optical frequency to a microwave frequency. The Division has performed this transfer in the past, but all would agree that this is a difficult thing to do routinely. Thus, it is important to initiate development of a simple, reliable chain (frequency division or multiplication) linking the microwave and optical regions. This will also provide for improvements in our realization of the meter and in optical frequency metrology which will in turn support coherent optical communication systems. A modest reorganization within the Division now provides a specific programmatic effort in this direction (see section VIII on Laser Frequency Synthesis).

The development of a fully engineered frequency standard based on trapped ions must await further understanding of the physics involved, and thus is a number of years away. NBS-6 is now 13 years old and operating at an accuracy level which is marginal for current requirements. Thus, the Division has committed resources to the development and construction of an advanced cesium beam standard (NBS-7) based on optical state selection and detection techniques. The goals are to improve accuracy to about one part in 10^{14} and to simplify and automate accuracy evaluation so that it can be accomplished more often.

Time Scale

The imminent improvements in primary frequency standards place additional requirements on the NIST time scales. The current time scale, acting as a flywheel, varies in frequency on the order of 1 part in 10^{13} per year, thereby setting the current requirement for time-scale calibration by NBS-6 at once per year. At an accuracy level of 1 part in 10^{14}, calibration must occur about once each month. In order to assure reliability in dissemination of time and frequency signals, time-scale performance should be improved to increase the period between calibrations. Efforts should continue to upgrade both the stability and reliability of the ensemble. One aspect of system reliability will be addressed with the replacement by the end of this fiscal year of the ten-year-old time scale computer. Many other time scale components have been upgraded, but the stability requirement can only be handled by acquisition of more stable standards. Research on time-scale algorithms should also continue, since this can contribute significantly to both time-scale stability and reliability.

Time Transfer

Satellite time transfer has become the method of choice for international time coordination with NIST playing a key role through development of the GPS Common-View Method. With this advance, time and frequency transfer is now limited by the long-term performance of the primary standards themselves and the Division now uses the technique to support other applications (e.g., NASA Deep Space Network and studies of the Millisecond Pulsar). The Division is also working on two-way time transfer using commercial communication satellites, a method which should provide even higher-accuracy time transfer to support pending improvements in primary standards. Satellite time transfer has substantially altered the conduct of the Division operations and, in the future, will play a larger role in the synchronization of major systems.

Services

Because of the predictability of time delays, satellite broadcast of time and frequency signals will improve significantly upon ground-based broadcasts. NIST already operates a satellite broadcast service through the GOES weather satellites, but that broadcast is limited in accuracy to 100 microseconds by the broadcast bandwidth and the tracking information provided by operators of the GOES system. Communication satellites provide the potential for a very simple broadcast service with accuracy in the range of 0.1 to 1 μs. The Division and the National Research Council in Canada are both studying this concept and considering cooperation, since a single broadcast service might well serve both countries.

Discussions with the electrical power industry suggest the need for 1 μs synchronization of power networks. Deregulation of the communication industry poses synchronization problems at a similar level. The Division is interacting with the latter industry through their timing standards committee to support some collective resolution of the problems. A high-accuracy satellite service could be of value to both of these industries.

Another area of growing interest involves the automated setting of clocks in computers and other digital systems. This can be done using the radio broadcasts, but, with many computers already tied to the telephone system, transmission of a digital time code through telephone lines is clearly a desirable and cost effective solution. The new NIST Automated Computer Time Service (ACTS) was introduced to meet this interest. The service compensates for telephone line delays to a level of about one millisecond and even better precision may be achievable. Discussions with users suggest that there are a number of applications which can be fulfilled with this service, but there are potential applications requiring a much higher level of precision. These could be met by a satellite dissemination service (see discussion above in this section).

Measurement of Phase Noise

The aerospace industry is now starting to see procurements for space hardware with specifications for components of very low phase noise. Phase-noise measurements have been well developed at a few specific frequencies for characterization of frequency standards, but little work has been done on the methodology for such measurements in other regions of the electromagnetic spectrum. The Division is now working to develop and demonstrate phase-noise measurement systems in other important spectral regions. This effort is coordinated with the work in the Electromagnetic Fields Division on broadband-thermal-noise standards. The phase-noise work naturally involves the development of stable reference oscillators and low-phase-noise multipliers, components which are important in the Division's work on primary standards and frequency synthesis.

B. BASIC AND APPLIED RESEARCH OPPORTUNITIES

The Division has developed a number of specialized experimental capabilities which provide unique opportunities for certain basic and applied research projects. These include: (1) systems for trapping and cooling of ions; (2) highly stable lasers and microwave sources for high resolution studies of atoms and molecules; (3) well-characterized atomic beams; (4) high-resolution systems for imaging atomic particles; and (5) satellite-timing receivers and transmitters. The Division also has a strong tradition of very accurate frequency measurement across the electromagnetic spectrum and an excellent background in the statistical characterization of high-stability oscillators. Considering these strengths, we list the following examples which are appropriate areas for research in the Division.

Atomic Physics

In the area of atomic physics, Division programs are centered on strengths in ion trapping, cesium beams and accurate frequency (length) measurements.

1. Tests of Relativity Theory - Such tests can involve accurate measurement of the gravitational red shift or comparisons of fundamentally different oscillators with varying spatial orientation of quantization axes (Hughes-Drever type experiment).
2. Measurement of Light Shifts - Both the influence of black-body radiation and electric fields (ac-Stark shift) can be studied. The latter might possibly provide the basis for an ultraviolet power standard.
3. Study of Atomic/Nuclear Distortion by Magnetic Fields - This involves accurate measurements on ions in Penning traps to provide tests of theoretical predictions.
4. Study of Radiation Statistics of Atomic Systems - Here, we observe transitions in systems involving one or a few atoms where cooperative effects and nonclassical statistics such as antibunching and sub-Poissonian can be studied.
5. Study of Influence of Radiation Fields on Atoms - Here we can compare predictions of quantum and semi-classical theory and study radiation damping and frequency pulling in cavities.
6. Precision Measurements in Hydrogen - Important quantities to be obtained from accurate measurements in hydrogen include the electron-to-proton mass ratio, the Rydberg constant and the Lamb shift.
7. Search for Violation of Time-Reversal Invariance - A search in an alkali metal (e.g., cesium) for a static electric dipole moment could

provide a really exacting test of this important principle.

8. Precise Measurements of Mass Ratios - Laser fluorescence mass spectroscopy developed within the Division could yield measurements of such ratios as He/T, M_e/m_p and $p/\bar{p}$, as well as g-factor measurements.

Molecular Physics

Spectroscopy is being performed with coherent radiation using tunable far-infrared (TuFIR) and laser magnetic resonance (LMR) systems. Both of these provide for highly accurate and very sensitive measurements of atomic and molecular spectral line frequencies as well as line shapes. Such measurements are important not only as secondary frequency and wavelength standards, but also in atmospheric physics and astrophysical research, areas in which the Division interacts strongly. The Division capability can be used to observe and characterize spectra of unusual and rare molecules, molecular ions and free radicals which heretofore have not been observable in the laboratory. The dependence of line shape (and width) on temperature and pressure can also be precisely determined.

Optical Physics

Studies in optical physics revolve around the need to develop very narrow-line sources of radiation at a variety of frequencies (from the microwave to the visible) and to accurately measure optical frequencies. Laser studies involve gaseous lasers, dye lasers solid-state lasers and semiconductor lasers. The standard approach to measuring optical frequencies involves frequency multiplication which requires the development of an understanding of mixers such as Schottky diodes, metal-insulator-metal (MIM) diodes, nonlinear crystals, vacuum-tunnelling diodes and, perhaps, superconducting (Josephson or quasiparticle) junctions composed of the new high-T_c superconductors. Another approach to the problem involving synchrotron division offers the opportunity to study laser excitations of a single relativistic electron in a Penning trap.

Laser cooling and Doppler-free (two-photon) spectroscopy are traditionally categorized under optical physics and should be included as areas of research, since they constitute major components of the Division program.

Plasma Physics

Stored ion clouds of beryllium and magnesium (which are being studied as frequency standards) constitute very interesting nonneutral plasmas. These plasmas have distribution functions which are closely related to those for neutral plasmas. Under proper laser-cooling conditions, such plasmas become very strongly coupled and can enter the liquid and solid states. Important experiments to consider involve study of Bragg scattering, ion diffusion, phase transitions, Coulomb clusters, and multispecies ion plasmas. Such studies are also relevant to the development of frequency standards since a full understanding of the dynamics of ions in these systems provides the basis for estimating systematic errors (primarily Doppler shifts) arising from ion motion.

Satellite Timing

One of the primary limitations to accuracy of satellite time transfer is the uncertainty in signal propagation time which arises from variations in the index of refraction of the troposphere and in the electron density of the ionosphere. Knowing the stability of the reference clocks, one can gain understanding of these delays through the additional uncertainties which they add. Alternately, they can be studied by using several carrier frequencies. The multifrequency method is particularly interesting as it applies to precise geophysical (length) measurements both between ground stations and satellites and between separated ground stations. Another important area for study involves the magnitude and the stability of delays which can be attributed to system hardware or to interfering signals.

Time Series Analysis

Over the last two decades, the Division has led the development of the statistical analysis of time-series data using the two-sample (Allan) variance. In a preliminary way, these techniques have been applied in other disciplines, e.g., standard volt cells and mechanical gage blocks. It appears that significant insight into the long-term stability of these systems can be gained through these methods. The more common use of the standard deviation is not always justified, particularly where the behavior of systems is observed over long periods (as is done with standards) where assumptions about noise properties are usually incorrect. To take advantage of time-series methods requires further development of the treatment of unequally spaced data. Furthermore, the ideas must be simplified if they are to be widely used.

Optimal Use of Ensembles of Clocks

The NIST time scales are based on an algorithm which intelligently combines the outputs of many clocks to arrive at a smooth time scale which is more stable and reliable than any of the constituent clocks. It is clear that further study and development of such algorithms can improve the robustness of the clock ensemble and yield even better ensemble performance. Research in this area is needed to support comparisons between earth-bound atomic clocks and the regular pulsations of the Millisecond Pulsar. Such comparisons could ultimately result in the detection of gravitational waves.

III. TIME AND FREQUENCY SERVICES

The Time and Frequency Services Group provides the Division's direct support to science, industry, other government agencies and the general public. Division broadcast services, the Frequency Measurement Service, and the Time and Frequency Bulletin all fall within their responsibility. In addition to these on-going services the Group is working on two other projects: synchronization of clocks using two-way satellite time transfer, and timing for space-borne communications nodes. The Group's work is described in more detail below.

Staff:
D. W. Hanson, Project Leader
D. A. Howe
J. L. Jespersen
G. Kamas
M. A. Lombardi
R. E. Beehler (Broadcast Manager)

WWV, WWVB, Ft. Collins	WWVH, Hawaii
J. E. Folley (Part-time)	A. Fabro (Part-time)
J. M. Maxton	E. F. Farrow
J. B. Milton, Chief Eng.	M. Ferguson (Part-time)
C. S. Snider	N. Hironaka, Chief Eng.
A. R. Trevarton	D. Okayama

Convenient access to NIST standards of time and frequency is accomplished for the majority of users through the radio broadcasts of stations WWV, WWVH, and WWVB and a time code broadcast by the GOES satellites. NIST also provides telephone time-of-day services (voice), a new digital telephone service designed for automated setting of computer clocks, publications of time and frequency values of other radio stations as received at NIST, portable clock comparisons and calibrations. Seminars concerning time and frequency metrology are regularly scheduled to acquaint users with techniques for characterizing oscillators and distributing frequency and time signals. Examples of important applications of time and frequency services are given below.

Navigation

Celestial navigators need time to determine their precise location. An error of 2 s could cause a ship to miss its destination by about 1 km. Thus, military and commercial shipping and small boat owners depend in a life and death sense on the availability of the signals from WWV and WWVH. More sophisticated electronic navigation systems such as LORAN-C and the

Global Positioning System (GPS) must maintain time much more accurately. An error of only 3 μs could produce the same 1 km error for the navigator.

System Control and Synchronization

The electric power industry uses both frequency and time information in the management of generation and distribution of electric power. Frequency measurement has been fundamental to the industry for many years and is satisfied by signals from WWVB and GOES. Time is becoming increasingly important in the location and analysis of fast occurring events (faults), measurement of power flow, and the control of systems to minimize losses and avoid outages caused by exceeding stability limits.

Radio and TV stations need accurate frequency to broadcast signals at exactly their assigned frequencies. They need accurate time to set clocks so they can join the networks at the right instant. The aviation and aerospace industries need accurate time for aircraft traffic control systems and for synchronization at satellite and missile tracking stations.

The telecommunications industry needs time accurate to 1 μs and better to synchronize communication's nodes spread over wide geographical areas. Divestiture by AT&T along with the growth of other major carriers poses significant difficulty for synchronous transfer of calls through the interfaces between companies. Increasing data rates in the newer digital communication systems will further complicate system synchronization.

Data Acquisition

The FAA records accurate time on its audio tapes along with the air-to-ground communications from airplanes. Having an accurate record of when particular events occur can be an important factor in determining the cause of a plane crash or equipment malfunction.

Geophysicists and seismologists studying lightning, earthquakes, weather, and other geophysical disturbances need time to synchronously and automatically obtain data from wide geographical areas and to label geophysical events. Other scientists use time for controlling the duration of physical and chemical processes while astronomers use time for labeling astronomical events, such as lunar occultations, eclipses, and pulses.

Science and Metrology

Manufacturers need time and frequency to calibrate counters, frequency meters and test equipment. Accurate spectra of molecules including information on pressure broadening are needed to accurately determine atmospheric concentrations of important pollutants. Laser frequency measurements provide accurate calibration frequencies for spectroscopists and for radio astronomy as well as the means for realization of the meter.

OBJECTIVE: Provide radio and satellite broadcast services.

NIST offers several around-the-clock time and frequency dissemination services to the general public. In 1923, radio station WWV was established by NIST and has been operated since that time. A sister station, WWVH was established in 1948, on the Hawaiian Island of Maui, and relocated to Kauai in 1971. In 1956, WWVB began low frequency broadcasts. WWV's signal is also offered by a telephone, not toll-free, by dialing (303) 499-7111. A similar service from WWVH is available by dialing (808) 335-4363 in Hawaii. Broadcasts from WWV and WWVH can be received on conventional shortwave receivers nearly anywhere in the world. Broadcast frequencies include 2.5, 5, 10, and 15 MHz for both stations and 20 MHz from WWV only. Accuracies within 1 ms can be obtained from these broadcasts if one corrects for the station's distance from the receiver. These services also provide standard frequencies, a BCD time code, astronomical time corrections, and certain public service announcements from other government agencies. The telephone service offers the capability of obtaining NIST time and audio frequency signals. The caller can receive a time signal, accurate to 30 ms or better, about the maximum delay in cross-country telephone lines. WWVB offers a direct path signal of greater accuracy than WWV or WWVH, but a special 60-kHz low frequency receiver is required. WWVB's signal includes a binary coded system, needing special decoding equipment. The WWVB broadcast covers the North American continent. These broadcast services are coordinated with similar operations in other countries through active participation in the international CCIR organization.

NIST time and frequency signals have been relayed through the GOES geostationary satellites since 1975. The GOES broadcast covers North and South America as well as major portions of the Pacific and Atlantic including parts of Europe. More than 10 years of experience has shown that such a system provides continuous time and frequency reception with more dependable propagation characteristics than HF and LF broadcasts. The satellite position broadcast with the time permits automatic correction for variations in path delay resulting in time accuracy of 100 μs.

A new digital telephone service, the Automated Computer Time Service (ACTS), was initiated in March of 1988. This service provides for automated setting of computer and other clock systems with optional compensation (to the 1 ms level) for telephone line delays.

FY 1988 Plans and Accomplishments

Procure and install new energy-efficient transmitters for WWV. This will include acceptance testing at the manufacturer's site and Fort Collins. The objective is to replace outdated equipment and to reduce energy costs. The savings should pay for the transmitters over the course of five years.

Accomplishment - Procurement of the transmitters is complete. The contractor is currently eight months behind schedule and is not likely to deliver and install the new transmitters before October 1988. All necessary preparations for the installation at WWV are complete.

Prepare a final report on the findings of survey of users of services.
<u>Accomplishment</u> - Questionnaire responses from about 6000 users of the various services have been tabulated in a database format. Extensive analysis of the results is nearly complete and the final report should be available early in FY 1989.

After the voice-synthesis equipment becomes operational, perform on-the-air tests of the equipment. Determine acceptability of broadcasts by users and, if successful, investigate options for acquiring additional systems for Fort Collins and Hawaii to replace outdated magnetic recording systems.
<u>Accomplishment</u> - The project has been redefined and rescheduled because: (1) the National Weather Service and DEC reduced their support of the project and (2) the current primary and backup announcement systems, no longer supported by the manufacturer, failed requiring a crash effort to quickly develop alternate systems. The DECTALK-3 equipment has been purchased by NIST and a new engineer at WWVH will explore the potential for an improved announcement system based on it.

Maintain reliable broadcasts from WWV, WWVB, WWVH and the GOES satellites.
<u>Accomplishment</u> - All services operated reliably with down-times of less than 0.1%. The only exception was some degradation of the special Other Agency announcements due to the failure of both the primary and backup recording systems.

Develop documentation for and lead U.S. Study Group 7 (Time and Frequency Services) of CCIR. Head U.S. delegation to 1988 Interim Meetings of the International CCIR Study Group 7. Contribute NIST input to CCIR handbook on satellite timing methods and resources.
<u>Accomplishment</u> - Major NIST accomplishments in standards, time scales, services, new satellite time transfer methods, and laser metrology were documented in appropriate documents of CCIR Study Group 7. For this study group, a series of U.S. preparatory meetings were organized and led by a staff member who also headed the U.S. delegation to the Interim Meetings in April 1988.

<u>FY 1989 Plans</u>

Install, evaluate, and place into regular operation the new transmitters for WWV as soon as they become available from the manufacturer.

Procure and install modern, custom-designed time code generator systems at WWV and WWVH. Implement requested format changes and additions after consultation with receiver manufacturers.

Complete construction, testing, and evaluation of two new voice announcement approaches for other agency announcements on WWV.

Complete final report on the results of the user survey.

Maintain reliable broadcasts from WWV, WWVH, WWVB, and the GOES satellite time code.

Conduct a series of U.S. meetings in preparation for the final meetings of the international CCIR Study Group 7. Provide NIST input to the documents of the study group as well as input on timing methods for a CCIR handbook.

OBJECTIVE: Provide seminars and measurement services on a reimbursable basis.

Frequency Measurement Service

The frequency measurement service is automated, modest in cost, and provides traceability to NIST at a level of one part in 10^{12}. The service is based on common-view reception of low frequency signals from stations such as WWVB or Loran-C. This service provides the user with a data logger and a low frequency receiver which is appropriate to the particular location. A typical system contains a receiver, microcomputer, disc units and printer-plotter. The user provides a dedicated phone line and modem so that the system data can be compared with data recorded at NIST providing assurance that the users reference is accurate. To assist the user in getting the most out of this system, the Division provides training on use of the equipment.

Time and Frequency Bulletin

The Division continues distribution of it's Time and Frequency Bulletin to over 500 service users. The bulletin provides information on the performance of many useful references and notes events and service changes of interest to users. It was expanded to cover new services.

Seminars

The annual Division seminar provides industry and other agencies with information and training on the use of frequency standards. Special effort is made to have the seminar support the introduction of new services and to be of particular interest to the nations's calibration laboratories.

FY 1988 Plans and Accomplishments

Continue operation of the Frequency Measurement Service.

Accomplishment - Operation of the service continues with users now numbering 52. New training and retraining due to transfers and reassignments involved 24 personnel from the user organizations. Primary contact with the users has been maintained through the NCSL.

Provide a comprehensive Time and Frequency Seminar (reimbursable). Develop an improved method for demonstrating time-domain and frequency-domain measurement systems to the large seminar audience.

<u>Accomplishment</u> - The seminar, held on June 14, 15 and 16, 1988, was attended by 33 people. Measurement systems were demonstrated at the Boulder labs, but lectures were given at a local hotel. Better interactions with attendees in the demonstration sessions were provided by reducing the size of the visiting groups. Attendees comments were favorable.

<u>FY 1989 Plans</u>

Continue operation of the Frequency Measurement Service. Modify systems to improve the match to the calibration lab needs.

Provide a comprehensive Time and Frequency Seminar (reimbursable) in 1989. This seminar will be held in conjunction with the Frequency Control Symposium which will be in Denver.

OBJECTIVE: Develop advanced methods for time transfer.

The use of communications satellites for time transfer at all levels of performance appears to be widely accepted. In a recent annual report, the BIPM/BIH urged further development of the concepts. Much of this is due to improvements in the available technology and significant reduction in the cost of components and leased transceivers on satellites. At the higher levels of performance, work reported by Japan and unpublished tests involving NIST, USNO, and COMSAT Laboratories have demonstrated one-half nanosecond time comparison precisions using two-way time exchanges through a satellite and comparable accuracy is expected when all systematic effects are evaluated. Additional tests have indicated that 20 ps comparisons are possible using the same techniques with higher transmission power levels. NIST, USNO and the NRC in Canada have informally agreed to develop a permanent time-transfer network to serve the three laboratories. All of the necessary equipment has been acquired and preliminary tests have begun.

<u>FY 1988 Plans and Accomplishments</u>

Perform two-way time comparisons between USNO, NRC and NIST using a domestic communications satellite.

<u>Accomplishment</u> - During the last 12 months, NIST has been performing two-way time transfer experiments with the U.S. Naval Observatory (USNO) using the SBS-3 satellite. The National Research Council (NRC) in Canada participated in the comparisons for a much shorter period of time. All comparisons achieved a precision of better than 0.5 ns. The comparisons are performed three days each week with 100 seconds of data providing sufficient resolution.

Procure, assemble and license a mobile KU-band earth station for calibration of the two-way satellite facilities of NIST, USNO and NRC.

Accomplishment - A mobile earth station was procured, equipped for two-way calibrations, licensed with the FCC and successfully operated in communication with the 6.1 meter NIST earth station through the SBS-3 satellite.

Begin trans-Atlantic time comparisons following availability of INTELSAT satellite (to be launched).

Accomplishment - The INTELSAT satellite launch was delayed many times until successful launch and positioning at 307° East longitude in mid August. Application to COMSAT to access this satellite has been made. As required by COMSAT, special measurements using the 6.1 meter earth station and this new INTELSAT satellite have been initiated.

FY 1989 Plans

Begin transAtlantic time comparisons using the INTELSAT V(F-13) satellite at 307° East longitude.

Calibrate the NIST and USNO earth stations using the mobile earth station. Include NRC in this calibration if they have received permission to reactivate their time transfer system.

Evaluate the reciprocity of the atmospheric delays in two-way time transfer at the frequency assignment of 14/12 GHz for the Fixed Satellite Service.

Continue development of the two-way time transfer system. Standardize the earth station equipment and operating software.

IV. TIME SCALE AND TIME AND FREQUENCY COORDINATION

This Group has the responsibility for the operation and further development of the NIST time scales and for coordination of these time scales with other timing centers and the International Bureau of Weights and Measures (BIPM). These time scales are, of course, a key responsibility since they not only provide the basis for all services, but also serve as the stable reference against which much of the Division gauges it's research. The Group has developed a coordination scheme based on common view of the Global Positioning System (GPS) satellites which is now the de facto coordination approach for the world.

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OBJECTIVE: Generate NIST time scales UTC(NBS) and TA(NBS).

NIST atomic time is generated from an ensemble of approximately twelve commercial and one laboratory cesium-beam-frequency standards and two laboratory hydrogen masers. The time of all the clocks is automatically measured every two hours with a precision of a few picoseconds. The UTC(NBS) and AT1 time scales are computed following each measurement cycle using a weighted-average algorithm. The small dispersion of the clocks during the two hour interval between measurements makes it possible for NIST to provide UTC(NBS) with 1 ns accuracy at all times. Coordinating with the BIPM, UTC(NBS) is steered toward and kept within 1 μs of UTC. AT1 is a metrology tool, unsteered in time or frequency, and made to be as stable and uniform as possible.

At the end of each month, the TA(NBS) time scale is computed using a Kalman algorithm. This computation is optimum in the statistical sense for clocks having both white frequency noise and random-walk frequency noise, a good model for the clocks in the NIST ensemble. The second of TA(NBS) is steered toward NIST's best estimate of the SI second based on periodic calibrations of the ensemble by the primary frequency standard, NBS-6.

FY 1988 Plans and Accomplishments

Test and document the performance of the NIST Time Scales in order to evaluate their performance for the most stringent of measurements, e.g. comparisons with the millisecond pulsar.

Accomplishment - NBS(AT1) has been documented to be more stable than International Atomic Time (TAI) for sampling times out to a year. UTC(NBS) has been kept within the one microsecond goal and has been documented as sufficiently stable for all uses except for the measurements on the millisecond pulsar PSR 1937+21. In cooperation with other laboratories a significant humidity dependance of the frequency of commercial cesium beam frequency standards has been documented. This effect could cause an annual term of a few hundred nanoseconds in UTC.

Contingent on the availability of funding, proceed with the acquisition of a new time-scale computer.

Accomplishment - The bid process has been completed and a delivery date of December 1988 has been set. Preparation for installation of the computer is now in process.

Complete the semi-rigid coaxial connections for both the back-up and the primary measurement systems and implement necessary software adaptations.

Accomplishment - The primary and back-up measurement systems have been reworked (including replacement of coaxial cables) and both systems are now being used to archive time scale data. Further modifications of the software will now await installation of the new time scale computer.

Train several Division staff on the De Marchi alignment techniques for commercial cesium standards.

Accomplishment - Evaluation of alignment procedures has not yet been completed, so this task has been delayed.

FY 1989 Plans

Study use of the cooled-beryllium ion standard in providing periodic calibration of the NIST time scales at the targeted accuracy of 1×10^{-14}.

Finish the installation and put into operation the newly acquired time-scale computer and supporting work stations.

Develop plans for acquisition of advanced clocks for the time scale in order to improve stability and reliability.

Continue with the De Marchi C-field tuning experiments to improve performance of cesium standards in the NIST time scales.

Prepare the proceedings for the Third International Atomic Time Scale Algorithm Symposium and continue with atomic time-scale algorithm research and development.

OBJECTIVE: Maintain international time and frequency coordination.

A satellite-based, time-transfer system developed by the Division is now in operation. Receivers are operating at: PTB in Braunschweig, West Germany; LPTF and OP in Paris, France; Goldstone, California; Madrid, Spain; Canberra, Australia; NRC in Ottawa, Canada; IEN in Torino, Italy; CRL, NRLM and TAO in Tokyo, Japan; VSL in Delft, The Netherlands; NPL in England; NPL in Israel; CSIRO in Australia; TUG in Austria; USNO in Washington, D.C.; and NIST in Boulder. A computer-based, automatic-data-collection network acquires data from the receivers. This data is combined with data from the NIST Atomic Time Scale so that the time of the remote clock is known with respect to UTC(NBS) to a precision of better than 10 ns after one day of averaging. The Jet Propulsion Laboratory employs three receivers developed by NIST in the same mode to provide frequency calibrations at a few parts in 10^{14} between the sites of the NASA Deep

Space Network. The GPS receivers at most of the national timing centers now transfer their data via the common-view technique to the International Bureau of Weights and Measures (BIPM) in Sevres, near Paris. This new system has replaced Loran-C as the principal time and time-interval transfer link for the SI second and the generation of the International Atomic Time Scale (TAI).

FY 1988 Plans and Accomplishments

Cooperate with BIPM, USNO and the Naval Research Laboratory on calibration and evaluation of GPS receivers for optimum time and frequency transfer.

Accomplishment - A NIST calibrated receiver was carried to USNO where NRL brought their calibrator; then it was carried to some key sites in Europe including the BIPM to which NIST loaned a receiver two years ago. The delay change over two years was less than two nanoseconds.

Assist other national timing centers as appropriate with the use of GPS common-view time transfer.

Accomplishment - A NIST receiver was carried to Japan in June and, for the first time, a measurement of the accuracy of GPS common-view transfer was completed with three Japanese laboratories. The NIST GPS common-view technique has been widely accepted and a cooperative, internationally authored paper has been published. Cooperation among international timing laboratories has been excellent.

Develop the hardware and software needed to implement major improvements in GPS common-view time transfer including evaluation of system biases.

Accomplishment - The software was developed and the results of the analysis documenting some of the biases in the GPS Kalman state estimates were reported at an international conference. Above the level of 1×10^{-15}, the biases are not significant for long-term clock comparisons. The hardware portion of this effort is not yet complete.

Develop software to further streamline and automate international time comparisons with the goal of weekly estimates of the world time ensemble.

Accomplishment - Periodic analysis of the GPS common-view data base has led to several important insights. Evidence of non-zero correlation terms between two of the new Hewlett Packard mercury ion frequency standards built for USNO were found. Evidence of similar correlation problems indicating existence of an annual term between the two primary cesium beam standards at the PTB were also found. The BIPM developed a special, retrospective scale which has been helpful in documenting an upper limit of about one part in 10^{14} to the stability of the millisecond pulsar. Since the primary standards at PTB are heavily weighted in this special scale, there is the possibility that it also has an annual term.

Additional Accomplishment - At the last CCIR meeting, the US made a recommendation that the time scales (UTCs) of all participating countries be synchronized with UTC to within one microsecond. The previous guideline was one millisecond. The recommendation, which was made possible by development of the GPS common-view concept by NIST, was accepted by Study Group 7 and should be formally approved by CCIR next year.

FY 1989 Plans

Work with Lewandowsky of the BIPM (who will be a guest researcher for six months of this FY) to develop means for more efficient use of GPS common-view time and frequency transfer to take advantage of the future addition of new GPS satellites.

Cooperate with PTB and BIPM in the determination of the source of possible annual terms in the respective time scales.

Compare the NIST time scales with other research clocks to determine relative performance. Use the comparisons as the basis for development of a global research time scale to be used in study of the millisecond pulsar.

OBJECTIVE: Develop metrology for precise time, frequency and length measurements.

Techniques for Measurement of Frequency and Frequency Stability

The Division has been a world leader in the development and dissemination of the measures of frequency stability and their practical implementation. The Division developed the de facto international standard for practical specification of frequency stability and played a major role in the development and test of the dual-mixer concept for measuring time, frequency, and frequency stability providing for simple, precise (picosecond) measurement of the difference between state-of-the-art frequency standards. Work on the effects of phase noise on frequency multiplication provided an explanation for the many previous failures at precision infrared synthesis. This new understanding of the multiplication process then stimulated considerable improvement in the phase noise of crystal oscillators and signal processing equipment. In the rf region, the lowest noise crystal oscillators, buffer amplifiers, isolation amplifiers, and frequency multipliers presently available are a direct outgrowth of prototype designs and analysis developed at NIST. These low noise devices have many applications in precise measurement as well as in the development of new frequency standards such as the passive hydrogen maser, the stored ion standard, and cesium standards.

Techniques for Characterizing Noise in Clocks

Memory of the rate of the primary standard is stored in a time scale, an ensemble of commercial cesium standards. The clocks in the time scale don't have the accuracy of NBS-6, but they do have very good frequency stability. The stability of a clock ensemble can be improved by increasing the number of clocks, by improving the stability of individual clocks, by wisely utilizing the clocks available, or by a combination of these approaches. The Division has chosen to use a modest number of clocks ensuring sufficient reliability, redundancy and variety (to avoid systematics from a particular manufacturer), but then to characterize the clocks with enough care so that the algorithms which average the clocks make optimum use of the performance of individual members of the ensemble.

The algorithms which control the time scale have evolved to their current state through considerable work over a long period. UTC(NBS) is generated by an algorithm which can be traced back 20 years. In order to estimate the performance of this algorithm, several studies were conducted. Using Kalman filters, a method was developed to model atomic clocks and obtain maximum likelihood estimates of the model parameters from data on the ensemble of clocks. Tests for the validity of the model and confidence intervals for the parameter estimates were made and shown to be statistically correct. A study was then made of the statistical significance of frequency drift and this yielded additional important insights. A second major development was a Kalman (or recursive) algorithm for estimating time from the ensemble of atomic clocks. The algorithm allows for the addition or deletion of clocks and provides for automatic error detection and correction. This Kalman algorithm is now used to generate the time scale TA(NBS). During this effort the earlier algorithm which generates UTC(NBS) was found to be very near optimum in its performance. Over the last year it's stability was shown to be of the highest order as it was found to be the most stable reference for the characterization of the stability of the millisecond pulsar.

FY 1988 Plans and Accomplishments

Evaluate the NIST time scales and algorithms to ensure confidence in measurements such as comparisons with the millisecond pulsar.

Accomplishment - Because the stability of NBS(AT1) measured against other time scales and the millisecond pulsar has been so good, effort has been placed on understanding just why this is so. It appears that an important feature of the algorithm contributing to this performance is it's adaptive nature which allows it to deal with changes in clock performance induced, for example, by environmental perturbations. Another feature of consequence is the detection of frequency steps in each clock and the associated process of reducing the weight of an individiual clock to limit the effect on the scale. Working with two other groups on their time scales, the advantages of this algorithm were substantiated and the results published.

If funds and staff are available, continue study of the use of time-series-analysis techniques in other disciplines. A joint proposal with the Statistical Engineering Division was made to management on this subject.

Accomplishment - Funding for this project was not available.

Additional Accomplishment - An IEEE subcommittee has written and approved a new standard on the characterization of frequency stability. Staff members from NIST participated in a major way on this committee. The standard was circulated widely for comments and published in a conference proceedings. It is now before the IEEE for approval.

Additional Accomplishment - The dependance of the frequency of the NIST ensemble clocks on relative humidity was measured and found to be significant. Humidity control was installed on one of the two clock chambers. The second chamber still needs to be controlled.

FY 1989 Plans

Continue support of adoption by IEEE of the frequency stability characterization standard.

Continue study of the influence of environmental factors on the NIST time scales and those of other laboratories.

Study short term performance of the NIST time scales and consider options for improvements.

OBJECTIVE: Provide seminars and measurement services on a reimbursable basis.

Global Time Service

The Division now offers a service, based upon a NIST designed receiver, which provides for highly precise time and frequency transfer to a users site. A receiver, located at the users facility, communicates data automatically to an NIST computer which stores the data, determines which data elements are suitable for time-transfer calculations and provides an optimally filtered value for the time and frequency of the user's clock with respect to the NIST Atomic Time Scales. The user is given an account on the NIST computer through which he can access the results of the NIST analysis. Tests between receivers in Colorado, Canada, Germany, France, Spain, Washington, DC and California have demonstrated time comparisons with precisions of better than 10 ns using an averaging time of 13 minutes and frequency comparisons with a precision of 1 part in 10^{14} for averaging times of four days.

Calibration of Atomic Standards

In conjunction with development of the time scale algorithms the Division has developed a time and frequency measurement system with exceptional performance. Clocks are now calibrated and characterized through comparisons with the ensemble clocks using the same measurement system which reads the ensemble clocks. This system is used as a reference for research within the Division as well as for reimbursable calibrations.

FY 1988 Plans and Accomplishments

Expand the time scale measurement system to allow for additional input ports for clock calibrations.

Accomplishment - The twenty-four-hour-clock-back-up system was completed and tested. Additional computer software supporting this back up needs to be written. This will done when the new time scale computer is installed.

Continue participation on GPS committee with the goal of minimizing the effects of GPS degradation on the transfer of time and frequency.

Accomplishment - Through a system called selective availability, GPS management plans to intentionally degrade the performance of the GPS signals. A civil GPS service (CGS) committee has been organized to coordinate with DOD in order to minimize the effects of S/A on the civil sector. The Division representative to this committee has played a key role in formulating recommendations which will be incorporated in a more general DOD document on GPS use. The committee recommendation provides for access which would not degrade the accuracy of time transfer. Through the efforts of this representative, an additional representative from BIPM was added to the committee. Final decisions on the committee recommendations have not yet been made.

Develop and implement methods for eliminating or minimizing bias effects which have been identified in GPS measurements.

Accomplishment - Two papers documenting the biases in GPS have been presented and published. These papers describe proposed methods for resolving the problems. Some of the solutions have been implemented.

FY 1989 Plans

Continue work on the CGS steering committee to minimize the impact of GPS selective availability on the civilian uses of the system.

Continue work on a ionospheric calibrator in order to increase the common-view ,time-transfer accuracy.

Increase the capacity of the time scale measurement system to accommodate additional time scale clocks and to allow for more special calibrations.

OBJECTIVE: Advise industry and government agencies on time and frequency metrology.

FY 1988 Plans and Accomplishments

Continue to assist the Joint Program Office at Air Force Space Division on methods for GPS time steering.

Accomplishment - The steering is now being successfully implemented.

Provide consultation to Israel supporting the request for assistance in implementing the NIST UTC steering approach on their time scale.

Accomplishment - With consultation from NIST the Israel National Physical Laboratory has developed the measurement system and the software to proceed with software construction and the steering of UTC(INPL).

Assist the Joint Program Office with consultation on proper methods for utilizing clock ensembles and combining algorithms to improve reliability and stability of the GPS reference systems.

Accomplishment - The hardware and software for ensemble measurements and clock operation for the master control station for GPS has been installed by NRL. It is patterned after the NIST system.

Additional Accomplishment - In anticipation of the need for establishing a GPS ensemble time for cross-link ranging, NIST studied a clock ensemble composed of clocks on the available GPS satellites. The frequency stability of this ensemble was shown to be better than that of many of the international timing centers, and, because this ensemble is not subject to the same set of environmental effects as those that affect earth systems, this clock ensemble has proved to be a very useful metrology tool.

FY 1989 Plans

Provide measurement support and advice to the AF Space Division and the Master Control Station for GPS on the performance of the Block 2 satellites as their launch sequence starts in December of 1988.

Prepare a review paper on the AT1 algorithm and its philosophy of construction in response to rising interest on the subject.

Study the effects of a variety of measurement conditions on time-domain data analysis as part of an effort to properly treat the problem of unequally spaced data in a time series.

Serve as general chairman of the 1989 Frequency Control Symposium to be held in Denver.

V. PHASE NOISE AND HYDROGEN MASERS

In past years, the primary goal of this Group has been the development of a passive hydrogen maser with good medium-term to long-term stability for DOD requirements and for use in the NIST clock ensemble. The project, which was funded by the Navy, has been quite successful. Two masers are currently operating in the ensemble and they have been out-performing the commercial cesium standards by a wide margin. The maser technology has been transferred to industry through the Industrial Research Associate Program. The project has also addressed other issues of importance to the Division. These include: line-center errors in high-performance servo systems and phase noise in frequency multipliers and synthesizers.

More recently the program emphasis has shifted to measurement of phase noise where emerging technology is pushing the state of the art. The Group has just made a long-term commitment to the Department of Defense to develop and demonstrate phase-noise measurement systems in the microwave and millimeter-wave regions of the spectrum. This work should result in improved measurement systems for NIST and lower-phase-noise, microwave and millimeter-wave synthesis to support development of primary standards as well as frequency synthesis into the optical regions of the spectrum.

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OBJECTIVE: Generate NIST time scales UTC(NBS) and TA(NBS).

Active hydrogen masers have long been touted for their excellent short-term stability, but long-term stability has generally been poor. The NIST maser project has focussed on improving long-term stability in a passive maser which is simple and small. The goal has been a system which will fit into a package equivalent to that of a commercial cesium standard.

The results obtained have been quite good. The best of these masers provides medium-to-long-term stability equivalent to that of a cesium ensemble of approximately 20 high performance tubes. The fundamental design advance has been the servo locking of the physical cavity resonance to the hydrogen reference. The system also locks the slave oscillator to the same atomic resonance. The obvious conclusion is that the long-term stability of active hydrogen masers has been severely degraded by cavity pulling effects and that variations in the wall shift are extremely small relative to the present accuracy of primary standards.

FY 1988 Plans and Accomplishments

Through the Industrial Research Associate Program, test the performance and environmental sensitivity of the commercial passive hydrogen maser.

Accomplishment - The electronics for the commercial system was evaluated for several months and several small problems were found. Further engineering work is needed to achieve the full potential performance. When this is completed we will finish the evaluation.

Pursuant to positive results in the above tests, purchase a commercial passive hydrogen maser for the time scale.

Accomplishment - No action taken since development work is not complete.

Continue to assist the Cesium Group in the design of accurate servo systems for NBS-7. This will include the evaluation of new modulator(s).

Accomplishment - We have assisted in the development of systems for generating low-distortion reference signals needed for testing of phase modulators. We have also assisted with a concept for a phase modulator which uses the frequency shift of a SC-cut resonator with electric field. Most of the electronics including the ovens have been design, built and are nearly ready for full evaluation. We have developed new software for evaluating and optimizing servos for new frequency standards. This software allows one to compute the frequency stability for various servo designs or to calculate the frequency stability of standards from the measured phase noise data. We have also developed a new understanding of the effect of high frequency noise in passive frequency standards and how to reduce its influence on the measured frequency or timing stability.

FY 1989 Plans

Finish testing of the sine wave phase modulator. If satisfactory, construct several units for use in NBS-7 and other cesium standards. If unsuccessful we will probably go to slow, square-wave-frequency modulation.

OBJECTIVE: Provide seminars and measurement services on a reimbursable basis.

Measurement of Phase Noise

The improved phase stability of components developed for the passive maser have enhanced the Division capability to provide special calibrations of phase noise in oscillators, amplifiers, frequency multipliers and synthesizers from 5 MHz to 700 MHz. The new DOD contract for development of phase-noise metrology through the microwave and into the millimeter-wave region will permit increased automation of measurements. The goal is to eventually cover the region from 5 MHz to 60 GHz for oscillators, amplifiers, multipliers, dividers and synthesizers. The emphasis will be on the development of sound measurement methodology and transfer of this methodology to industry and government laboratories.

FY 1988 Plans and Accomplishments

Complete automation of the 5 MHz to 1 GHz, phase-noise-measurement system to include an automated calibration of the accuracy to approximately ±1 dB.

Accomplishment - We have developed a new concept for measurement of phase noise using a new phase modulator. A patent disclosure has been submitted for evaluation. This new phase modulator permits us to achieve accuracies of better than ±0.6 dB over this entire band. The automation has been demonstrated, but full implementation will not be realized until early in FY 89. This may be the most significant advance in this field in the past 20 years.

Complete automation of the 1 GHz to 26 GHz, phase-noise-measurement system.

Accomplishment - See above. The accuracy at 10 GHz is now better than ±0.6 dB out to 500 MHz from the carrier and about 1.5 dB at 1 GHz from the carrier. This is to be compared to the best commercial systems with accuracy of 2 to 6 dB with Fourier frequency range of 40 MHz.

Assemble and test a 33 GHz to 50 GHz, phase-noise-measurement system with a 1 GHz bandwidth. The accuracy goal is ±1 dB to 30 MHz and ±2 dB to 1 GHz.

Accomplishment - This system was completed. The accuracy is similar to that of the 1 GHz to 26 GHz system described above. Automation of the system will be completed soon.

Build and test a multiplier system to lock the 10.6 GHz microwave oscillator to a quartz oscillator at 100 MHz. The 100 MHz oscillator will then be phased locked to a 5 or 10 MHz oscillator for normal analysis.

Accomplishment - The prototype has been successfully tested. We are now mounting it in a magnetically shielded box for further evaluation.

Additional Comment - We have discovered that there is little or no documentation on the statistical uncertainty for phase noise measurements except for the case where the frequency noise is white. A small study contract was let to investigate this question.

FY 1989 Plans

Complete documentation and automation for the systems covering 5 MHz to 1 GHz, 1 to 26 GHz, and 33 to 50 GHz.

Deliver prototype phase-noise-measurement systems to DOD sponsors for evaluation.

Fabricate an additional 10.6 GHz oscillator system for frequency synthesis.

Investigate the statistical uncertainty of phase noise measurements as a function of the number of measurements. This will establish the uncertainties in a way similar to that used for $\sigma_y(\tau)$ and help standardize the uncertainty as reported by various laboratories and vendors.

OBJECTIVE: Establish the second and meter for the International System.

FY 1988 Plans and Accomplishments

Assist the Frequency Synthesis Group with development of synthesis systems connecting the microwave region to the optical region.

Accomplishment - We successfully multiplied a 72 GHz klystron signal, phase locked to the low-noise 10.6 GHz source, to 2.25 THz using a thin-film Schottky diode. The signal-to-noise ratio was 47 dB in a 3 kHz bandwidth! At lower frequencies we demonstrated frequency multiplication by as much as 201. Both accomplishments are very important in developing robust frequency synthesis from the microwave to the optical region. For further details see section VIII.

FY 1989 Plans

Investigate phase locking of Gunn diodes. These are much noisier than klystrons but last longer and are easier to use because voltages are lower.

Study concepts for multiplication to 4.25 THz.

OBJECTIVE: Advise industry and government agencies on time and frequency metrology.

Hydrogen Maser Technology

The passive hydrogen maser developed at NIST with partial military funding has demonstrated exceptional frequency stability from a few seconds to a few weeks. Based on 2 months of data, the stability is $\approx 5 \times 10^{-15}$ at 1 day and $\approx 3\text{x}10^{-15}$ at 8 days. At a level of resolution of $\pm\ 3\text{x}10^{-16}$/day, the drift is not observable. The time dispersion per day is a factor of 4 to 5 times better than the best available commercial cesium frequency standards. Several Industrial Research Associates have worked with NIST on this program. This cooperation continues and the first passive hydrogen maser to be constructed in this collaboration is now in operation.

Quartz Crystal Resonators

Vibration sensitivity is presently one of the most severe difficulties encountered when using a frequency standard in non-laboratory environments. Although NIST no longer has an experimental quartz crystal research program, consulting support is being provided to the U.S. Army and its industrial contractors. A new method for temperature control of clocks which was developed in the hydrogen maser project would appear to offer promise for quartz resonators. Interactions with industry on this concept will continue.

The Division has provided support to the quartz industry's effort to develop standards permitting interchangeability of quartz oscillators. Two workshops on the subject were organized in Boulder and the result appears to be a rather simple measurement procedure based on impedance measurements using commercial coaxial standards as references. The method provides full traceability to National standards and forms the basis for solid U.S. leadership in the development of standards at the international level.

Phase noise

With the initiation of new work on measurement and control of phase noise, the Division is providing significant consultation on the subject to science, industry and other government agencies. The Division has a clear opportunity to provide a solid basis for phase noise metrology.

FY 1988 Plans and Accomplishments

Continue consultation with industry and governmental agencies on methods for measurement and control of phase noise.

Accomplishment - We have modified a commercial quartz oscillator to hold the humidity and pressure approximately constant. We achieved a frequency stability of 3 x 10-13 for measurement times from 0.03 s to 21 d. This demonstrates that the random walk frequency noise can be removed at least for measurement times out to 21 days for the one particular oscillator. Additional tests on other oscillators show improvements in long-term frequency stability by factors of 2 to 10. This modifies our basic understanding of noise in quartz resonators. This should be very important for many communication and satellite application where power and weight requirements exclude use of atomic standards.

FY 1989 Plans

Assist government laboratories and industry in implementing the new NIST concept for high accuracy phase noise measurements.

VI. ATOMIC BEAM STANDARDS

This Group is responsible for operation of the current primary frequency standard, NBS-6 and the development of NBS-7, the next generation primary frequency standard which will be based on optically pumped cesium.

The objective is a standard which can be easily operated in a nearly continuous mode with semi-automatic assessment of systematic errors at an accuracy level of 1 part in 10^{14}. The project is built upon successful tests of the concept on field-size standards pumped by laser diodes.

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OBJECTIVE: Establish the second and meter for the International System.

Operation of the U.S. Primary Frequency Standard

Since 1968 NIST has designed and developed three new cesium devices: NBS-4, NBS-5, and NBS-6. NBS-4 has a medium-length cavity of 50 cm, and was built to test new ideas for improving the stability of cesium devices. This standard is one of the most stable cesium clocks in the world, achieving a stability of $7\text{x}10^{-15}$. It should be noted here that no previous NIST cesium frequency standards directly drove a clock; instead, they were used periodically to calibrate the frequency of an ensemble of commercial cesium clocks that. NBS-4, because of its excellent stability, has served as a working clock in the time-scale ensemble.

NBS-5 was built on the framework of NBS-3 and in turn served as the basis for NBS-6, completed in 1975. The refinements incorporated include greatly improved components to provide narrower resonance lines (25 Hz), the ability to reverse direction of the atomic beam (which allows errors due to asymmetries in the cavity to be diagnosed), and other features aiding analysis of performance. NBS-6 has an accuracy of $8\text{x}10^{-14}$; more accurate but not quite as stable as NBS-4. Used together, these two standards generate the U.S. standard second. A clock ensemble is used to carry the second forward in real time so that it is continuously available.

FY 1988 Plans and Accomplishments

Complete current evaluation of NBS-6.
Accomplishment - The evaluation of NBS-6 was completed early in FY88.

Recharge NBS-4 with cesium and bring it back into operation.
Accomplishment - The cesium oven was recharged and the beam optics were realigned. The signal level, background and resonance symmetry

are now better than they have been for years. There are still some problems with the servo system. The priority on development of NBS-7 precludes full time work on this system, but it will be completed and returned to service as time allows.

Study potential reduction of the uncertainty specification on NBS-6 and determine the advisability (limited resources) of attacking this project.
Accomplishment - The work on NBS-7 and NBS-4 has been more time consuming than expected forcing a delay in this task.

FY 1989 Plans

Complete work on NBS-4 and return it to service in the time scale.

Study potential reduction of the uncertainty specification on NBS-6 and determine the advisability (limited resources) of attacking this project.

Initiate another evaluation of the systematic uncertainties in NBS-6.

OBJECTIVE: Perform research and development on new primary frequency standards.

Primary Cesium Standard Development

The known limitations to the accuracy of NBS-6 lie with the microwave cavity phase shifts, exacerbated by the velocity dispersive nature of the state selection magnets. In addition, there are unknown shifts of the cesium clock frequency associated with systematic effects which cannot be readily studied in conventional systems. Replacing the magnets in a cesium standard with optical pumping and detection using laser diodes should allow the reduction of cavity-phase-shift uncertainties, and permit a better understanding of the limitations of cesium standards. A small laboratory version of the optically-pumped, cesium-atomic-beam frequency standard has been constructed and performance demonstrated at $\sigma_y(\tau) < 7\text{x}10^{-12}\tau^{-\frac{1}{2}}$.

A larger test bed for the optically pumped standard has been designed and the major components have been fabricated and assembled. This test bed will serve as the basis for NBS-7. The system features a longitudinal C-field and a novel Ramsey cavity which minimizes errors caused by distributed cavity phase shift. The optical pumping concept provides the means for minimizing errors due to end-to-end cavity phase shift.

FY 1988 Plans and Accomplishments

Complete integration of all of the clock subsystems.
Accomplishment - We have constructed a prototype demodulator which meets the stability and offset specifications. A modulation drive source has been developed and it meets the system requirements (47 Hz

sine wave with second harmonic 140 dB below the fundamental). The modulator has proven to be more difficult. We have constructed our third generation modulator and it awaits testing. Most other components of the system are complete and the integration of these components has started.

Determine the signal-to-noise performance and stability for the various optical pumping schemes.

<u>Accomplishment</u> - Using a small test bed at NIST and in joint experiments at the National Research Laboratory of Metrology (Japan), the optical-feedback-stabilized lasers and the fluorescence collection optics have been shown to perform adequately, that is, to permit realization of the full noise performance of the system. These experiments constitute the first such demonstration of the concept.

Initiate evaluation of the systematic uncertainties of the standard.

<u>Accomplishment</u> - Several delays in procuring components, in having machine work done, and in adequately electrocleaning the vacuum chamber have prevented the assembly of the complete system.

Initiate test of servo system concepts for locating the line center.

<u>Accomplishment</u> - This test cannot be performed until the standard is assembled.

<u>FY 1989 Plans</u>

Electronics. Complete development of and test the final prototype linear modulator. Fabricate the package for all of the electronic subassemblies. Fabricate the final servo electronics for control of the lasers.

Lasers. Complete final design of and fabricate the laser housings. Assemble the latest version of the optical-feedback-stabilized lasers for use in optical pumping and optical detection in the system.

Beam Tube. Complete assembly of the beam tube. Initiate evaluation of the light-shift and Majorana effects.

OBJECTIVE: Advise industry and government agencies on time and frequency metrology.

<u>Cesium Beam Technology</u>

Recent advances in cesium beam technology, including the optical pumping concept, could improve the performance of commercial devices. For example, this research could improve both the long-term stability and the reproducibility after turn-on of satellite based cesium clocks. These improvements involve the use of laser diodes, cesium heat pipe ovens, optical pumping, and fluorescence detection of atoms. In addition, with the assistance of a guest researcher, the Division has identified methods for improving performance of commercial standards through optimal tuning.

Much of this work is performed under contract from other government agencies. In addition, the Division has formed an Industrial Research Agreement with a manufacturer of cesium clocks. This agreement permits the transfer of NIST research results to the private sector, and also brings guest scientists from industry to the NIST laboratories.

FY 1988 Plans and Accomplishments

Continue collaboration with industry on the development of optically pumped cesium standards.

Accomplishment - As the optical pumping techniques have matured, Division interactions with industrial research projects has decreased. We continue to serve as technical consultants for DOD sponsored work.

Complete fabrication and testing of the hybrid recirculating oven.

Accomplishment - The design for this system is complete and the parts have all been ordered. Assembly will be initiated when other components of the beam tube and electronics are near completion.

Contingent on funding, develop improved methods for optimal tuning of commercial frequency standards and study the application of third-order-servo systems as a means for completely eliminating Rabi-pulling effects.

Accomplishment - Only part of the funding for this project was received. A study of the reliability and durability of the special tuning is in progress. The study of the third-order servo has not yet been started.

FY 1989 Plans

Continue collaboration with industry and government agencies on the application of optical pumping methods to field standards.

Complete fabrication and testing of the hybrid recirculating oven.

Test a commercial version of the recirculating oven.

Continue development of methods for improving the performance of commercial cesium standards. This includes direct methods for reducing Rabi-pulling effects and the study of the third-order-servo system.

VII. ION STORAGE

The long-term plans for primary frequency standards for the Division involve an eventual shift to ion storage and radiative cooling. For the present, the effort of this Group is being directed toward study of the physics of the concepts. The Group has already demonstrated a Be^+ ion clock which operates at a performance level equal to that of NBS-6, the present primary standard. While the focus of the work is ion standards, the techniques are also applied to other problems of fundamental interest.

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OBJECTIVE: Perform research and development on new primary frequency standards.

Atomic Clock Based on Stored Ions

As a step towards realizing a primary frequency standard based on stored ions, the Division has developed a clock based on a ground state hyperfine transition in $^9Be^+$. The combined uncertainties in all systematic frequency shifts (such as those due to Doppler effects) have been demonstrated to be at the same level as those of the present U.S. primary time standard, NBS-6 which has an uncertainty of about one part in 10^{13}.

In these experiments, a few hundred $^9Be^+$ ions were confined in a Penning trap and laser cooled to temperatures less than 1 K. An oscillator was locked to a magnetic-field-independent hyperfine transition (~ 300 MHz) using an optical-pumping, double-resonance technique. The measured stability was about equal to that of a commercial cesium clock. Frequency stability and accuracy performance can be improved in the future by using an ion with a higher hyperfine frequency.

Farther in the future, it appears that the most accurate clocks will be based on optical transitions in atoms or molecules. The main reason for this conjecture is that the Q's for such transitions can be extremely high ($Q \geq 10^{15}$). With this in mind, the S→D quadrupole transition in Hg^+ has been studied. The transition was observed for the first time in a miniature rf trap on a single Hg^+ ion. The present linewidth is limited by magnetic field instabilities which broaden the line, but this transition has a fundamental Q of about 0.5×10^{15} (radiatively limited).

Trapped Ion-Cloud Studies

Studies are made of ion dynamics and the relation of these dynamics to trap design. It appears that the principle limitation to accuracy of a frequency standard based on many ions stored in a Penning trap will be the uncertainty in the second-order-Doppler (time-dilation) frequency shift due to the rotation of the ion cloud. This rotation is a non-thermal effect and is independent of the internal temperature of the cloud. Therefore, detailed studies of ion-cloud temperature, density and rotation are being made using a two-laser, optical-optical, double-resonance technique.

A new concept for a frequency standard based on "sympathetic cooling" is being studied theoretically and experimentally. In sympathetic cooling, one ion species is cooled by Coulomb coupling with another ion species which is laser cooled. This was proposed and demonstrated (on the Mg^+ isotopes) a few years ago at NIST and has now been studied in more detail using Hg^+ and Be^+. The advantage is that the "clock" ions can be continuously cooled, but ac Stark shifts from the cooling radiation can be made negligibly small. This should result in substantially narrower linewidths (less than 1 mHz) and reduction of errors due to the second-order Doppler shift.

FY 1988 Plans and Accomplishments

Improve the spectral purity of the 282 nm source for the Hg^+ optical frequency standard. The basic approach is to frequency stabilize an existing laser to an ultra-stable, high-Q cavity.

Accomplishment - The laser system has been locked to a well-isolated cavity to a precision of 1 Hz. The spectral purity of the laser will therefore be governed by the stability of the cavity. Measured linewidths on the $^{198}Hg^+$ S→D transition (1.07×10^{15} Hz) are about 3 kHz, but are limited by magnetic field fluctuations. We are now switching to $^{199}Hg^+$ where field-independent transitions exist.

Make first measurements of field-independent hyperfine transitions in $^9Be^+$ or $^{25}Mg^+$ with the new Penning trap in the superconducting magnet. The goal is an accuracy exceeding one part in 10^{13}.

Accomplishment - $^9Be^+$ was sympathetically cooled by simultaneously stored-and-cooled $^{26}Mg^+$. A $^9Be^+$ linewidth of 0.0009 Hz was observed. The signal-to-noise ratio was improved by approximately a factor of 10 by using a laser/rf, quadruple-resonance scheme. These results should eventually provide for an order-of-magnitude increase in the stability and accuracy of the $^9Be^+$ clock which was studied previously.

FY 1989 Plans

Lock the local oscillator to the $^9Be^+$ hyperfine transition and evaluate all systematic effects.

OBJECTIVE: Perform basic studies in areas related to future frequency standards.

As an outgrowth of studies on ion clouds stored in Penning traps for possible frequency standard application, several closely related basic studies have been undertaken. Two examples are given below.

Search for Spatial Anisotropy

Frequency standards, including those based on atomic or nuclear (Mossbauer) transitions, have traditionally played an important role in testing gravitational theories. One example is measurement of the gravitational red shift. In addition, the very high resolution attained in trapped ion spectroscopy enables other sensitive tests of the Einstein Equivalence Principle (EEP). As a test of the EEP the frequency of the $^9Be^+$ "clock" transition $(M_J = 1/2, M_I = -3/2) \rightarrow (M_J = 1/2, M_I = -1/2)$ has been compared to the frequency of a passive hydrogen maser to see if a correlation can be found with orientation in space. With a resolution better than 0.1 mHz, no variation was observed. These results decreased previous experimental limits by a factor of 300, but were superceded by work at the University of Washington. A projected gain of a factor of 1000 over our previous measurements should be achievable using $^{25}Mg^+$ or $^9Be^+$ in the superconducting magnet. Such measurements are a fairly easy extension of searches for systematic frequency shifts in an ion frequency standard.

Non-Neutral Plasmas

In the language of plasma physics, the ion clouds in a Penning or rf trap comprise a one-component, non-neutral ion plasma. In a small plasma of laser cooled $^9Be^+$ ions stored in a Penning trap, we have observed behavior which is indicative of the liquid state. In this case the Coulomb coupling constant Γ was as high as 100. Calculations predict that at $\Gamma \simeq 2$, the pair correlation function should begin to show oscillations characteristic of a liquid, and at much larger values of Γ ($\Gamma \simeq 170$) crystallization may take place. In our experiment a second laser was used to probe the ion plasma and measure the temperature of the ions from the Doppler broadening of the optical probe transition. The ion number density was determined by measuring the (ExB) cloud rotation frequency. Because the trap electric field and magnetic field were known, the space charge electric field was extracted from the cloud rotation frequency and used to determine the ion number density. Ion number densities of $\approx 2 \times 10^7/cm^3$

and temperatures of ≈ 10 mK produced values of $\Gamma \simeq 100$. Values of Γ large enough to observe a liquid-solid phase transition should be accessible in future versions of this experiment. If the theoretical cooling and density limits can be obtained, values of Γ as large as 15,000 are perhaps possible for Be^+ ions. Because experimental information on three-dimensional, strongly-coupled plasmas is almost non-existent, these experiments can provide some useful tests of the theoretical calculations. The development of a clear understanding of ion-cloud dynamics is fundamental to the estimation of systematic errors in frequency standards arising from motions of the ions.

FY 1988 Plans and Accomplishments

Hg^+ Single Ions. (1) Initiate sideband cooling studies to reach the zeroth quantum level. (2) Complete studies of lifetime and branching ratios using quantum-jump spectroscopy. (3) Investigate the spectrum of pseudomolecules formed by two or more ions in a trap. (4) Develop narrower laser linewidth for higher resolution studies of quadrupole resonance.

Accomplishment - (1) A single $^{198}Hg^+$ ion was cooled to the zero-point energy of motion and a paper on the result has been submitted. (2) The studies of the lifetime and branching ratios via quantum jumps were completed and the results were published. (3) Pseudomolecules and their spectra were observed and the results published. (4) The narrow-linewidth laser was developed (see above). (5) Studies on antibunching and sub-Poissonian statistics were completed and the results published. (6) A precise experimental test of quantum jumps in single Mg^+ ions was made and the results were published.

Ion Plasmas. (1) Investigate Bragg scattering on $^9Be^+$ plasmas. (2) Look for order in plasmas by imaging plasmas onto a photon-counting imaging tube. A shell structure is predicted by theory. (3) Study ion plasmas in an rf trap with emphasis on reducing rf heating. (4) Investigate non-neutral plasmas using macroscopic (10 μm diameter) particles in an rf trap.

Accomplishment - (1) The Bragg-scattering experiment was postponed because of stray light problems. (2) The shell structure and smectic phase in nonneutral Be^+ plasmas in a Penning trap were observed and a publication has been submitted. (3) Ion "clusters" and shells were observed in rf traps. (4) Macroscopic particle clusters were observed in a low-frequency rf trap. We need more work to control the charge and mass accurately. (5) Theoretical and experimental studies on laser cooling in Penning traps was completed and the results were submitted for publication. (6) A detailed comparison of theory and experiment on static properties of ion clouds in Penning traps was performed and the results reported.

Synchrotron Frequency Divider. Assemble first test apparatus to isolate single electrons in a new superconducting-magnet apparatus.

Accomplishment - The design of the apparatus has been completed and preliminary tests have been performed.

FY 1989 Plans

Single (Or Few) Ions. Initiate experiments on interference, radiation spectra and intensity correlations in the scattered radiation from one, two or more ions. A small trap with inner dimensions of 50 μm is under construction for these experiments.

Ion Spectroscopy. (1) Redo the spatial anisotropy measurement on $^9Be^+$. (2) Compare the results of the $^9Be+$ hyperfine-splitting measurements in the superconducting magnet with those done in the conventional magnet. This comparison tests the existence of a long-range, spin-spin interaction mediated by classes of hypothetical particles such as axions. (3) Investigate fundamental atom-cavity interactions using trapped ions.

Strongly Coupled Plasmas. Experimentally investigate anisotropic diffusion in strongly coupled ion plasmas contained by a Penning trap.

Synchrotron Divider. Assemble the newly designed synchrotron-divider apparatus and perform experimentally tests of its performance.

VIII. LASER FREQUENCY SYNTHESIS

This Group retains the expertise and facilities which were used in earlier measurements of the speed of light and the subsequent work which led to the redefinition of the meter in terms of the second. More recently, this frequency synthesis has proven to be extremely useful as a basis for frequency and wavelength spectroscopic standards in the infrared and far infrared. Of particular note is the generation (synthesis) of tunable far infrared radiation (TuFIR) using either second-order or third-order mixing on the metal-insulator-metal, point-contact diode. The generated radiation completely covers the far infrared part of the spectrum. The Group continues to improve devices and concepts for frequency synthesis from the microwave to the visible regions of the spectrum. This synthesis will be needed to support the stored ion standard in the optical part of the spectrum.

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OBJECTIVE: Provide reference frequencies from the microwave to visible regions.

Frequency References (Measured with Respect to the Cesium Standard)

The advances made by the Laser Frequency Synthesis Group in extending direct frequency measurements from the microwave to the visible portion of the spectrum are now being used to determine the frequencies of atomic and molecular transitions. These measurements are hundreds of times more accurate than the old wavelength measurements. The knowledge of the frequencies of selected species allows the spectroscopist, astronomer, or atmospheric scientist to calibrate spectrometers and receivers with appropriate atomic or molecular frequencies (or wavelengths).

The generation of reference frequencies with requisite accuracy involves accurate heterodyne frequency measurements and the reliable fitting and analysis of the spectral data. The CO_2 laser which is stabilized to CO_2 itself furnishes the main frequency grid for all of these measurements and is widely used for reference purposes.

The far infrared (0.1 to 7.5 THz, 3 mm to 40 μm)

The frequencies of several hundred optically pumped lasers have been measured and frequencies of > 800 lines have beenpublished last year in a review paper. Rotational frequencies of CO, HCl,HF, and HBr have been measured using the TuFIR technique.

The Infrared Region (25 to 200 THz, 12 to 1.5 μm)

The frequencies of hundreds of lines of OCS, DBr, CO, CO_2, N_2O, and NO now furnish reference grids for this region. The methane line used to stabilized the He-Ne laser is an especially accurate secondary standard. Atlases and tables of reference frequencies covering selected infrared regions are available.

FY 1988 Plans and Accomplishments

Measure the 1372 cm^{-1} hot-band of OCS leading to molecular constants and standard frequencies in the 520 and 2412 cm^{-1} region as well.
Accomplishment - These measurements have been completed and a publication is in preparation.

Measure frequencies of spectral lines near 1635 cm^{-1} in N_2O for use as standard reference frequencies.
Accomplishment - These measurements have been completed and a publication is in preparation.

Measure hot-band features in OCS near 1700 cm^{-1} OCS as standard references.

Accomplishment - These measurements have been completed and a publication is in preparation.

Make accurate measurements on H_2O in the far infrared so that "impurity" absorption at low pressure can be used to calibrate Fourier transform spectrometers.

Accomplishment - This objective has been dropped. The replacement project involved stabilization of the CO laser to a CO frequency. This stabilized laser can be used as a major reference just as we use the CO_2 laser.

FY 1989 Plans

Measure the OCS band at 2062 cm^{-1} as standard reference frequencies.

Measure the SO_2 band at 1320 cm^{-1} as standard reference frequencies.

Improve the spectrometer instrumentation by adding a White cell and a Brewster angle fringe spoiler. The latter item would help to eliminate standing waves in the spectrometer.

OBJECTIVE: Establish the second and the meter for the International System.

Frequency Measurements Suitable for Realizing the Definition of the Meter

In October of 1983 the General Conference of Weights and Measures approved a change in the definition of the meter, namely that: "The meter is the length of the path travelled by light in vacuum during a time interval of 1/299 792 458 of a second." With this definition the meter can be realized from the wavelength of any laser which is stabilized to a narrow atomic or molecular absorption for which the frequency is known. The wavelength λ is determined from the relation $\lambda=c/\nu$, where c is the fixed value of the speed of light and ν is the measured frequency of the laser. Thus, the realization of the meter requires measurement of the absolute frequency of spectral lines in the visible region. To this end, the Division has performed two accurate frequency measurements of hyperfine transitions in molecular iodine used for laser stabilization.

The absolute frequency of a dye laser stabilized on the o-hyperfine component of the $^{127}I_2$ 17-1 P(62) transition at 520 THz (576 nm) in iodine was measured with respect to the CH_4 stabilized 88 THZ (3.39 μm). The measured I_2 frequency was 520 206 808.547 MHz with a total uncertainty of 1.6 parts in 10^{10}. The absolute frequency of the 473 THz He-Ne laser (633 nm), stabilized on the i-hyperfine component of the $^{127}I_2$ 11-5 R(127) transition was measured with respect to CH_4. The measured frequency of 473 612 214.789 MHz for the i-hyperfine component was also done with a total uncertainty of 1.6 parts in 10^{10}. These frequencies, when used to realize the new meter, represent a 25-fold improvement over the krypton length standard. However, for scientific purposes, another order of magnitude in accuracy is needed.

OBJECTIVE: Develop methods for precise time, frequency and length measurements.

Measurement of Frequency and Frequency Stability

Frequency metrology from the far infrared to the visible has been greatly stimulated by work in the Division. An extremely important aspect of this work was the first frequency measurement of the 3.39 μm line of CH_4 followed by the wavelength measurement of the line. The product is a value for the speed of light nearly 100 times more accurate than the previously accepted value. Coupled with frequency measurements of visible lines, this has led to replacement of the krypton lamp as the length standard and the assignment of an exact value for the speed of light.

Recent work on the MIM diode has expanded the range over which frequency-difference measurements can be made in the visible by a factor of 100. This is expected to greatly simplify frequency metrology because it reduces the number of frequency reference lines needed to cover this important spectral region.

Techniques for Laser Frequency Synthesis

Frequency synthesis is achieved in a non-linear device which adds, subtracts and multiplies the frequencies of the radiations incident on it. The Division has used W-Ni, metal-insulator-metal (MIM) point contact diodes as detectors, harmonic generators, and mixers of coherent radiation from the microwave to the visible region of the spectrum. The MIM diode played a major roll in the frequency synthesis chain which connected the cesium clock to the visible, I_2-stabilized lasers and hence provided the realization of the meter from the new definition.

The MIM diode has been used for the past 20 years and the mechanical and electrical engineering improvements have been steady. Recent use of conical coupling along with off-axis parabolic focusing mirrors has led to an exciting new technique of generating tunable far infrared radiation. Six tenths of a microwatt of cw, tunable-far-infrared radiation has been generated by mixing 100 mW of radiation from each of two CO_2 lasers in a MIM diode. The difference frequency radiated from the MIM diode was detected in a calibrated germanium bolometer. The use of a third-order MIM diode to add microwave sidebands to the CO_2 difference produces a greater frequency tunability and provides a complete coverage of tunable cw radiation in the entire far infrared band from 100 to 6000 GHz. Recently, the HCl, CO, and HF spectra from 0.5 to 5.5 THz have been measured and these simple molecules now provide for excellent calibration standards in this frequency range.

FY 1988 Plans and Accomplishments

Investigate the use of special high-frequency, Schottky diodes for frequency synthesis in the far infrared.

> Accomplishment - Frequency multiplication by a factor of 201 using a thin-film Schottky diode was demonstrated. We have also characterized the signal-to-noise performance versus harmonic number. It should be possible to multiply by a factor of about 50 to 4.5 THz with a good signal-to-noise ratio.

Using the best available mixer, attempt to synthesize about 0.5 THz from X band. This will be the first link in the new chain connecting the microwave to the optical region where the stored ion standard will operate.

> Accomplishment - The frequency of a 72 GHz klystron, phase locked to our very low noise X-band source, was successfully multiplied to 2.5 THZ using a thin-film Schottky diode. The signal-to-noise ratio was 47 dB in a 3 kHz bandwidth. This eliminates the need for a 0.5 THz laser in the frequency chain, a substantial simplification. The thin-film Schottky diode is very robust and should provide high reliability in a continuously operating synthesis chain.

FY 1989 Plans

Phase lock the 70 μm methol alcohol line (4.5 THz) to the high-purity, X-band oscillator using a Schottky diode as the mixing element.

Study concepts for stabilizing an oscillator near 1.5 μm, a region important for optical communication.

Investigate methods for stabilizing a Gunn oscillator at 80 GHz with a wideband servo system.

Set up a new frequency measurement laboratory dedicated to research in frequency synthesis and frequency measurements in the optical region.

IX. GEOPHYSICAL MEASUREMENTS

This is a small program conducted in JILA by Time and Frequency Division staff. One of the projects involves construction and demonstration of an apparatus for measuring intermediate baselines (25 km to 50 km) with an uncertainty of 1/2 cm or less. The multiple-wavelength technique that is used is closely related to satellite navigation and timing problems which also require a complete accounting for atmospheric dispersion. A second project involves use of an array of tilt detectors to study properties of the earth's mantle and core-mantle boundary. These tiltmeters are also installed in a seismic zone in Southern California to investigate the utility of tilt measurements for earthquake prediction. A third program involves the use of GPS signals for geodesy. This is a joint effort involving 7 universities and funded by the National Science Foundation.

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OBJECTIVE: Develop methods for precise time, frequency and length measurements.

Distance Measurement Techniques

The need to accurately determine the lengths of baselines on the surface of the earth arises in many different contexts, ranging from the calibration of tracks used for rocket tests to estimation of the relative motions of large geographical regions in seismically active zones. This work is particularly timely, since the use of timing techniques for such distance measurement is expected to grow and a key roadblock to improved resolution involves an understanding of the dispersion of the atmosphere.

Geodesy from the GPS Satellites

Using signal time of flight from GPS satellites and radiometric corrections for atmospheric and ionospheric dispersion, it appears that very accurate geodetic measurements can be accomplished. A major program, funded by NSF, involves collaboration between a number of universities to utilize this concept. This NIST Group has assumed responsibility for hardware and software developments involving the GPS satellites and for some aspects of the initial data reduction and analysis.

FY 1988 Plans and Accomplishments

Conduct longer baseline tests of the multiple-wavelength system. Initial tests will focus on stability and reproducibility, so that an a-priori knowledge of the baseline length is not necessary. Subsequent measurements will be made over calibrated baselines. Install additional microwave hardware to complete the microwave measurement of the water vapor (the existing system is really only a 2.5 wavelength system).

Accomplishment - The multiple wavelength system was run for 150 days using water vapor data from the NOAA tower at Erie and for about 14 days using a direct microwave measurement of the water vapor. With a baseline of about 24 kilometers, the reproducibility from day to day is about 2 millimeters (0.08 ppm) and the standard error for the entire data set is about 5 mm (0.2 ppm). Further reduction in the long-term error is expected as the microwave measurement is refined.

Develop software to improve the analysis of GPS data. This will include incorporation of data obtained by water vapor radiometers. The data provides real-time measurement of the atmospheric-water-vapor correction. A radiometer, obtained from JPL, will be incorporated into the system.

Accomplishment - A standard processing algorithm was completed and a universal format for the data was developed. The algorithm was used to process over 1000 tapes representing observations of several hundred baselines located in many different areas.

Continue GPS data analysis for measurements at various sites including recent campaigns in Southern California in collaboration with MIT and measurements in Hawaii in collaboration with Peter Bender and others. The measurements are motivated by geophysical considerations. Measurements of several baselines near Boulder will also be made. This series of baselines ("The Colorado Triangle") is designed to test improvements in the analysis software and the importance of water-vapor corrections.

Accomplishment - Completed campaigns involve measurements at sites in Southern California, Yellowstone National Park, Hawaii, the South Pacific, Greenland, Southwestern United States (New Mexico and Texas), South America, and the Colorado Triangle (performed several times).

Geophysical Tilt Measurements

FY 1988 Plans and Accomplishments

Continue operation of several tiltmeters in Southern California and in Yellowstone National Park. Contingent on funding, install additional instruments at a site (Durmid Hill) that is deemed to have a significant probability for an earthquake in the near future. The NIST instruments have been incorporated into several regional networks to provide real-time comparisons of data from different instruments. The proposed instruments at Durmid Hill will be included in this network, and this data will be sent directly to the USGS central analysis system in Menlo Park.

Accomplishment - The tiltmeters continue to operate and generate data in Yellowstone and Southern California. For Southern California, the data analysis is in progress, but not yet complete. Analysis of data for Yellowstone was completed and published.

FY 1989 Plans

Three-Color Geodimeter. Incorporate microwave instrumentation in the geodimeter system. Conduct full-scale tests over a known baseline and compare the results with those using GPS. Conduct measurements in Southern California on the western side of the San Andreas fault.

Tiltmeters. Install a third instrument in Southern California. Continue analysis of the output data.

Geodesy using GPS. Cooperate in the conduct of campaigns in Turkey, South America, the Colorado Triangle and Southern California. Using CDROM disks, improve the systems for archiving GPS data.

X. SPECTROSCOPIC MEASUREMENTS

This program focusses on the application of high-resolution, frequency measurements to the study of atomic and molecular spectra in the far infrared region of the spectrum. The emphasis is on the development of new and improved spectroscopic methods and on the application of these methods to the study of free radicals and other interesting molecules which are significant in upper atmospheric research and in astronomy.

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OBJECTIVE: Measure spectral frequencies of atoms and molecules.

High resolution spectroscopic measurements in the far infrared have been advanced significantly through development at NIST of two measurement techniques. These permit laboratory measurements which have bearing on atmospheric and astronomical studies.

Laser Magnetic Resonance (LMR) spectroscopy has been developed into an ultrasensitive technique (i.e., several orders of magnitude more sensitive than microwave spectroscopy) for observing new atomic and molecular species and measuring reactions involving them. LMR techniques are singularly effective in measuring chemical reactions necessary to model the effects of pollutants (e.g., fluorocarbons, nitric oxide, etc.) in the atmosphere.

The new techniques of Tunable Far Infrared (TuFIR) spectroscopy promises to enhance the LMR technique by measuring frequencies of some of the same free radicals without a magnetic field. These field measurements will have greater accuracy. The technique, an outgrowth of NIST frequency synthesis work involving MIM diodes, also allows the measurement of all far-infrared-active molecules, not just paramagnetic ones.

FY 1988 Plans and Accomplishments

Continue improvements in TuFIR spectroscopy and search for new species interesting to radio astronomers and atmospheric spectroscopists. Install a new photoconductive detector in the spectrometer to enhance sensitivity.

> Accomplishment - The spectrum of HO_2 at 93 cm^{-1} was recently observed. A few lines of this spectrum had been observed previously using LMR, but the more complete spectrum observed this year is needed by NASA for studies of the upper atmosphere. Measurements of the pressure broadening of several important spectral lines of OH and O_2 were also completed. Work was started on installation of the photoconductive detector in the TuFIR spectrometer, but completion has been delayed by resource constraints.

Build a higher power CO_2 laser to pump the FIR laser and install a beam splitter in the FIR laser.

> Accomplishment - The new CO_2 laser has been completed and the beam splitter was installed in the FIR laser. Both are operating well.

Continue LMR spectroscopy of metastable molecular species to obtain new information on previously unknown species.

> Accomplishment - New spectra observed this year include those of FeH, CoH, NiH and CrH.

Search for the elusive H_3O^+, H_2D^+, and NH^+ molecular ions.

> Accomplishment - We have observed spectra for H_3O^+, D_2H^+ and H_2D^+, but not yet seen NH^+.

FY 1989 Plans

Install a cooled grating prefilter in the TuFIR spectrometer.

Study the third-order-mixing process in the MIM diodes.

Analyze recently obtained data on NiH, FeH and CoH.

Study pressure broadening and temperature dependence of the spectral lines of OH and HO_2.

Search for new ions such as NH^+, NeH^+ and HeH^+ and measure more lines of H_2D^+ and D_2H^+.

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NBS Time and Frequency Seminar, June 14-16, 1988, Boulder, Colorado.

SPECIAL REPORTS

J.L. Jespersen and D.W. Hanson, Space Communications Timing, RADC-TR-88-9 Final Technical Report, 270 pages, March 1988.

PARTICIPATION AND LEADERSHIP

D.W. Allan, Study Group VII, International Radio Consultative Committee (CCIR)

D.W. Allan, IEEE IM TC-3 Frequency and Time

D.W. Allan, NASA Team Member for Shuttle Timing Experiment

D.W. Allan, URSI, Commission A

R.E. Beehler, Chairman of U.S. Study Group 7, CCIR

J.C. Bergquist, Director, Adriactico Research Conference on "Coherent Sources for Frontier Spectroscopy," International Center for Theoretical Physics

K.M. Evenson, URSI Commission D

D.A. Jennings, Member CCDM

J.L. Jespersen, Chairman IRIG Timing Committee

J.L. Jespersen, member of TIXI.3 subcommittee on timing and synchronization

G. Kamas, Measurement Assurance Subcommittee, National Conference of Standards Laboratories

J. Levine, Chairman, Electronic Shops

J. Levine, NBS Computer Users Committee

J. Levine, Member NBS Research Advisory Committee

D.B. Sullivan, URSI Commission A

D.J. Wineland, Committee for NBS Precision Measurement Grants

D.J. Wineland, Organizing Committee for 4th Symposium on Frequency Standards and Metrology, Ancona, Italy

D.J. Wineland, Chairman, Gordon Conference on Atomic Physics, June 1989, New Hampshire

D.J. Wineland, Air Force Studies Review Committee for Antimatter Technology, JPL

D.J. Wineland, JPL Ion Storage Program Review Committee

INVITED TALKS

D.W. Allan, "Modern Technology and Precise Time," Pyro Chemical Engineering, Denver, CO, November 1987.

D.W. Allan, "High Precision Time Standard: Application to Satellite Geodesy," Austin, TX, Applied Research Laboratories, February 1988.

D.W. Allan, "Precise Time and Frequency Standards: Use and Accuracy," Applied Research Laboratories, Austin, TX, February 1988.

D.W. Allan, "Millisecond Pulsar Rivals the Best Atomic Clock's Stability," Raytheon Company, Lexington, MA, April 1988.

D.W. Allan, "Standard Terminology for Fundamental Frequency and Time Metrology," 42nd Annual Frequency Control Symposium, Baltimore, MD, June 1988.

D.W. Allan, "Standard Terminology for Fundamental Frequency and Time Metrology," Fourth Symposium on Frequency Standards and Metrology, Ancona, Italy, September 1988.

R.E. Beehler, "NBS Time and Frequency Dissemination Services," 2nd Conference on Use of Time and Frequency in the Electric Power Industry, Ft. Collins, CO, September 1987.

J.C. Bergquist, "Quantum Jumps and High Resolution Spectroscopy of a Single Ion," Argonne National Laboratory, Chicago, IL, October 1987.

J.C. Bergquist, "Quantum Jumps and Spectroscopy of a Single Ion," University of Notre Dame, Notre Dame, IN, October 1987.

J.C. Bergquist, "High Resolution Spectroscopy of a Single, Laser-cooled Ion," NBS Gaithersburg, MD, November 1987.

J.C. Bergquist, "Laser Cooling (and freezing) of Stored Ions," University of California at Santa Cruz, April 1988.

J.C. Bergquist, "Laser Cooling (and Freezing) of Stored Ions", Cornell University, Ithaca, NY, June 1988.

J.C. Bergquist, "Single Ion Optical Frequency Standard," Conf. on Precision Electromagnetic Measurements, Japan, June 1988.

J.C. Bergquist, "High Resolution Optical Spectroscopy of a Single Trapped Hg Ion," Fourth International Laser Science Conference, Atlanta, GA, October 1988.

J.C. Bergquist, "Hg^+ Single Ion Spectroscopy," Fourth Symposium on Frequency Standards and Metrology, Ancona, Italy, September 1988.

J.C. Bergquist, "Generation of Ultrastable cw Optical Sources," Adriatico Research Conference, Trieste, Italy, September 1988.

J.J. Bollinger, "Ordered Structures of Cold, Stored Ions," Spring Meeting of the American Physical Society, Baltimore, MD, April 1988.

J.J. Bollinger, "Applications of Laser-cooled Ions in Traps," AT&T Bell Laboratories, Murray Hill, NY, May 1988.

J.J. Bollinger, "Liquid and Solid Behavior of Strongly Coupled Plasmas," Workshop on New Directions in Plasma Engineering, Berkeley, CA, June 1988.

J.J. Bollinger, "Experiments with Laser-cooled Trapped Ions," Adriatico Research Conf. on Frontier Sources for Frontier Spectroscopy, Trieste, Italy, September 1988.

J.J. Bollinger, "Penning Trap Frequency Metrology," Fourth Symposium on Frequency Standards and Metrology, Ancona, Italy, September 1988.

J.J. Bollinger, "Observation of Shell Structures with Ions Stored in Traps," Workshop on Crystalling Ion Beams, Wertheim/Main, West Germany.

R.E. Drullinger, "An Optically Pumped Cesium Primary Frequency," Fourth Symposium of Frequency Standards and Metrology, Ancona, Italy, September 1988.

K.M. Evenson, "Far Infrared Spectroscopy of Free Radicals and Molecular Ions," University at Carbondale, Carbondale, IL, January 1988.

K.M. Evenson, "Far Infrared Spectroscopy of Free Radicals and Molecular Ions," University at Carbondale, Carbondale, IL, January 1988.

S.L. Gilbert, "Plasma Characteristics of Laser-cooled $^9Be^+$ Stored in a Penning Trap," University of California, La Jolla, CA, December 1987.

S.L. Gilbert, "Shell Structure in Strongly Coupled Ion Clouds. A Smectic Phase?" NBS Gaithersburg, MD, April 1988.

S.L. Gilbert, "Liquid and Solid Phases of Laser Cooled Ions," Eleventh International Conference on Atomic Physics, Paris, France, July 1988.

S.L. Gilbert, "Liquid and Solid Phases of Laser Cooled Ions," Physics Colloquium, University of Notre Dame, October 1988.

L. Hollberg, "Optical Stabilization of Diode Lasers," Frontier Sources for Frontier Spectroscopy, Trieste, Italy, August 1988.

L. Hollberg, "Stabilization of Semiconductor Lasers with Optical Cavities, Fourth Symposium on Frequency Standards and Metrology, Ancona, Italy, September 1988.

W. Itano, "Spectroscopy of Laser-cooled Ions, Institut Laue-Langevin, Grenoble, France, July 1988.

W. Itano, "Coulomb Clusters in Paul Traps," Workshop on Crystalling Ion Beams, Wertheim, West Germany, October 1988.

W.M. Itano, "Spectroscopy of Single, Laser-Cooled Hg^+ Ions," Los Alamos National Laboratory, Los Alamos, NM, October 1988.

D.A. Jennings, "Tunable Far Infrared Spectroscopy," University of Nevada, Reno, Nevada, June 1988.

J. Levine, "Measurement of a 23 Km Baseline without a 3 Wavelength Distance Measuring System," American Geophysical Meeting, San Francisco, CA, December 1987.

T.K. Peppler, "Ensemble Time and Frequency Stability of GPS Satellite Clocks," 42nd Annual Frequency Control Symposium, Baltimore, MD, June 1988.

F.L. Walls, "The Influence of Pressure and Humidity on the Medium Term Frequency Stability of Quartz Oscillators," 42nd Annual Symposium on Frequency Control, Baltimore, MD, June 1988.

F.L. Walls, "Stability of Frequency Loops," Fourth Symposium on Frequency Standards and Metrology, Ancona, Italy, September 1988.

D.J. Wineland, "Ion Storage Experiments at NBS," Las Alamos National Laboratory, Las Alamos, New Mexico, March 1988.

D.J. Wineland, "Liquid and Solid Plasmas," National Academy of Sciences, Washington, D.C., March 1988.

D.J. Wineland, "Strongly Coupled Stored Ions; Coulomb Clusters, Liquid and Solid Plasmas," MIT, Cambridge, MA, April 1988.

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D.J. Wineland, "Spectroscopy of Single Ions," Univ. of Nevada, Las Vegas, May 1988.

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D.J. Wineland, "Frequency Standards in the Optical Spectrum," Symposium on the Hydrogen Atom, Pisa, July 1988.

D.J. Wineland, "The Digital Atom and Optical Pumping," Symposium in honor of Jean Brossel, Paris, July 1988.

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D.J. Wineland, "Spectroscopy of Laser Cooled Ions," Univ. of Texas, Austin, TX, September 1988.

QUANTUM PHYSICS DIVISION

SUMMARY OF ACTIVITIES

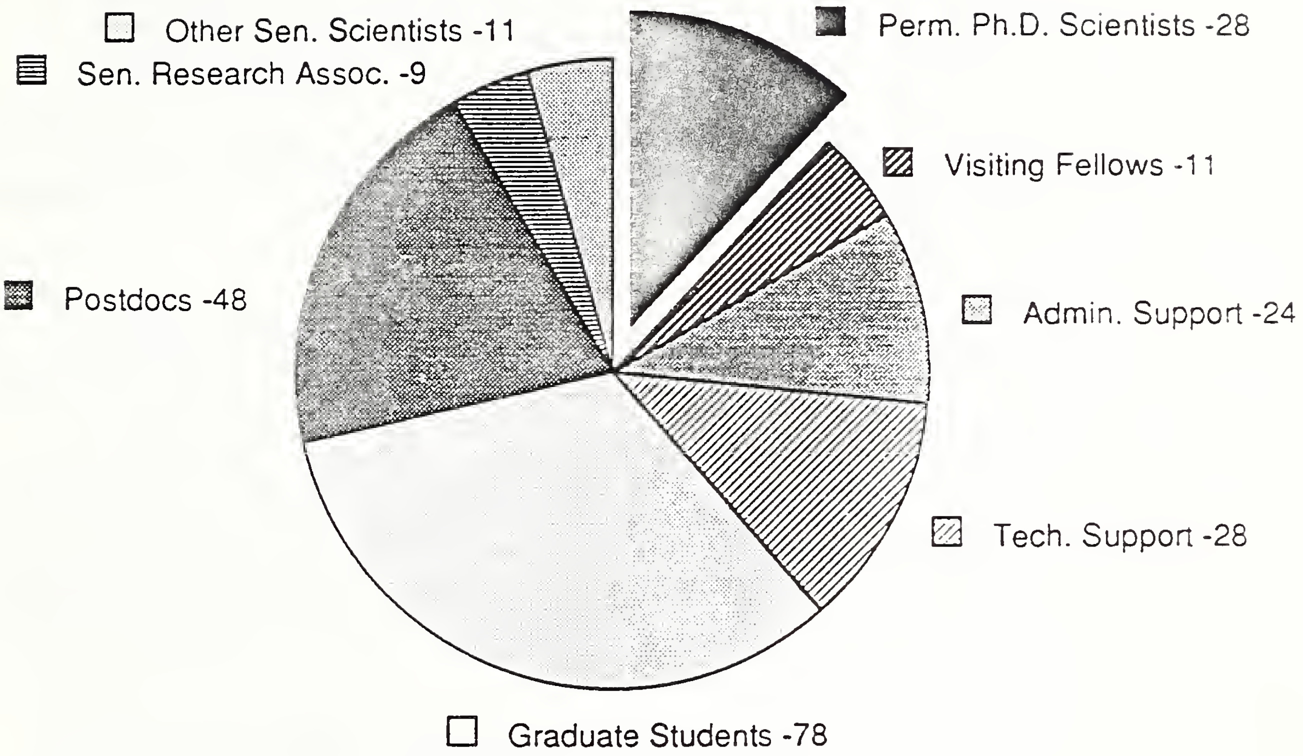
FISCAL YEAR 1988

OVERVIEW

Through the Quantum Physics Division, NIST participates in the Joint Institute for Laboratory Astrophysics, a cooperative enterprise between NIST and the University of Colorado (CU). In collaboration with University faculty and visiting scientists, the Division conducts long-term, high-risk research in support of the Nation's science and technology. The Division's objectives include:

- Developing the laser as a refined measurement tool and applying it to tests of fundamental postulates of physics such as special and general and relativity.
- Improving the theory and instrumentation required to measure astrophysical and geophysical quantities such as the cosmic distance scale, the acceleration of the Earth's gravity, and the long distances involved in determining crustal movements.
- Researching new techniques for measuring interactions involving atoms and molecules, to provide data essential in areas such as thermonuclear fusion, high power switches, advanced lighting, and laser development.
- Developing and applying measurement techniques to advance fundamental understanding of microscopic molecular processes such as those that occur in combustion and laser-initiated chemical reactions.
- Interacting with University faculty and visiting scientists to maintain expertise at the forefront of research in physics.
- Transferring the results of its research and the technology developed to the Nation's industries, universities and other government agencies.
- Exchanging ideas and skills with other scientists in NIST through visits, seminars and longer-term interchanges of personnel.

A direct outgrowth of the national space program in the early 1960s, JILA was formed in response to a report of the Space Science Board of the National Academy of Sciences. That report pointed to serious gaps in our basic understanding of the behavior of atoms and molecules in terrestrial, planetary, solar and stellar atmospheres. The unifying theme for the Institute therefore became the physics of gaseous atmospheres. Since then, however, JILA has responded to changing national needs and to the requirements of its parent organizations. Thus the Institute has become a world leader not only in atomic and molecular science and astrophysics but also in precision measurement, laser physics, and certain areas of geophysics.



JILA STAFFING 1988-1989

TOTAL - 237

The permanent senior scientists or "Fellows of JILA", of which there are currently 25, form a governing body that sets policy, subject to review by the Director of NIST and the President of the University. A Chairman, elected every two years by the Fellows, has much the same role as the chairman of an academic department. Assisted by an executive committee, he is responsible for operating the Institute within the policies set out by the Fellows. Of the 25 Fellows, 13 are full-time faculty members in the Departments of Physics, Chemistry, or Astrophysical, Planetary and Atmospheric Sciences; 12 are NIST employees, 11 in the Quantum Physics Division and 1 in the Time and Frequency Division. Although these scientists work side by side, sharing facilities and responsibility for the success of the Institute, each remains officially responsible to his respective employer, NIST and its Director in one case, CU and the academic department in the other.

Through their adjoint faculty appointments, NIST scientists at JILA have both the opportunity and responsibility to teach courses and participate in other faculty activities. This gives them access to graduate and undergraduate students, some of whom become interested in pursuing research directed toward NIST goals. Of 79 graduate students in JILA, 40 are supervised in their research by NIST scientists; of 48 postdoctoral research associates, 31 work with NIST scientists. Some have subsequently joined NIST and now occupy positions of leadership; others are carrying the knowledge and skills acquired at NIST to the Nation's industries, universities and other government agencies. Of over 100 graduate students and research associates supervised by NIST staff at JILA during the past 8 years, 20% are now in industry, 20% in government agencies, and the remainder largely in universities.

Besides the graduate students and postdoctoral research associates, the Visiting Fellows Program is probably the single most important factor in maintaining an atmosphere of change and excitement in JILA. The Program provides partial funding for some ten internationally distinguished scientists a year to spend up to twelve months at JILA collaborating with resident scientists. Since its inception 25 years ago, the Program has become internationally renowned. More than 230 senior scientists from 29 foreign countries as well as the U.S. have participated. The number of applicants exceeds the number of positions typically by a factor of four. In accordance with the Memorandum of Understanding, applicants are chosen according to scholarly achievement, demonstrated interest in the scientific and technical objectives of JILA, and the recommendations of their peers.

For NIST and University researchers alike, perhaps the greatest attraction of JILA is the large concentration of scientific talent in atomic and molecular physics and closely related areas. Neither institution, one with a broad responsibility for measurement, the other for education, could justify such a large number of senior scientists in a single area. Together these researchers are able to collaborate, exchange ideas and attract visiting scientists in a way that would be impossible for two smaller groups operating separately.

This has been a particularly exciting year for the JILA scientists and staff:

- Some 300 friends and supporters helped JILA celebrate its 25th Anniversary and dedicate its new building on April 8. Speakers included Colorado Governor Roy Romer, University of Colorado President E. Gordon Gee, and NIST Director, Ernest Ambler. A scientific symposium featured Norman Ramsey, Richard Zare and Craig Wheeler. Lewis Branscomb was the after-dinner speaker.

- Gordon Dunn's highly successful term as Chairman of JILA will come to an end on December 31, allowing him to return to research full-time. He will be succeeded by Peter Conti, Professor in the Department of Astrophysical, Planetary and Atmospheric Sciences.

- JILA is pleased to welcome two new Fellows: Robert Parson, an Assistant Professor in the Department of Chemistry, and Andrew Hamilton, an Assistant Professor in the Department of Astrophysical, Planetary and Atmospheric Sciences. Parson's research in theoretical chemical dynamics includes studies of collision-induced intra- and intermolecular energy transfer in gas and condensed phase, vibration-rotation dynamics in strong radiation fields, and the role of bending vibrations in triatomic photodissociation. Hamilton's principal research interest is the interstellar medium, with particular emphasis on supernova remnants.

- Quantum Physics Division scientists have received the American Physical Society's two major prizes in the fields of atomic, molecular and chemical physics. John L. Hall was awarded the 1988 Davisson-Germer Prize, "For his pioneering studies in optical physics and his achievements in elevating laser spectroscopy to new heights of precision". Stephen R. Leone received the 1989 Herbert Broida Prize "For his outstanding contributions to our understanding of the reaction dynamics of excited state, radical and ionic species". Leone currently enjoys a John Simon Guggenheim Fellowship for his research in chemical dynamics.

- Jeffrey Linsky has been awarded NASA's Medal for Exceptional Scientific Achievement for his contributions tot he study of the solar-stellar connection and the atmospheres of cool stars.

- David Nesbitt is using his Alfred P. Sloan Fellowship to study infrared photofragmentation of cluster ions.

- During the past year, Quantum Physics Division scientists have:

  - Developed laser stabilization techniques to produce sub-Hertz dye laser linewidths using a stabilizer completely external to a commercial dye laser.

- Used satellite laser ranging to measure a 30 ± 3 mm decrease in the length of the 884 km baseline that runs nearly parallel to -- but crosses -- the San Andreas Fault.

- Used the 300 m Erie Tower east of Boulder to obtain data that will provide a definitive test of deviations from a $1/R^2$ gravity dependence.

- Used a new equation of state to obtain agreement between theoretical and observed low frequency oscillations in the Sun, a long-standing problem for solar seismology.

- Obtained the first measurements of magnetic field strength in the coolest class of stars.

- Initiated the first calculations for vibrational excitation of the hydrogen molecule by electron impact to include *ab initio* and simultaneously the three essential effects of internuclear dynamics, electron exchange, and polarization/correlation forces.

- Measured the angular dependence of the partial Zeeman cross sections in electron excitation of the sodium atom.

- Developed a technique to measure the distribution of depositing radicals throughout a silane plasma.

- Observed and measured for the first time the ionization process, resonant-excitation-double-autoionization, which is directly analogous to dielectronic recombination; also observed resonant-excitation-triple/quadruple-autoionization.

- Developed a new laser absorption technique for measuring electric fields in electrical discharges important for plasma processing.

- Made the first direct measurement of the dipole moment function of the atmospherically important OH radical from flash kinetic spectroscopy, resolving a long-standing controversy between experiment and theory.

- Developed laser photofragmentation time resolved Fourier transform emission method used to study radicals and diatomic products with high resolution.

FUNDAMENTAL AND PRECISE MEASUREMENTS

Laser Stabilization and Stopped Atoms - J. L. Hall

The application of stable laser techniques to fundamental spectroscopic problems requires the availability of stable - but widely tunable - cw dye lasers. The *a priori* incompatibility of high stability with wide tunability (not to mention with the rapidly-flowing intracavity free dye stream) has greatly prolonged the development of such lasers. A key new technology being developed in Hall's lab arises out of a collaboration with Professor T. W. Hänsch, formerly of Stanford University. The method can work with the output of any cw laser since the active transducer is located outside the laser cavity. The technique uses both an electro-optic phase modulator and an acousto-optic frequency shifter to provide effective frequency/phase correction of the laser field *after the laser has produced its output*. The present effort is to integrate this concept with the controller of a commercially-available stabilized dye laser system. In addition to frequency correction, the system provides optical isolation against optical feedback to the laser source and can be configured to provide effective intensity control as well. The recent availability of a new type of operational amplifier, not subject to a gain bandwidth product conservation law, has made it possible to achieve a large improvement in the operation of this system. In the 1988 International Conference on Quantum Electronics Hall and Hλnsch were able to report cavity-locked operation in the sub-Hertz linewidth domain, and later in the summer we achieved phase-locked operation. This capability will be of fundamental importance to users of tunable dye lasers serious about ultranarrow linewidths, for example colleagues studying sharp optical transitions in a trapped ion. There is strong commercial interest in this device, and a joint patent with Stanford University has recently been granted.

An interesting application of the JILA tunable sideband technique is the conversion of an atomic beam to a static gas sample at millikelvin equivalent temperature. The velocity deceleration of the atomic beam is provided by the directed momentum transfer from the laser to the counter-running atomic beam, about 30,000 absorption/random-emission events being required to suppress the initial thermal velocity and stop a beam of sodium atoms dead in their tracks. During this process, the changing velocity-induced Doppler shift sweeps through about 100 resolvable natural linewidths. The availability of the inertia-free sideband frequency sweeping capability (using a swept frequency oscillator to feed the broadband electro-optic modulator) has been fundamentally useful in this work, enormously simplifying the interpretation of these atom-cooling experiments. Hall's group obtained a three-dimensional residual velocity distribution of 3 m/s RMS, equivalent to a kinetic temperature of about 8 mK, which was in quantitative agreement with the fundamental limit imposed by the natural linewidth. Hall and his student M. Zhu now follow this stage with a period of post-cooling, pumping a 20-fold weaker line to obtain higher resolution. This work is opening qualitatively new regimes of "atomic beam" physics, including gravity effects as a first-order consideration, atom bouncing, and atom aggregation with "atom mirrors" formed by pulsed, reversing curved wavefronts. One of the most exciting prospects for spectroscopy implicit in this work is the availability of long perturbation-free coherent interaction times, certainly 10s to 100s of milliseconds, bringing the prospect for Hz-level resolution. Interaction times are limited at present by collisions with background gas as well as a previously-undiscussed velocity inhomogeneity.

As an adjunct to this work, Hall and his group are pressing the limits of laser stabilization to a passive material optical reference cavity. Lowering the noise and drift rate of such a locked source will allow slower servo loops in guiding onto an atomic resonance. The lower bandwidth there will thus lead to lower frequency noise of the system. In addition, the cavity locking techniques are interesting in their own right because of possible application in inertial guidance (passive laser-driven ring resonator gyroscopes), local oscillator stabilization for space satellite communication, and as the optical reference source for gravity wave detectors based on interferometry. The scientists in Hall's group have generated and measured beat stability of two independent lasers below the 50 millihertz level, which would correspond to laser linewidths of the same value if the cavity used for the locking were equivalently stable. By means of heterodyne techniques with a laser stabilized on an I_2 reference line, they find that the reference cavity is subject to a small long-term drift, about 1 Hz/sec or $\approx 10^{-7}$/yr. A new cavity support/isolation structure has helped reduce sensitivity to leveling of the vibration-isolation table. An improved Peltier cooler-based thermal controller located inside the vibration/acoustic/thermal isolation box ("quiet house") gives temperature variations of ± 2.5 mK, which are further attenuated and filtered by the thermal controller on the reference cavity structure. The presently observed 100 Hz amplitude at 24-hours period will allow ≈ 500-fold improvement on the Kennedy-Thorndike experiment, which checks that the velocity-dependent transformation of time and length are equivalent.

In collaboration with Professor H. J. Kimble of the University of Texas (Austin), Hall has made the first measurements and demonstration experiments in which a practical, significant level of "squeezing" has been obtained. Rather than the 7% effect reported by the initial Bell Labs team, they have shown a factor of 2.5 effect. The collaboration presently is trying to observe the so-called "quantum non-demolition" detection in which the amplitude of an electromagnetic signal is repeatedly read out by a carefully-prepared quantum system. The goal is to show that the perturbation implicit in quantum measurement can be confined to the variable conjugate to the one being observed. While the full metrological implication of these results may only become clear over a half-decade timescale, it is already obvious that dramatically enhanced measurement sensitivity will be available for important national objectives such as Earth-based searches for gravitational radiation.

Laser Gravitational-Wave Observations in Space - P. L. Bender and J. E. Faller

The basic concept for a Laser Gravitational-Wave Observatory in Space (LAGOS) is now well established. Work on the conceptual design for such an observatory has been carried out for the last three years under support to the University of Colorado from the NASA Innovative Research Program, as well as under earlier and continued support from NIST. Based on this work, a single-page summary of suggestions to NASA on the type of program needed to develop LAGOS was prepared (Figure 1).

As discussed previous reports, studies of expected gravitational wave signals due to binary star systems have been carried out by D. Hils, R. F. Webbink (former JILA Visiting Fellow) and Bender. To summarize briefly, it appears that the power spectral density of signals due to different types of binary star systems will be above the instrumental sensitivity for frequencies from roughly 10^{-5} Hz to 10^{-2} Hz. Since about 10^{8} binaries in our Galaxy contribute to the signals, it will not be possible to resolve individual sources unless they are unusually close by. Exceptions are double neutron star binaries and close white dwarf binaries with frequencies above about 3×10^{-4} Hz, for which the number in the galaxy per cycle/yr resolution bin is less than 1. The reality of the gravitational wave signals can be checked by observing the change in signal strength as the plane of the galaxy goes through one of the nulls in the antenna pattern, which correspond to the plane bisecting the two baselines and a perpendicular plane. Information on the location of resolvable sources can be obtained in the same way.

Recent work on the conceptual design for the LAGOS antenna has been focused particularly on the requirements for minimizing the spurious accelerations of the test masses in the three separate spacecraft that form the antenna. A preliminary error budget of 2×10^{-15} $\mathrm{cm/sec^{2}/Hz^{0.5}}$ has been established for such spurious accelerations over the frequency range from 10^{-5} to 10^{-3} Hz. A substantial part of the disturbances will come from random molecular impacts on the test mass, even for a 10^{-11} torr vacuum in the cavity surrounding the test mass. Another important disturbance source will be 10^{-4} cm displacements of the spacecraft with respect to the test mass, coupled with spacecraft distortions due to variations in the solar intensity. The error budget level was chosen to permit observation of a number of kinds of galactic binaries. This appears to be achievable, but a great deal more work is needed in order to verify this.

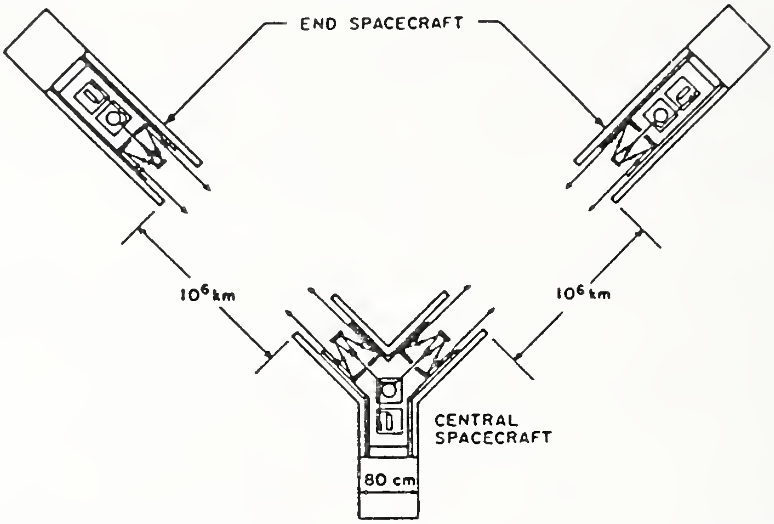
The LAGOS project now appears ready to go into a technology development phase. This would include particularly the following: Disturbance Avoidance (Compensation) System for the test masses; the thermal design for the spacecraft; the thruster and fuel storage system for counteracting the solar radiation pressure and solar wind forces on the spacecraft; and a 2 watt laser with high stability, reliability and efficiency. NASA is planning to start supporting a small amount of work under their Advanced Development Program on possible future gravitational wave observations in space. Support is being sought for work in several of

Figure 1

Laser Gravitational-Wave Observatory in Space (LAGOS)
(Gravitational Waves)

Program Summary: NEW AND UNIQUE CAPABILITY TO SEARCH FOR PULSES FROM VERY MASSIVE BLACK HOLE FORMATION OR COLLISIONS AND TO STUDY CLOSE BINARY SYSTEMS.

- L-shaped array of 3 spacecraft forms the LAGOS antenna
- Lasers measure the 1 million km arm lengths
- $10^{-21}/\sqrt{Hz}$ maximum sensitivity
- High sensitivity from 1 sec to 1 day period
- Physics of collapse/ early universe/compact binary systems
- Mission duration: 10 yrs.
- Target launch date: 2000
- Mass in solar orbit: 400, 300, and 300 kg
- Estimated cost: TBD



Science Objectives:

- Measure sinusoidal signals from many individual cataclysmic variables, neutron star binaries and white dwarf binaries in our galaxy
- Determine directions to individual sources from sharp nulls in the antenna pattern
- Measure stochastic background due to many main sequence binaries with unresolved frequencies
- Observe universal background from compact extragalactic binaries at short periods, if possible
- Search for gravitational wave pulses with periods longer than 1 sec from possible exotic sources, such as gravitational collapse of very massive objects near the era of galaxy formation

Mission Description:

- The LAGOS antenna is located 30 or 60 degrees behind the Earth in solar orbit.
- Orbits of the two end spacecraft are somewhat eccentric ($e = .0033$) and inclined ($i = .0058$) to keep their distances from the central spacecraft constant to 1% over 10 yrs.
- Gravitational waves change the difference in length of the two antenna arms.
- One watt of laser power is transmitted in each beam through 50 cm diameter telescopes.
- Phase-locked lasers at the two end spacecraft provide the return beams.
- Distance measurements are made between test masses in each spacecraft which are very carefully shielded from spurious forces.
- Spacecraft are held centered on test masses to 10^{-4} cm to reduce gravitational force changes.
- The slowly changing solar irradiance and spacecraft orientation will be used with careful thermal insulation to minimize thermal disturbances of the test masses.

Technology:

Pacing:

- Greatly improved Disturbance Compensation System with 2×10^{-15} cm/sec$^2/\sqrt{Hz}$ performance from 0.01 to 1 mHz
- One watt laser diode pumped Nd:YAG lasers with high stability, reliability, and efficiency.

State of the Art:

- Laser measurements of distance changes with 5×10^{-11} cm/$\sqrt{Hz}$ accuracy from 0.001 to 1 Hz
- Thermal insulation of critical components to achieve 1 to 5 day time constants

Science Strategy: LAGOS IS REQUIRED FOR OBSERVATIONS OF MANY IMPORTANT GRAVITATIONAL WAVE SOURCES IN THE 10 μHZ TO 1 HZ FREQUENCY RANGE.

the above areas, in cooperation with R. T. Stebbins and Hils (University of Colorado).

Optical Imaging Interferometry in Space - P. L. Bender and J. E. Faller

Some preliminary work on a specific concept for an optical imaging interferometer in space was carried out a year ago by Stebbins, Bender and Faller, and has been published. The basic idea is to use roughly 15-meter long sections of graphite-epoxy truss structure or other low-expansion material for the basic interferometer structure. Three such sections could be used in a Y-shaped configuration, with about 5 afocal telescopes located along each arm. The light from each telescope interferes with that from a number of the other telescopes to give an optical image. Careful thermal design would make the distortion rate for the interferometer relatively small. Laser measurements from two control blocks located on a mast perpendicular to the plane of the Y would be used to monitor the overall distortion and provide corrections for the optical paths with 10^{-2} wavelength stability over a typical observing time of roughly two hours. The laser measurement system is similar to that planned for the POINTS (Precision Optical Interferometry in Space) astrometric interferometer being developed by R. D. Reasenberg and others at the Harvard/Smithsonian Center for Astrophysics.

With 50-cm diameter telescopes, the aperture coverage would be dilute. However, quite high magnitude sources could still be observed with good spectral resolution. The spatial resolution would be nearly an order of magnitude better than for the Hubble Space Telescope at the shortest wavelength of about 150 mm observable with the interferometer.

More extensive work on a similar concept for an optical imaging interferometer in space has been done in the last year by JPL. Fortunately, their conclusions also support the viability of the basic concept. One area they do not expect to pursue actively is the laser metrology part of the interferometer. With their encouragement, Bender and Faller have submitted a new proposal with Stebbins (University of Colorado) under the NASA Innovative Research Program for work on this part of the problem. Under the proposal, we would design and carry out preliminary tests of a prototype laser distortion-sensing system for a 3-aperture segment of one interferometer arm. This would be done on a 1/5th scale model of one arm and the mast.

1-30 Hz Isolation Systems for Ground-based Gravitational Wave Detectors - P. L. Bender and J. E. Faller

The performance of existing and contemplated ground-based gravitational wave detectors could be extended through augmented seismic isolation. For example, the ground noise spectrum, which increases toward lower frequency, establishes the low frequency limit in present interferometer designs. Extending the operating band down to 1 Hz through better vibration isolation would afford access to a band that may contain signals indicative of massive black hole formation or collisions in galactic or pre-galactic times. An isolation factor of 10^{-5} to 10^{-6} appears to be needed in order to bring the vibrational noise at the support points of the test mass pendulums down to the desired level at 1 Hz in interferometric detectors such as the proposed 4 km Cal Tech and MIT instruments.

We are interested in investigating with Stebbins, C. C. Speake, a visitor from the BIPM, and D. B. Newell, whether a two- or three-stage isolation system can be designed that will provide the necessary isolation without introducing too much thermal noise. The required noise level is not well known, but is in the range 10^{-11} to 10^{-13} cm/Hz$^{-0.5}$ at 1 Hz. Each isolation stage needs to attenuate oscillations in all six degrees of freedom in order to avoid cross-coupling between the different types of motion. The horizontal translations are relatively easy to handle, but precision rotating pivots are needed in inertial sensors such as torsion pendulums for detecting tilt and rotation. The precision requirements for these angular degrees of freedom appear to mandate the use of solid flexures. Springs or flexures also are needed for vertical translation isolation.

Unfortunately, both results obtained by T. J. Quinn and Speake and preliminary measurements in Bender's and Faller's lab indicate that the damping coefficient due to internal friction in various materials goes up as the frequency goes down. This is a serious problem for long period, high Q mechanical suspensions. It is particularly serious in terms of thermal noise generation in flexures and springs.

Since both the restoring force and damping of practical flexures arise from their bending, we have developed a servo system to eliminate the bending by twisting the support structure to follow the motion of the rotating part, as suggested by Stebbins. A simple servo system can sense the movement of the pendulum mass with respect to the lab frame and then rotate the supporting structure so that the flexure does not bend. An increase in the period of a flex pivot by a factor 5 by this method has been demonstrated by M. Ashby and Stebbins. However, this does not avoid the thermal noise problem. Investigation of the inherent mechanical energy losses in different types of materials will be needed in order to minimize the thermal noise in low-frequency vibration isolation systems of modest size.

High Accuracy Atomic Mass Measurements - G. H. Dunn

S. Jefferts (University of Colorado) and Dunn are pursuing their new program of ultra-high precision atomic mass measurements. Their goal is to develop a technique to measure atomic masses initially to parts in 10^{10}, but eventually to parts in 10^{12}. These measurements will have a role in the determination of the neutrino mass, the determination of Avogadro's number, the physics of nuclear isomers and the chemistry of chemical isomers, and the masses of superpositions of states. The high field (7 T), high uniformity magnet has been obtained and tested for long term stability. The experimental insert has been designed, obtained and installed. Much of the electronics have been built or procured, including development of an ultra-quiet cascade amplifier. A major project during the past year has been development of a special metal alloy with a magnetic susceptibility near zero at 4 K. Dunn and his colleagues worked with various percentages (near 4%) of Ni in Cu before arriving at an alloy more than two orders of magnitude better than OFHC Cu at that temperature. The trap structure has been designed in detail, and prototypes are under construction using first Al and then Cu as the material. Ingots of this "magic metal", have now been cast and are ready for machining. Diamond tooling will be used for the final cut on the magic metal to avoid any chance of leaving ferromagnetic tool chips in the surface. Thus, great care is being taken to insure minimal perturbations of the magnetic field by the trap structure itself. Dunn is hoping that the first mass measurements will be obtained during the coming year.

GEOPHYSICAL MEASUREMENT METHODS

Geophysical Measurements Related to the Suggested 5th Force - J. E. Faller

In the January 6, 1986, issue of *Physical Review Letters*, an article appeared by Fischbach *et al.* which suggested, based on an analysis of a number of data-types, the possibility of a new short-ranged component to gravity. This suggested new component of gravity was dubbed the "fifth force". As a result, a number of experimental studies have subsequently been undertaken with the aim of testing this suggestion. The results of the experiments performed to date do not agree with each other; either nature is more cunning than we suspected or some -- perhaps even all -- of these experiments contain some subtle and as yet undiscovered sources of systematic errors. Though the majority of the experiments reported to date would seem to rule out the possibility of a material-dependent fifth force, the possibility of a deviation from the inverse square law of gravity remains.

During the past year, a number of target-of-opportunity experiments have been carried out or are still being worked on -- all designed to test experimentally some aspect of the fifth-force suggestion.

T. Niebauer (University of Colorado), McHugh and Faller have used the dropping chamber from the JILA absolute gravimeter, together with first the Finnish and later the DMA/NGS dropping chambers, to carry out a Galilean test of the fifth-force hypothesis using U_{238} and Cu as the free-falling dropped masses. They measured no differential acceleration down to 5 parts in 10^{10}, thereby establishing better experimental limits on any material-dependent fifth force over the range 0.2 km to 10^4 km.

Faller and McHugh have constructed a fluid-float Eötvös experiment using Cu and Pb as the test masses to test the material-dependent fifth-force hypothesis over the short 1 - 10 meter range. This target-of-opportunity experiment has resulted in the temporary suspension of their gravity gradiometer float studies. But as these two experiments are complementary in terms of possible error sources and experimental limits of precision, they are also making progress with gradiometer studies. During the past year, systematic error sources having to do with rotating the entire apparatus by 180 degrees, a necessity for fifth force studies using the room as the test mass, have been under investigation.

The Erie tower, located 20 km east of Boulder, is now being used to repeat the AFGL "North Carolina Tower Experiment", which appeared to indicate the presence of both a 5th and a 6th force, and the recent "Greenland Hole-in-the-Ice Experiment" which, it is stated, yielded evidence of a 6th force. Because of their convenient access to the 300 m tower, Niebauer and Speake have been able to acquire good up-and-down-the-tower gravity data using a number of Lacoste & Romberg relative gravimeters. They are now acquiring the difficult, extremely dense data set necessary to carry out the $1/R^2$ "upward continuation" that will yield predicted Newtonian values of gravity in the tower to compare with their actual measurements. They would like to believe that this effort will allow them to report either that Newton is saved on the plains of Colorado -- or that our understanding of gravity needs a major overhaul.

Short Path Atmospheric Refraction (SPARC) - P. L. Bender

S. J. Walter (University of Colorado) and Bender are working under NASA funding to develop a microwave-optical system to improve the accuracy of the correction to microwave distance measurements due to atmospheric water vapor. Since optical distance measurements are affected much less by water vapor, the difference between microwave and optical measurements to an aircraft at about 6,000 meters altitude would serve to determine the microwave distance correction. A 35.25 GHz microwave carrier from a Gunn diode oscillator and a roughly 830 nm optical carrier from a laser diode are modulated at 1.5 GHz in the transmitter. The modulation signals are recovered in the receiver, amplified, filtered, down-shifted to 15 kHz, and then compared in phase. The accuracy goal for the calibrator is 2 to 5 mm. It will be used in joint measurements with water vapor radiometers and radiosondes to determine improved line shape and strength information for the 22 GHz atmospheric water vapor line.

Ground tests of SPARC have been carried out in the last year over 0.14 km, 1.5 km, and 12 km ground paths. The stability of the instrument seems good despite strong scintillation of the optical signal. Comparisons of the results with end point meteorological measurements are being made. Construction of two image motion compensators for use in the later airborne measurements is now over 50% complete. One image motion compensator will direct the signal from the 1.5 GHz modulated laser diode in the aircraft toward the receiver on the ground. The other compensator will automatically direct the light received from the aircraft onto the avalanche photo-diode detector, despite rapid and irregular tilts of the aircraft.

GPS Measurements in the Hawaiian Islands - P. L. Bender

Signals from the Global Positioning System (GPS) satellites have been used during the period 28 March - 12 April, 1987, to measure the distances between sites on Kauai, Oahu and Maui in the Hawaiian Islands.

The main scientific goal was to obtain a direct measurement of the vector distance between the satellite laser ranging station on Maui and the NASA Very Long Baseline Interferometry station on Kauai. These stations are both used in measurements of the motion of the Pacific Plate with respect to the North American Plate, the Australian Plate, and other plates.

The GPS data have been analyzed during the last year by X. Wu (University of Colorado). He was able to resolve the phase ambiguities in the measurements over the 386 baseline from Kauai to Maui by using, in addition, the group delay measurements. Over a two-week period, nine days of data yielded day-to-day repeatability of 1.5 cm (0.04 ppm) for the baseline length, 2.7 cm for the height difference, and 1.6 cm for the transverse component. An ionospheric modeling approach to the ambiguity resolution problem was also shown to work most of the time for this baseline, but with worse precision. The accuracy of the baseline results is limited mainly by the uncertainties in the best available GPS satellite orbits for the observation period.

Translocation Method for Analyzing Satellite Laser Range - P. L. Bender

A modified translocation method has been used with laser range data to the Laser Geodynamics Satellite (LAGEOS) to determine changes in an 884 km baseline in California. This baseline between Quincy in northern California and Monument Peak near San Diego crosses the San Andreas fault system, and the components of its rate of change are of strong interest in understanding how the relative motion between the Pacific and North American plates is taken up near the boundary. The starting point for the analysis was the set of range residuals from an 11.7 year orbit for LAGEOS computed at the Center for Space Research of the University of Texas. Corrections to the initial orbit elements for each pass observed from both laser ranging stations were solved for, along with corrections to the baseline components for each six months' block of data. However, the orbit element corrections were constrained to avoid large changes from the initial orbit. Most of the work on the analysis was done by M. A. Vincent (University of Colorado) and A. Stolz, a JILA Visiting Fellow.

The results for the baseline components and their changes during the eight half-year periods from 1984-1987 were remarkably consistent. The range residuals were reduced by the fitting process from over 60 mm rms to under 10 mm rms. The rate of shortening of the baseline was 30 mm/a, and the rate of change in the transverse component agreed with the Minster-Jordan RM-2 model. The vertical component showed no significant change with time. The rms scatters for the half-year values were 4 mm, 11 mm, and 9 mm for the length, transverse, and vertical components. For data from

1982-1983, it was not possible to reduce the post-fit range residuals below about 30 mm rms, and the scatter in the baseline components was larger.

ASTROPHYSICAL MEASUREMENT

The Physics and Application of Radiation Transport - D. G. Hummer

Hummer's program addresses the basic physics of the transport of radiant energy through matter and its application to the determination of physical parameters in radiating gases from analysis of the emitted radiation. His work encompasses a wide variety of physical phenomena from radiation transport and spectral line formation on the one hand to the development of the equations of state and the calculation of opacities for stellar material on the other. His program currently comprises the following elements.

Approximate Lambda Operator Method for Radiative Transfer. - G. Rybicki (Center for Astrophysics) and Hummer have recently developed a powerful new method for radiative transfer calculations that appears to surpass all existing methods for *multi-level* problems. The basic idea is to replace the *non-local* operator that gives the mean intensity from the source function by a *local* operator that can be solved trivially, and then to correct for the difference iteratively. They have developed a very fast method of generating this optimal approximate operator, and have succeeded in incorporating this approach into the equations of statistical equilibrium in a way that maintains the linearity of the problem. This approach has the advantages of speed, simple analysis and ease of coding, and is ideally suited to parallel processing; it appears that 10^4 spectral lines in non-LTE situations can be treated in this way. The method provides the basis for a new generation of stellar atmosphere codes, which can treat non-LTE line-blanketing essentially exactly (see below).

Advanced Stellar-Atmosphere Modeling (Phase 1). - The stellar atmosphere code written by I. Hubeny (JILA Visiting Fellow) is sufficiently general and powerful to allow us to incorporate elements such as C, N, O, and Si -- in addition to the usual H and He -- including all the bound-free and selected free-free transitions. Hummer has outlined a program with Hubeny to carry out these calculations, and has started to assemble the necessary atomic data (mainly from the Opacity Project) and to incorporate it into Hubeny's code. Their treatment of He is much more accurate than all existing work. This project is still in an early stage.

Advanced Stellar-Atmosphere Modeling (Phase 2). - The approximate lambda operator technique described above is being applied by W. Schmutz (JILA Postdoc on three-year fellowship from Swiss NSF) and Hummer to construct model stellar atmospheres with full non-LTE line blanketing. This work will require an enormous amount of atomic data, which is now available from the Opacity Project. The analysis and general planning of the code are underway.

Free-free Gaunt Factors for Hydrogenic Ions. - The standard source for these quantities has been the paper of Karzas and Latter, where the results are presented graphically. To facilitate computer calculations, such as those involved in obtaining opacities in the Opacity Project (see below), Hummer repeated the calculations of Karzas and Latter, fitting the results to an efficient two-dimensional Chebyshev expansion in scaled frequency and temperature variables. In the course of this work, it became clear that the equations published by Karzas and Latter were computationally inadequate, requiring the development of new analytical results. It is probable that they interpolated graphically across the regions of parameter space in which their primary method failed to converge.

Parameters of Hot Stars. - A major part of Hummer's effort in the past six months has been devoted to this long-term project with D. Abbott, B. Bohannan and S. Voels (University of Colorado). The goal is to exploit the new generation of astronomical detectors to obtain very high signal-to-noise line profiles, which are then analyzed using photospheric models that incorporate all physical processes thought to be of possible relevance (see above). The purpose of this work is to provide sufficiently accurate constraints on the theory of stellar evolution that the effect of the physical uncertainties (i.e., convective overshooting, mass-loss, and opacities) in that theory can be evaluated and ultimately removed. The errors in current determinations are much too large for this purpose. Voels has completed and successfully defended his thesis, which contains the most accurate available parameters for eight O-type stars.

This work yielded stars with abnormally high helium abundances, which could not be modelled with the existing code. Voels and Hummer developed a technique which they call "Collisional-radiative switching" that improves the convergence properties of the method so that arbitrarily large helium abundances could be treated.

Although Abbott and Hummer showed several years ago that the effective temperature of stars hotter than about 3×10^4 K cannot be determined from measured continuum fluxes, this issue has remained controversial. Hummer, Abbott, Voels and Bohannan have taken the temperature of a well-observed star as determined by the chief proponent of the continuum method and showed that while the continuum fits all of the observations, the line spectrum is completely discrepant, i.e., the continuum is extremely insensitive to the effective temperature.

This program is a collaborative effort with the University of Munich to determine accurate stellar parameters for at least 30 stars each in our Galaxy and the Large and Small Magellanic Clouds. Two recent trips to Munich advanced the analysis and modelling of the excellent spectra of stars in the Clouds. These data are almost ready to be used in the method devised a few years ago for determining distances to isolated hot stars by purely spectroscopic means.

Stellar Opacities and the Equation of State. - Hummer has developed codes for calculating exactly the photoionization cross sections and

Einstein coefficients for hydrogenic ions, which have been incorporated in the Opacity code, along with the free-free subroutine mentioned above. This code is used, not only for hydrogenic ions but also for levels of other elements with large values of the quantum numbers n and l. Although Hummer is not directly involved in writing the opacity code, he had a role in its design and in the inclusion of other atomic processes. At present Hummer is trying to understand how to include Rayleigh scattering exactly without counting contribution in the vicinity of lines twice.

Although most of the work on the equation of state was completed previously, Hummer has refined the calculation of the internal partition function and compared it with unpublished results from Livermore, which he has now shown to be unphysical. In a recent preprint by J. Christensen-Dalsgaard, W. Dappen and Y. Lebreton, it was shown that the atomic partition function developed by Hummer leads to a significant improvement in the agreement between the frequencies of calculated and observed low frequency, global solar oscillations.

Collisional-radiative Recombination Spectra of Helium. - The cosmic abundance of helium, which sets a strong constraint on the conditions in the very early Universe, is best determined from the recombination spectrum of helium in nebulae. For this purpose the theoretical line strengths are necessary. Hummer has been working with P. Storey (University College London) for about two years on an accurate determination of the theoretical line strengths. The main problem here is with the atomic data, for although excellent radiative data is now available from the Opacity Project, the collisional rate coefficients are not available for most transitions of interest. Recently Berrington and Kingston computed cross sections for all transitions among levels with principal quantum number as large as four. Storey has computed the collisional rates from this data, and Hummer has computed Chebyshev coefficients for each transition. Hummer has then incorporated these coefficients into a subroutine that returns the rates at any specified temperature. The largest remaining problem concerns collisional coupling of the singlet and triplets systems, which up to now have been taken as independent. There is reason to believe that collisional coupling between singlets and triplets for large n is important. As no data on this process are available, Hummer and Storey have recently computed the necessary rate coefficients using classical theory, which should be good for the highly-excited states of importance. The code is largely written, but because of its complexity, testing will require several months. Hummer hopes to obtain definitive results early in 1989.

Previous work on the collisional-radiative spectrum of hydrogenic carbon, nitrogen and oxygen has recently been published. Previous work on H and He+, along with work on carbon ions carried out in 1982 has been used by L. Smith and Hummer to determine the He and C abundances in a number of Wolf-Rayet stars, using Smith's spectra taken for this purpose.

Sobolev Method with General Redistribution. - Recently Rybicki and Hummer generalized their earlier work, which was limited to uniform expansion, to spherically symmetric flows with velocity laws of the form v(r). The programming has gone slowly as the calculation is extremely complex. Rybicki is currently at the Institute of Astronomy in Cambridge, England, where this method seems to be of considerable interest in a variety of contexts, and is now being applied there by Rybicki in collaboration with various people there.

Radiation-driven Stellar Winds with Optically-thick Continuua. - In collaboration with J. Puls (Munich), Hummer has derived the correct expression for the force on the gas in a high-speed flow from radiation when the continuum is optically thick. Hummer noticed that the force became infinite if the line profile had a Lorentzian component and the background opacity was zero. This suggests that in a real case with some appreciable background continuum, the force could be substantially enhanced if the true line profile were used instead of the universally-assumed Doppler profile. Hummer believes that this could play a major role in the dynamics of winds of Wolf-Rayet and Luminous Blue Variable stars. He is now working on the evaluation of the very difficult triple integrals which enter into the expression for the radiation force in this case. These expressions will be used by Hummer on his coming visit to Munich in the stellar wind code developed there to evaluate this mechanism.

Measurements of Magnetic Fields in Cool Dwarf Stars - J. L. Linsky

Linsky and his former Ph.D. thesis student, S. Saar, are pursuing a major program to measure surface magnetic fields on stars cooler than the Sun. They have already obtained results on stars cooler than had previously been possible to measure; they have also developed an analysis technique to take into account for the first time the saturation of optically thick absorption lines.

These measurements confirm the hypothesis that magnetic fields are at the heart of solar-like phenomena by showing that stars with the most energetic phenomena, for example flares and enormous starspots, also have the strongest measured field strengths and spatial coverage. Three additional conclusions may be drawn from these measurements and the field parameters in somewhat warmer stars. First, the field strength is determined by hydrodynamic processes in the photosphere and not by dynamo field creation processes in the stellar interior. Second, stars with energetic or widespread magnetic-related phenomena have fields that cover nearly the whole star, indicating a high rate of field production in the stellar interior. Third, the fraction of the stellar surface covered by magnetic fields depends on the stellar rotation, as would be expected if fields were amplified by the dynamo process.

Microwave Measurements of Stars - J. L. Linsky

Linsky and S. Drake (Goddard Space Flight Center) have several projects underway to study microwave emission from stars. They have now completed a survey of microwave emission from 39 of the closest stars that are more luminous and cooler than the Sun. This survey at 5 and 15 GHz was made using the National Radio Astronomy Observatory's Very Large Array (VLA). The purpose was to measure mass loss rates for a class of stars (giants and supergiants of spectral types G, K, and early M) for which there was little data heretofore. Microwave emission from these stars is thermal bremsstrahlung from the ionized component of the circumstellar gas leaving the star. Drake and Linsky have now extended this program to study the mass loss from the coolest M giant stars, many of which are SiO maser emitters.

Linsky and Drake have just completed an extensive survey of microwave emission from the hot coronae of close binary systems called RS CVn systems, named after the prototype. These systems are interesting because rapid rotation and internal convection combine to create enormous magnetic fields that both heat the plasma in extensive hot coronae surrounding the stars and may also accelerate electrons to relativistic energies. They have arrived at a new interpretation of the radiation from these stars in which the low level microwave radiation is due to synchrotron emission from the same distribution of thermal electrons responsible for the observed soft X-ray emission, whereas the high level of microwave emission observed during flare events is due to synchrotron emission from relativistic electrons accelerated in the magnetic fields of these stars.

Linsky and J. Bookbinder (University of Colorado) have begun a large survey of microwave emission from the coronae of low mass flaring stars called M dwarfs. The goals of this ambitious project are to understand the microwave emission mechanisms and coronal heating processes by studying an unbiased volume-limited sample of stars with differing masses, ages, and rotation rates.

Models for the Outer Atmosphere Layers of Stars - **J. L. Linsky**

Linsky and colleagues C. Jordan (Oxford University) and A. Brown (University of Colorado) have completed work on a set of detailed models for the outer atmosphere of solar type stars. These models describe the amount of emitting material in the chromosphere, transition region and corona. The models were constructed to match ultraviolet emission line fluxes observed by the International Ultraviolet Explorer satellite and X-ray fluxes observed by the Einstein X-ray Observatory.

Doppler Imaging of Active Regions on the Surfaces of Stars - **J. L. Linsky**

Linsky and J. Neff (University of Colorado) are obtaining maps of the surface structure of stars using a technique they developed called Doppler imaging. This technique involves the analysis of high spectral resolution, high signal-to-noise (by astronomical standards) profiles of emission lines from rapidly rotating stars obtained at a large number of aspect angles (phases). As a star rotates, bright regions (called plages) on its surface first appear at one limb with a large blue shift, then move across the visible surface with increasing Doppler shift and then disappear over the receding limb with a red shift corresponding to the rotational velocity of the star. This new technique can be used to infer the existence of plages, their spatial location, size, and brightness contrast, information essential for modelling their atmospheres.

Planning for Future Space Observatories to Obtain Ultraviolet and X-Ray Astrophysical Data - J. L. Linsky

Linsky is participating in the detailed planning of several future astronomical missions. The most immediate is the Hubble Space Telescope to be launched in 1990. Linsky has been a Co-investigator on the High Resolution Spectrograph (HRS) since 1978 and he has participated in the major decisions that have led to the design and construction of this instrument. The HRS will obtain spectra with resolution up to 10^5 covering the spectral region 110 -320 nm. Linsky is also a Co-investigator on the Space Telescope Imaging Spectrograph (STIS), now being designed to replace the HRS five years after launch. This instrument will have high spatial imaging capability as well as high spectral resolution over the extended spectral range 110 - 1100 nm.

In 1985 Linsky was appointed an Interdisciplinary Scientist and member of the Science Working Group for the proposed Advanced X-Ray Astrophysical Facility (AXAF). This 1.2-m grazing incidence telescope is being planned to obtain high resolution X-ray spectra of stars and galaxies in the mid-1990's. The AXAF Program has just been approved by Congress as a new start. Linsky's specific interest is high-throughput spectroscopic observations of stars to measure stellar coronal temperatures, densities, and flow velocities.

Linsky collaborated with colleagues at several universities and the NASA Goddard Space Flight Center to write a proposal to NASA to study a proposed far ultraviolet spectroscopic explorer satellite called LYMAN. This satellite, which is now in its Phase A study, would contain a grazing incidence telescope and spectrograph to cover the 10 - 200 nm spectral range at both low and high spectral resolution.

ATOMIC AND MOLECULAR PHYSICS

Electron-Molecule Interactions - D. W. Norcross

This theoretical program is devoted to large scale computational studies of bound and continuum states of electrons interacting with simple molecules. The reaction process can take several forms and have a variety of products, e.g., rotational and vibrational excitation of the molecule, capture of the electron to form a molecular negative ion, or dissociation of the molecule into other atomic and molecular fragments. The effort is primarily developmental -- inventing and extending numerical techniques for more rigorously representing the electron-molecule interaction, and for treating ever more complicated molecules and processes -- but opportunities to produce useful data are not overlooked. Results apply to studies of many practical and fundamental processes, e.g., laser modeling, physics of the interstellar medium, and in studies of chemical reaction dynamics.

Production work in the recent past has included detailed calculations in the adiabatic nuclei approximation of cross sections for vibrationally elastic scattering of electrons by HF, HCL, CO and (linear) HCN; for ro-vibrational excitation of HF and HCL by electrons, and of CO by positrons; and calculations of the attachment energies of the three lowest negative ion states of HCl^- as a function of internuclear distance.

Owing to the presence of sharp threshold structures in vibrational excitation of polar and many nonpolar molecules, an accurate computational treatment of this process demands complete and rigorous inclusion of the effects of nuclear dynamics in the theoretical formalism. To this end the partial-wave coupled scattering code has been generalized to allow further for the coupling of a manifold of lower vibrational states, while still incorporating reliable treatments of the tricky exchange interaction and the complicated correlation and polarization forces. Preliminary calculations of the 0-1 vibrational excitation cross section in HF, within Sigma symmetry, show good agreement with experimental results. Preliminary runs for H_2, an important and oft-studied molecule for which the best current theoretical and experimental results (crossed beam and swarm) are in serious disagreement, have been completed and tend to support the crossed beam measurements.

An improved package for the calculation of asymptotic solutions of scattering equations has been completed and successfully married to the molecular scattering code. This will permit the first practical and realistic calculations of the binding energies of weakly bound and diffuse molecular negative ion states, and perhaps also highly excited states of neutral molecules. The richest prize will be new results for the lowest bound states of HF^-, HCl^-, and HCN^-. This will finally uncover the full spectrum of the infinite number of bound states that can be trapped in the field of a polar molecule, and provide the first systematic connection between negative ion resonances and true bound states as a function of internuclear distance. As a test case, SCF calculations for H_2^- have been completed.

Electron Impact Excitation of Atoms and Atomic Ions - D. W. Norcross

This group is pursuing several fundamental and applied problems in the theory and computational physics of electron impact excitation. Excitation by electron impact is a primary source of energy transfer and radiation emission in both fusion and astrophysical plasmas. The needs for a vast amount of data for these processes, for both modeling and diagnostic purposes, are well documented, and the impossibility of generating all the necessary data by measurements is almost universally, if reluctantly, accepted. Since theory must be relied upon to provide the bulk of the data, it must be tested against measurements for carefully selected special cases. These cases, in turn, must be designed either to test or stretch particular aspects of the theory (e.g., transitions near thresholds, involving excited states, resonances, or state-selected projectiles or targets), or to check out particular novel experimental techniques under development (e.g., photometric calibration, recoiling- and merged-beam techniques, and angular distribution measurements).

A systematic series of calculations has been completed for Be^+. It has now been shown that neither an elaborate multi-configuration expansion for the electron-core interaction, nor an exhaustive treatment of virtual excitation into the continuum, has any significant impact. While the long-standing discrepancy in the polarization of the fluorescence radiation associated with this excitation has been resolved (ancient theoretical formalism was found to be in error), a stubborn 18% difference with Dunn's high precision measurements for the total cross section remains.

Detailed calculations for ions in the sodium and potassium isoelectronic sequences have been initiated with work on the doubly-charged ion Al^{++} and Ca^+. The scattering code has been used in a mode with all channels closed to compute binding energies for many of the low-lying bound states of Al^+, for which inclusion of polarization leads to much improved predictions of the ionization energies. For Ca^+, agreement of both the fluorescence polarization and the excitation cross section with the results of measurements by Dunn's group, is excellent.

Electron-Atom and Atom-Atom Collisions Processes - A. C. Gallagher

The electric breakdown and conduction of a gas and the radiation from the resultant plasma are of importance in lasers and area lighting, in switching and power generation, and in the diagnostics of man-made and astrophysical plasmas. The radiative and electrical properties of these hot gases depend on electron-atom and atom-atom collision processes, which couple the kinetic energies of the particles into radiative transitions and vice versa. During this year, Gallagher has collaborated with postdoctoral research associates M. Harris and H. Werij, and graduate students D. Atkins, K. Gibble, X. Han, G. Schinn and M. Troyer, to study several kinds of collision and radiative processes that occur in these hot gases. As it is neither practical nor economical to investigate all specific species and processes of current or potential interest, these investigations are designed to obtain highly detailed diagnostics of a few specific processes, thereby guiding and testing basic understanding applicable to all similar processes. Specifically, Gallagher and his colleagues are carrying out the following experiments.

An experiment to measure fully differential electron excitation of Na atoms from the 3S to 3P state is largely completed. This experiment uses a powerful new approach, the detection of differential cross sections by Zeeman splitting and recoil Doppler shift, to allow measurements that are fully differential in M_ℓ, M_s, and θ. Excellent signals and accurate threshold-region partial cross sections with respect to M_ℓ and M_s have been obtained, and measurements of the θ dependence are in progress. These measurements test theories in the critical threshold region with immensely more detail than has previously been available.

Differential inelastic atom-atom energy-transfer collisions ($A^* + B \rightarrow A^{**} + B$ or $A^* + B \rightarrow A + B^*$) are being measured in a crossed-beam apparatus. Such measurements critically test understanding of the interactions and collisions. Gallagher and his colleagues use supersonic metal-atom beams with well-defined velocities and detect the energy transfer, by laser induced fluorescence from the final state (A^{**} or B^*). The recoil Doppler shift in the A^{**} or B^* absorption spectrum is analyzed to yield the differential cross sections with respect to scattering angle. They have now completed measurements of $Na(3P_{3/2}) + B \rightarrow Na(3P_{1/2}) + B$ where B is an Na(3S) or K(4S) atom, yielding the differential cross sections for the energy transfer. Additional alkali-pair experiments are underway.

Another experiment measures total atom-atom collision cross sections and stimulated radiation processes in Sr vapor. Here fluorescence transients following pulsed radiative excitation of Sr are diagnosed to establish radiative and collisional pathways between many excited states, leading ultimately to a highly excited and ionized vapor. As an example, $Sr^* + Sr^* \rightarrow Sr + Sr^{**}$ processes have been measured for many combinations of initial (Sr^*) and final (Sr^{**}) states.

Silane Neutral Chemistry - A. C. Gallagher

The quality and utility of hydrogenated amorphous silicon (a-Si:H) thin film photovoltaics have increased every year since their initial production in 1976. Efficiencies of 10% are now routinely achieved, compared with crystal silicon cell efficiencies that are now about 20%. Because a-Si:H can be deposited inexpensively from a discharge as a thin layer on large areas, it is a leading contender for solar power generating systems, as well as large-area photoconductors. It is also being developed by many companies for area display and reading. In spite of this impressive progress, major improvements in deposition rate, large-area reliability, stability, and efficiency are still believed to be feasible. Some of the advances also involve Si/C and Si/Ge alloy films.

Since 1979, Gallagher and his group have been studying the discharge and surface processes that lead to the film production in order to assist this progress with improved understanding of the microscopic processes. Working this year with J. Doyle, D. Doughty, M. He and G. Lin, he has developed methods to measure surface reaction probabilities and the spatial distribution of depositing radicals, and used these to establish radical behavior in the discharges, thereby testing and advancing models for the gas and surface chemistry.

Dielectronic Ionization - G. H. Dunn

In a collaboration with E. Salzborn and A. Muller, Dunn has observed and experimentally measured for the first time a process resulting in ionization, but which is directly analogous to dielectronic recombination. In a quest for "giant resonances" in electron-impact ionization of ions, they have measured over 25 ionization cross sections as a function of energy for single, double, and triple ionization of one, two and three times charged heavy metal ions. Though the giant resonances were seen in some cases, they turned out not to be the most exciting part of the work. Resonant-excitation-double-autoionization (REDA) was clearly identified as sharp resonances for the first time experimentally, and the newly hypothesized and named processes RETA and REQA (resonant-excitation-triple/quadruple-autoionization) were also seen. Figure 2 shows examples of both REDA (top row) and RETA (bottom row).

Electron-Ion Inelastic Collisions - **G. H. Dunn**

It has long been recognized that a new method must be found for the experimental measurement of cross sections for electron-impact excitation of ions. The bulk of the measurements to date have used crossed beams and a fluorescence detection technique, and only four measurements have been made for ions of charge greater than one. A new method has been needed to understand excitation of multiply charged ions and the role of resonances, as well as to study indirect processes in ionization of ions (Excitation-autoionization, Resonant-excitation-double-ionization, etc.).

To help meet this need, Dunn, C. Timmer, and other students and post-docs are using trochoidal merger-demerger analyzers to merge an electron and ion beam and disperse inelastically scattered (or ejected) electrons from excitation (or ionization). The dispersed electrons are detected on position-sensitive detectors. This approach yields detection efficiencies approaching unity compared to efficiencies of the order 10^{-4} or less in fluorescence or normal scattered electron configurations. The new method is promising primarily at energies near threshold for excitation.

Construction and trouble shooting of this apparatus has been a major project for the past three years. During the past year, the apparatus has been repeatedly tested, diagnosed, and re-worked. Major software acquisitions have led to much better modelling of apparatus particle trajectories, which in turn has led to the redesign and construction of some key electrodes. At the most recent testing, the apparatus pumped down to 10^{-10} Torr, the electrons followed proper trochoidal trajectories, and the ion beam was adequate. Despite the low vacuum, background signals were still high, though with enough patience measurements could conceivably have been taken. A decision was made, however, to add titanium sublimation pumping to try to achieve 2×10^{-11} Torr. Since the background signal is proportional to the background pressure, it would be down a factor 5 - 7 and experiments could be started! Thus, progress is slow but continuous on this very difficult experiment. Other laboratories (LRL and JPL) that began construction of similar apparatuses are also having problems, and Dunn and his colleagues believe they have a substantial lead at this stage.

Figure 2

Kinetics of Metastable N_2 - A. V. Phelps

Phelps and his colleagues are making measurements of collision processes responsible for the production and loss of molecular metastables in electrical discharges in H_2 and N_2. Such discharges are important in devices such as hydrogen thyratrons, negative ion sources using H_2, and high power gas lasers using N_2.

J. Borysow, A. B. Wedding (University of Colorado) and Phelps have completed measurements of the destruction and rotational coupling rate coefficients for the $a''^1\Sigma_g$ metastable state of N_2. This state has recently been proposed as the energy storage reservoir responsible for the onset of instabilities in high-power CO_2-N_2 lasers. Although the destruction rate coefficient is almost an order of magnitude smaller than for the H_2 metastables investigated previously, it is sufficiently large that it seems unlikely that this state plays a significant role in the growth of discharge instabilities in high-pressure, high-power discharges.

Borysow and Phelps have developed a new technique for determining the time-dependent electric field strength in the positive column of low-pressure, pulsed electrical discharges in N_2. A knowledge of this field is necessary for modeling the production and loss kinetics of the metastable N_2. They use a laser to measure the mean Doppler shift of the very weak absorption lines of the Meinel band of N_2^+ near 690 nm. The Doppler shift gives directly the ion drift velocity, which is a known function of the electric field strength.

Collision Processes in Electrical Discharges at Very High E/n - A. V. Phelps

Phelps and colleagues are making experimental tests of models they have developed to describe the behavior of electrons, ions and fast atoms in gas discharges at very high electric field to gas density ratios, E/n. The analyses of the spatial distribution of emission from steady-state, low- current discharges showed that the optically forbidden states of N_2 molecules and Ar atoms are being excited in collisions of fast neutrals with the gas. In the case of Ar the ionization produced in such collisions was shown to be the dominant gas ionization process in electrical breakdown at low pressures and very high voltages. The fast Ar atoms are produced in charge transfer collisions of Ar^+ with the gas atoms and have average energies of about > 100 eV at the higher E/n.

V. T. Gylys (University of Colorado), B. M. Jelenković (Inst. of Physics, Belgrade), and Phelps have completed measurements of the time dependent growth of current and light emission from N_2 at gas densities and voltages below breakdown. They have shown that in the case of N_2, a very simple model of electron motion and ionization can explain the observed current growth. Experimental current growth data for Ne have been obtained but not fully analyzed.

In collaboration with L. C. Pitchford of GTE Laboratories Inc., Phelps has continued calculations of electron transport and reaction coefficients in gases at very high electric fields. Their principal concern has been with the modeling of electron motion in the very high E/n experiment described above.

Collaboration with NIST/Gaithersburg - A. V. Phelps

One of the results of the exchange visits of Phelps to NIST/Gaithersburg in 1985 and 1987 has been a determination of a new and more accurate set of electron collision cross sections for the important electrical dielectric gas SF_6. A joint paper describing this work has been submitted for publication in collaboration with R. J. Van Brunt of the Applied Electrical Measurements Group.

JILA ATOMIC COLLISION CROSS SECTION DATA CENTER - Jean W. Gallagher

The JILA Data Center under Gallagher's direction has carried on an active program to compile and evaluate data in the areas of electron and photon collisions with atoms, ions, and simple molecules. Several projects entailed collaboration with Data Center visitors who participated in the review and evaluation of data in their fields of expertise.

FY 1988 Accomplishments

1. *Collisional Alignment and Orientation of Atomic Outer Shells. II. The Molecular Regime and III. Spin Polarized Studies.* N. Andersen, Klaus Bartschat, E. B. Campbell, Jean W. Gallagher, Ingolf V. Hertel

In collisional excitation, the alignment and orientation of the target charge cloud are represented by either four or five "natural parameters". Part I of this review series (recently published in *Physics Reports*) presented an extensive discussion of the physical meaning of these parameters and a comprehensive compilation of data for direct excitation by electron and ion impact. Work has started on Parts II and III, which will make a similar presentation for the special cases, respectively, of (II) the molecular regime that pertains only to atom-atom and ion-atom collisions where the interaction times are long compared to the internal atomic time scale and (III) studies where the details of electron spin dynamics are considered.

2. *Review of Electron Impact Optical Excitation Functions for Atoms and Atomic Ions.* D. W. O. Heddle and Jean W. Gallagher

In this article optical excitation function measurements for electron-atom and electron-ion collisions are reviewed. Sources of experimental error are discussed, and in cases where adequate documentation is provided, publications are reviewed for accuracy of experimental method. The effects of polarization of the emitted radiation and methods of normalization are considered. The reliability of specific reported data is discussed based on these considerations, on the results of consistency checks and, where possible, on comparison with other measurements. Data sources for 50 atoms and 20 atomic ions are identified. Comparative plots are presented for cases where enough data are available.

3. *Multiphoton Bibliography 1983-1986*, S. J. Smith, J. H. Eberly, and J. W. Gallagher

This publication supplements NBS Publ. LP-92 (and Suppl. 1 - 4). An indexed list of articles with complete references is presented.

Work in Progress

The Atomic Collisions Data Base

Work continues on developing an interactive retrieval program. Expansion of the Data Base content continues.

FY 1989 Plans

An update to the Bibliography of Swarm Data (last published in 1979) has been started. Swarm data will be added to the Atomic Collision Data Base.

Data that have been collected on index sequential files during the last ten years will be reformatted and entered in the Data Base. Work continues on identifying, ordering, and entering new material into the Data Base.

CHEMICAL PHYSICS

Ultra-low Temperature Ion-Molecule Reactions - G. H. Dunn

M. Schauer (University of Colorado) and Dunn have continued their study of ion-molecule collisions at ultra-low energies. The technique, which uses cooled ions held in a Penning trap, is to follow the decay of parents and rise of daughters in the trap, where temperatures are substantially lower than in other methods. During the past year, the apparatus was modified so that it could be physically warmed to temperatures up to about 80 K (from the low temperature of about 10 K), permitting studies over a broader energy range. Previous measurements with this apparatus had used kinetic driving of the ions in the trap (magnetron mode) to change the interaction energy. Other modifications include changing the materials for the gas manifolds and inlets to permit introduction of pure ortho- or para- hydrogen to study the effects of rotation on some of the low temperature reactions. Detailed measurements were made as a function of energy for the basic reactions of radiative charge transfer of He^+ with H_2 and dissociative charge transfer involving the same collision partners. The mean energy range covered was 1 meV to 7 meV. Neither the results for radiative charge transfer nor those for dissociative charge transfer agree with theory developed at JILA two years ago by Kimura. Results for dissociative charge transfer are in reasonable agreement with other experiments at the high end of the energy scale where measurements are available. Dunn's results seem to be the first clear measurements for radiative charge transfer of any species.

State-resolved Dynamics via Infrared Laser Absorption Spectroscopy - D. J. Nesbitt

Nesbitt is pursuing four areas of research into molecular structure and dynamics using ultra high sensitivity infrared absorption techniques: 1) Spectroscopy of weakly bound clusters in a supersonic molecular beam by direct absorption of a tunable difference frequency laser; 2) State-to-state energy transfer between colliding supersonic jet beams; 3) Intramolecular energy distribution in jet cooled hydrocarbon molecules; and 4) Kinetics and spectroscopy of transient radicals via laser flash photolysis followed by time resolved laser absorption.

C. Lovejoy, R. Lascola (University of Colorado) and Nesbitt have already obtained high quality spectra of several van der Waals and hydrogen bonded molecules. Study of these prototypical, weakly bound species provides new information on the nature of bonding, collisional energy transfer in the gas phase, and the extremely important issue of the time scale for intramolecular vibrational relaxation. Their novel technique uses time resolved, direct infrared absorption of a high resolution tunable difference frequency laser in a slit supersonic expansion. The slit expansion device provides a two-order-of-magnitude enhancement in absorption path length, but still allows the extreme cooling, lack of spectral congestion and propensity for cluster formation characteristic of a supersonic jet. In addition, much like a stream of water through a slit aperture, hydrodynamic effects in the slit expansion geometry serve to collimate the velocities along the plane of the expansion. This results in 10-20 fold reduced Doppler widths in an unskimmed molecular beam.

Using these techniques, Lovejoy and Nesbitt have obtained the first infrared spectra of a variety of complexes, including M-HX (M = rare gas, X = F,Cl), HFN_2, $HFCO_2$, HFN_2O, and HFH_2. Many different vibrational states in each complex have been elucidated, which permits study of intermolecular potentials and coordinates far from the equilibrium geometry. Some key observations resulting from these studies are: 1) Depending sensitively on the nature of the vibration, internally excited complexes can be extremely metastable even with up to 40 times the energy to dissociate; 2) In loosely bound complexes, large amplitude quantum motion leads to extensive vibrational averaging of observable quantities (such as molecular rotational constant) and hence a high dependence on particular ro-vibrational quantum state; 3) Isomers in molecular complexes can exist, and exhibit two different, stable structures with completely different and assignable spectra; 4) Particularly in systems containing H_2, tunnelling effects from weak multiple minima in the potential can be observed and analyzed by virtue of spectral doublings resolvable in the apparatus. These studies are raising new and challenging theoretical questions about the nature of full 3-dimensional solutions of the multibody Schrödinger equation in molecular systems near the dissociation limit.

A. McIlroy (University of Colorado) and Nesbitt are exploiting the novel properties of slit jet expansion to study the dynamics of vibrationally excited, but ultra cold, hydrocarbons. A given vibration in a molecule, if excited, can eventually relax into a linear combination of many other vibrational modes via intramolecular relaxation pathways. Spectroscopically, the fingerprint of this intramolecular relaxation is line broadening or excess fine structure in the spectrum, which is completely obscured at room temperature. Studies in the cooled jet environment, however, elegantly avoid this difficulty and permit a detailed spectroscopic investigation of intramolecular dynamics in a collision-free regime. Their studies have successfully revealed this excess fine structure in a homologous series of terminal acetylenes excited in the CH stretch region ($\approx 3.3\ \mu m$). Analysis of the fine structure indicates two major surprises: 1) Vibrations do <u>not</u> need rotation of the molecule to relax intramolecularly (i.e., Coriolis effects are important but not essential), and 2) The relaxation occurs to essentially all vibrational states equivalently. The spectra permit a prediction of the time dependence of these CH stretch detailed excitations which we now know to relax on a 100 psec timescale or less. The dynamics in these systems, however, may change dramatically from system to system, and therefore provide a rich opportunity to isolate the key features determining IVR phenomena.

A. Schiffman (University of Colorado), D. Nelson (NRC Postdoctoral Fellow) and Nesbitt have built a new experiment to study transient radicals by time and frequency resolved absorption spectra. A pulsed excimer laser is used to cleave photolytically appropriate molecular precursors in a fast gas flow to generate highly reactive radical species. By use of a tunable IR laser probe collinear with the photolysis beam, weak transient absorbance signals from the radicals can be detected, signal averaged and analyzed for the desired kinetics. First efforts have been directed towards OH in order to characterize the infrared integrated absorption strengths of this atmospherically important radical. A major success of this study has been to extract the dipole moment function for OH from purely the IR and microwave Stark data by itself. Recent efforts have focussed on the use of the transient OH absorption to study the kinetics of this atmospherically important radical. We now have developed methods for single frequency scanning the F-center under computer and servo loop control, as well as capturing transient IR signals for later analysis.

A new experiment is presently being built with M. Schuder (University of Colorado) and Nelson for diode laser probing of molecular species in supersonic jets. The diode laser will permit extension of their earlier efforts to a much wider region of the IR spectrum. In particular, we will be able to look at clusters containing the strong IR chromophores NO, N_2O, CO_2, CO, SO_2, and OCS. At present we are gaining experience in servo loop stabilizing and scanning single frequency diode lasers with respect to a reference cavity. The first molecular effort will be towards characterizing ArDCl and $HFCO_2$ in the region near 5 microns. The systems are of fundamental interest due to the overlap with the near infrared, difference frequency studies of weakly bound complexes.

Photofragmentation Dynamics - **S. R. Leone**

Photodissociation processes of molecules are providing some of the most detailed results of state-resolved chemical dynamics in recent years. These photofragment processes are particularly important because they are similar to the latter half of a collision, which in principle could represent a chemical transformation. While many groups have explored the use of laser-induced fluorescence to probe the states of diatomic fragments, few laboratories have considered the possibilities of detecting infrared emission, which can ultimately be extended to more complex polyatomic fragments.

R. Fletcher, E. Woodbridge (University of Colorado) and Leone have completed a major new apparatus to study photodissociation dynamics using time-resolved Fourier transform infrared (FTIR) emission spectroscopy. The method was recently shown in this laboratory to give highly precise results for the rotationally resolved product states of the HF diatomic from the photolysis of 1,1-CH_2CFCl. The technique was immediately extended to a study of the three body photodissociation of acetone to form two methyl radicals and CO. From the uniquely high excitation of the rotational states in the CO fragment, it is possible to determine that the acetone breaks apart in two steps, i.e., in a nonconcerted process. Recently, a complete spectrum of the methyl radical fragments has also been obtained. Spectra of the excited CCH radical from the photolysis of acetylene have also been analyzed in detail to determine the rotational dynamics of this decomposition.

Ion-Molecule Collision Dynamics - **S. R. Leone**

Several extremely exciting breakthroughs have been made this year to increase the powerful repertoire of methods to study ion dynamics.

A single mode dye laser technique has been used to study ion velocity distributions for the first time in a well-characterized electric drift field region, work carried out by S. Penn (NRC Postdoctoral Fellow), H. Beijers, V. Bierbaum, and Leone. The Ba^+ ion was drifted in He and Ar buffer gases in a flowing afterglow apparatus, and the velocity distributions were recorded by scanning the single mode dye laser and detecting laser-induced fluorescence. The measurements obtained several fundamentally new pieces of information. In addition to measuring the drift velocity as a function of field strength (and hence the mobility), the temperatures (i.e., spreading of the ion velocity distribution) both parallel and transverse to the electric field were obtained for the first time. According to theory, for a heavy ion in a light buffer, the spreading in the parallel direction should be significantly greater than in the transverse direction and the velocity distributions should be Maxwellian. This result has now been verified and the agreement with theory is excellent. In addition, theory describes a "skewing" of the velocity distribution for heavier buffer gases. This has also now been documented experimentally for the first time. These results open up a tremendous number of new possibilities to study ion velocity distributions optically under well-characterized conditions and to compare the measurements to theory and provide refinements to the theoretical analyses.

A discovery about Penning ionization processes and charge transfer has been made by D. Sonnenfroh (NRC Postdoctoral Fellow) and Leone. Using a novel apparatus in which metastable states of Ne or ions of Ar are reacted with rotationally cold N_2 molecules, a higher level of rotational detail has been revealed about these electron transfer processes. The rotational distributions within each vibrational level show strong bimodality when the nitrogen is initially cooled to 8 K. At room temperature, this bimodality is obscured. The two rotational distributions are accounted for by the fact that the potential surfaces for the electron transfers have two regions of electron transfer, for example, early in the collision and only after the distance of closest approach is reached. Collaborative investigations are underway (D. Clary, former Visiting Fellow) to calculate the dynamics that give rise to this fine detail in the rotational states.

Energy Transfer - S. R. Leone

Energy transfer processes are important in a wide variety of environments, including laser and discharge media, interstellar space, and the upper atmosphere. The most exciting results in this area (notwithstanding the energy transfer work involved in the Ba^+ velocity distributions mentioned above) have been in the study of alignment effects on electronic energy transfer of Ca and Sr atoms. In new experiments, L. Kovalenko and Leone have measured a wide variety of energy transfer processes in a complex system of states in Sr atoms. The orbital alignments of the states responsible for the energy transfer to seven near resonant levels have been obtained. There is a high degree of specificity both in the branching ratio and in the alignment effects. The results are accurately explained by the use of some molecular selection rules for the couplings between the various states. Theoretical work is ongoing with J. Delos (former Visiting Fellow) to study fine-structure changing collisions in atomic sodium.

Surface Dynamics - S. R. Leone

D. Oostra, B. Bourguignon, R. Smilgys and Leone are pursuing a program in surface scattering dynamics and the growth of semiconductors. This project involves the use of lasers as tools for determining the participation of individual vibrational and electronic states of the gas phase species in the epitaxial kinetics and dynamics of surface semiconductor growth. The first work involves the growth of GaAs semiconductors on silicon single crystals. Measurements have been made using laser induced fluorescence detection of Ga and In atoms as they scatter and desorb from a Si(100) crystal to determine the binding energies of the atoms on the silicon surface. The results show a high binding energy for Ga (2.9 eV) and somewhat lower for In (2.6 eV).

Leone and his colleagues have succeeded in probing the dynamics of the two different spin orbit states in the Ga, and have derived a model of the two-state desorption kinetics to explain the results. Whereas the Ga spin-orbit states appear to be strongly coupled on the surface, the In spin orbit states, which are split by a greater energy difference, do not. Structural studies using low energy electron diffraction show that the Ga forms ordered overlayers on Si up to coverages of one monolayer, most likely forming two bonds to the silicon surface and one Ga-Ga dimer bond. Structures for the Ga overlayers and the island growth behavior after one monolayer have been postulated. The results have important implications for the industrial considerations of the growth of GaAs on silicon. For example, the binding energy considerations show that both Ga and As have equal propensity to bind to the clean silicon surface, thus explaining the difficulties previous researchers had with antiphase domains, in which either As or Ga will start growing next to the Si substrate.

1987-1988 VISITING FELLOWS

Quantum Physics Division (577)

Visiting Fellow	Home Institution	Area of Work
David C. Clary	University Chemical Laboratory Cambridge University Cambridge, United Kingdom	Theory of molecular collision in processes in the gas phase.
James M. Farrar	Department of Chemistry University of Rochester Rochester, NY	Low energy ion-neutral interactions, crossed beam studies of reactive collisions.
Jack Feinberg	Department of Physics University of Southern California Los Angeles, CA	Optical computing; interactions of light with matter.
Juhan Frank	Max Planck Institut fur Astrophysik Garching, West Germany	Accretion in active galactic nuclei and binary systems.
Ivan Hubeny	Astronomical Institute Czechoslovak Academy of Sciences Ondrejov, Czechoslovakia	Stellar atmospheres, atomic processes, line scattering, numerical simulations.
Wm. Lowell Morgan	Lawrence Livermore National Laboratory Livermore, CA	Computer simulation of atomic and molecular processes, gas-surface interactions.
Per Ake Nordlund	Copenhagen University Observatory Copenhagen, Denmark	Dynamics of the solar atmosphere.
Artur Stolz	School of Surveying University of New South Wales Kensington, Australia	Global positioning system and laser ranging.

1987-1988 VISITING FELLOWS (cont.)

Visiting Fellow	Home Institution	Area of Work
John Weiner	Department of Chemistry University of Maryland College Park, MD	Inelastic collision dynamics in simple systems.
Peter Zoller	Institute for Theoretical Physics University of Innsbruck Innsbruck, Austria	Interaction of laser light with atoms, multiphoton processes, laser physics, quantum optics, electron correlation effects.
Burkhard Brehm	Institut fur Atom- und Molekulphysik Universitat of Hannover Hannover, West Germany	Photoionization and photofragmentation of molecules and angular distributions of photoelectrons.
John Briggs	Fakultaet fur Physik Universitaet Freiburg Freiburg, West Germany	Theory of highly excited states of two-electron atoms.
Fang Li Zhi	Beijing Astronomical Observatory Chinese Academy of Sciences Beijing, P.R.C.	Theoretical astrophysics and cosmology.
Gary Ferland	Astronomy Department Ohio State University Columbus, OH	Photoionization models of quasars and emission line models.
Ian Howarth	Department of Physics & Astronomy University College London, London, United Kingdom	Observational studies of stellar winds, interstellar media, x-ray and interacting binary star systems.
Stephen Lundeen	Department of Physics University of Notre Dame Notre Dame, IN	High resolution studies of atomic and molecular Rydburg states.

1988-1989 VISITING FELLOWS

Quantum Physics Division (577)

Visiting Fellow	Home Institution	Area of Work
Burkhard Brehm	Institut fur Atom- und Molekulphysik Universitat of Hannover Hannover, West Germany	Photoionization and photofragmentation of molecules and angular distributions of photoelectrons.
John Briggs	Fakultaet fuer Physik Universitaet Freiburg Freiburg, West Germany	Theory of highly excited states of two-electron atoms.
Fang Li Zhi	Beijing Astronomical Observatory Chinese Academy of Sciences Beijing, P.R.C.	Theoretical astrophysics and cosmology.
Gary Ferland	Astronomy Department Ohio State University Columbus, OH	Photoionization models of quasars and emission line models.
Ian Howarth	Department of Physics & Astronomy University College London, London, United Kingdom	Observational studies of stellar winds, interstellar media, x-ray and interacting binary star systems.
Stephen Lundeen	Department of Physics University of Notre Dame Notre Dame, IN	High resolution studies of atomic and molecular Rydburg states.
Alfred Maquet	Laboratoire de Chimie Physique Universite Pierre et Marie Curie Paris, France	Theoretical studies of collisions under the influence of radiation.
Takashi Sato	Department of Electrical Engineering Niigata University Niigata City, Japan	Laser stabilization and laser-induced particulate formation.

1988-1989 VISITING FELLOWS

Quantum Physics Division (577)

Visiting Fellow	Home Institution	Area of Work
George Schatz	Department of Chemistry Northwestern University Evanston, IL	Theoretical work on atomic and molecular collision processes and unimolecular decomposition.
Reinhard Schinke	Max-Planck-Institut fur Stromungsforschung Gottingen, West Germany	Theoretical dynamics of photodissociation of polyatomic molecules, molecular collisions.
John P. Simons	Department of Chemistry University of Utah Salt Lake City, UT	Electronic structure of negative molecular ions; dynamical behavior of anions.

CONFERENCES SPONSORED

Quantum Physics Division (577)

The Twelfth International Conference on General Relativity and Gravitation, University of Colorado, Boulder, Colorado, July 3-8, 1989. P. L. Bender and J. E. Faller are on the Scientific Committee.

SEMINARS AND COLLOQUIA

CELEBRATION SYMPOSIUM:

JILA's 25th ANNIVERSARY

April 8, 1988
2:00 to 5:00 pm

Richard N. Zare (Department of Chemistry, Stanford University) - The Laser Revolution in Chemistry.

J. Craig Wheeler (Astronomy Department, University of Texas-Austin) - Supernova 1987.

Norman F. Ramsey (Professor Emeritus, Harvard University) - The Frontier of High Precision.

JILA Colloquia

Arthur M. Wolfe (University of Pittsburgh and Mt. Wilson-Las Campanas Observatory) - Damped Lyman Alpha Absorption by the High Redshift Progenitors of Disk Galaxies, October 6, 1987.

David Clary (JILA Visiting Fellow, University of Cambridge) - Electron-Dipole Complexes, October 13, 1987.

Ivan Hubeny (JILA Visiting Fellow, Czechoslovak Academy of Sciences) - Radiative Transfer With Partial Redistribution, October 20, 1987.

William Gadzuk (NIST, Gaithersburg) - Elementary Chemical Dynamics at Surfaces, October 27, 1987.

Jim Anderson (Harvard University) - Free Radical Kinetics: Multipole Transition States and Antarctic Polar Vortices, November 10, 1987.

Frances Bagenal (HAO/NCAR) - The Peculiar Role of Io in Jupiter's Magnetosphere, November 17, 1987.

William Lowell Morgan (Lawrence Livermore National Laboratory) - Computer Simulation of Gas-Surface Dynamical Processes, November 24, 1987.

Jacob Shaham (Columbia University) - Low Mass X-Ray Binaries, Millisecond Pulsars, and Quasi Periodic Objects, December 1, 1987.

Joseph Demuth (IBM Yorktown Heights) - Atomic Imaging and Spectroscopy With the Scanning-Tunnelling Microscope, December 8, 1987.

Matt Malkan (UCLA) - Accretion Discs in Active Galactic Nuclei, December 15, 1987.

Daniel Kelleher (NIST, Gaithersburg) - In Search of Pauli Exclusion Principle Violating States in He, January 12, 1988.

Richard A. McCray (APAS/JILA) - Supernova 1987a: What Next?, January 19, 1988.

James M. Farrar (JILA Visiting Fellow, University of Rochester) - Ion Beam Studies of Chemical Reaction Dynamics: Collisions and Photochemistry, February 2, 1988.

Bohdan Paczynski (Princeton University Observatory) - Cosmic Gamma-Ray Bursts: Fact and Fantasy, February 9, 1988.

Peter Zoller (JILA Visiting Fellow, University of Innsbruck, Austria) - Atomic Transitions in Light Fields: Rydberg Wave Packets and Finite Bandwidth Squeezing, February 16, 1988.

Gary Ferland (Ohio State) - Thermal Emission From Quasars, February 23, 1988.

James A. Anderson (Harvard University) - Free Radical Reactivity and Catalysis: Of Multiple Transition States and Antarctic Polar Vortices, March 1, 1988.

Grote Reber (Tasmania, Co-Founder of the Science of Radio Astronomy) - The Big Bang Is Bunk, March 8, 1988.

Rick Smalley (Rich University) - C_{60}, March 15, 1988.

Dough N. C. Lin (Lick Observatory) - Star Formation in Globular Clusters and Dwarf Galaxies, March 22, 1988.

William Miller (University of California, Berkeley) - Recent Developments in the Theory and Application of Quantum Mechanical Reactive Scattering, March 29, 1988.

Steve Barry (University of Chicago) - Freezing and Melting and Fractals and Clusters, April 5, 1988.

Sasha Kashlinsky (University of Virginia) - Large Scale Structure and the Microwave Background, April 12, 1988.

Bob Mathieu (University of Wisconsin) - Stellar Kinematics of Star Forming Regions, April 19, 1988.

William Happer (Princeton University) - Laser Polarization of Noble Gas Nuclei, April 26, 1988.

Richard A. London (University of California, Lawrence Livermore National Laboratory) - Laser Produced Plasmas and Soft X-Ray Lasers, May 3, 1988.

Pat Thaddeus (Harvard University) - A CO Survey of Metallic Clouds in LMC, May 10, 1988.

George Schatz (JILA Visiting Fellow, Northwestern University) - Reactive Quantum Scattering Resonances and the Photodetachment Spectra of $ClHCl^-$ and IHI^- , September 6, 1988.

James Bayfield (University of Pittsburgh) - Highly Excited Atoms in STrong Microwaves: Classical Resonances, Localization, and Ionization, September 20, 1988.

Sun Kwok (University Calgary) - Evolution Form Red Giant to Planetary Nebula, September 27, 1988.

Lothar Frommhold (University of Texas, Austin) - Supermolecular Spectra: Principles and Astrophysical Interest, October 4, 1988.

Steve Lundeen (JILA Visiting Fellow, University of Notre Dame) - Spectroscopy of High L Rydberg States of H_2: A Sensitivae New Probe of the H^+ Molecular Ion, October 11, 1988.

John C. Raymond (CfA) - Diagnosing the Line Spectra of Interstellar Shocks, October 18, 1988.

James L. Kinsey (Rice University) - Spectroscopic Studies of Photodissociation Dynamics, October 25, 1988.

Ray Weiss (JILA Distinguished Visiting Scientist, MIT) - Recent Progress in Measurements of the 3 K Background, November 8, 1988.

James L. Valentini (University of California at Irvine) - State-To-State Dynamics: Do We Really Need All That Date?, November 15, 1988.

Dave M. Rank (Lick Observatory) - Recent Infrared Observations of Supernova 1987a With the Kuiper Astrophysical Observatory, November 29, 1988.

Joint JILA/Astrophysics, Planetary and Astronomical Sciences Colloquia

David J. Thomson (Bell Laboratories) - Multiple Window Spectral Analysis of Paleoclimatological Time Series, October 5, 1987.

Bruce R. Barkstrom (NASA Langley) - Earth Radiation Budget Experiment and Measurements, October 19, 1987.

Joseph J. Tribbia (NCAR) - On the Dynamics and Predictability of Atmospheric Motions With Timescales Larger Than One Month, October 26, 1987.

Jill Bechtold (Mt. Wilson - Las Campanas Observatories) - Quasar Absorption Line Controversies, November 2, 1987.

Max J. Suarez (Global Modeling and Simulation Branch, NASA/Goddard Space Flight Center) - The Time-Scale of El Nina/Southern Oscillation Variability, November 9, 1987.

David W. Rusch (LASP/APAS) - Ozone Trends in the Middle Atmosphere, November 16, 1987.

Catharine Garmany (JILA/CASA) - Massive Stars in the Magellanic Clouds: The Ones That Haven't Exploded, November 23, 1987.

Carolyn C. Porco (University of Arizona) - Eccentric Features in Saturn's Rings, December 3, 1987.

Robert C. Kennicutt, Jr. (University of Minnesota) - Giant HII Regions and the Formation of Populous Star Clusters, December 7, 1987.

Erast Gliner (Institute for Physics and Technology, Leningrad) - General Relativistic Problem of the Inflationary Cosmology, January 25, 1988.

Jens V. Villumsen (Ohio State University) - Cosmological Parameters From the Infra-Red Astronomical Satellite, February 15, 1988.

William D. Vacca (APAS) - Quasi-Periodic Oscillations in Low Mass X-Ray Binaries, February 22, 1988.

Michael A. Dopita (Mount Stromlo and Siding Spring Observatory) - Planetary Nebulae in the Large Magellanic Cloud, February 29, 1988.

Bruce R. Barkstrom (NASA Langley) - The Earth Radiation Budget Experiment (ERBE), March 7, 1988.

Gibor B. Basri (Berkeley) - Accretion Disks and Boundary Layers on T-Tauri Stars, March 14, 1988.

Tom R. Ayres (CASA) - Aerobatics With Stellar Spectra, March 21, 1988.

Isaac Shlosman (JILA) - Fueling the Black Hole in Active Galactic Nuclei, April 4, 1988.

Mitchell C. Begelman (APAS/JILA) - Active Galactic Nuclei on the Back of an Envelope, April 11, 1988.

Claire E. Max (Lawrence Livermore Laboratory) - Computer Simulation of High-Energy Astrophysical Plasmas, April 18, 1988.

Isidoros Doxas (University of Texas at Austin) - Numerical Study of the Current Sheet in a Magnetotail Model, April 25, 1988.

John W. Firor (NCAR) - Earth Climate and Greenhouse Effect, April 28, 1988.

C. Megan Urry (Space Telescope Science Institute) - What are Blazars Anyway?, May 2, 1988.

Stephen H. Lepp (CfA) - Polyaromatic Hydrocarbons (PAHs) in Astrophysics, September 12, 1988.

Amiel Sternberg (CfA) - The Infrared Response of Interstellar Molecular Hydrogen to Ultraviolet, September 19, 1988.

Leo Blitz (University of Maryland) - The Evolution of the Interstellar Medium, September 26, 1988.

James Liebert (Steward Observatory) - kWhite Dwarfs and thae Agae of the Galactic Disk, October 3, 1988.

Webster Cash (APAS/CASA) - Far Ultraviolet Rocket Observations of Supernova 1987a, October 10, 1988.

Tod Clancy (LASP) - Global Climatology of the 58-90 Kilometer Atmospheric Temperature, October 17, 1988.

John C. Raymond (CfA) - Diagnosing the Line Spectra of Interstellar Shocks, October 18, 1988.

Jim Green (Berkeley) - Detection of the He I Edge in the Interstellar Medium, October 24, 1988.

Eli Dwek (GSFC) - Infrared Emission From Supernova Remnants Observed by the Infrared Astronomical Satellite, November 7, 1988.

Joint JILA/Astrophysics, Planetary and Astronomical Sciences Colloquia

Joseph Nuth (GSFC) - Chemical Dynamics and Circumstellar Grain Formation, November 11, 1988.

John Cary (APAS) - Plasma Chaos, November 28, 1988.

Peter Quinn (StScI) - Dark Matter and the Hubble Sequence, December 5, 1988.

Peter Conti (APAS/JILA) - Numbers and Distributions of Wolf-Rayet Stars in the Local Group of Galaxies, December 12, 1988.

Special JILA Seminars

Brian Petley (National Physical Laboratory, Teddington, UK) - Toward the Limits of Precision and Accuracy in Physical Measurement, October 29, 1987.

Jean -Paul Richard (University of Maryland) - Laser Instrumentation for Gravitational Wave Antennas at the Multi-Mode Bar Type, February 12, 1988.

Chris Greene (Louisiana State University) - Conspicuous Effects of Weak Forces in Photodetachment, March 3, 1988.

V. P. Chebotayev (Institute of Thermal Physics, Academy of Sciences, USSR) - Recent Advances in High Resolution Spectroscopy and Frequency Metrology, March 8, 1988.

Steven A. Blundell (Institute for Theoretical Physics, University of California at Santa Barbara) - Parity Nonconservation in Atoms, March 10, 1988.

Bonnie Schumaker (Jet Propulsion Laboratories, Pasadena, California) - Ultra-Squeezed Light and Quantum Nondemolition Detection in Optical Fibers, March 24, 1988.

Anil K. Pradhan (JILA) - Atomic Processes in Laboratory and Astrophysical Plasmas, April 7, 1988.

Thad Walker (Princeton University) - Deexcitation of Metastable States of Ba and Ba^+, April 7, 1988.

Roger Herman (Pennsylvania State University) - A Novel Theory for Atomic Coherence Transport and the Structures of Spectral Lines in Laser Spectroscopy, April 14, 1988.

Shih-I-Chu (University of Kansas) - Atomic and Molecular Process in Strong Fields, April 14, 1988.

Peter Zoller (JILA Visiting Fellow, University of Innsbruck, Austria) - Light Statistics and Multiphoton Processes, April 21, 1988.

Anthony F. Starace (University of Nebraska), - Many-Body Effects on Multiphoton Ionization Processes, April 18, 1988.

Warren Warren (Princeton University - Effects of Pulse Shaping in NMR and Femtosecond, June 24, 1988.

Peter Schulz (MIT Lincoln Laboratory) - Ti: Sapphire Laser Dynamics, July 25, 1988.

Eric Eliel (University of Leiden, The Netherlands) - Progress in Light-Induced Drift of Alkali Atoms, July 22, 1988.

Dieter Hils (JILA) - Precise Locking of He-Ne Lasers to Stable Cavities, August 4, 1988.

Rajarshi Roy (Georgia Institute of Technology) - Stochastic Dynamics in Lasers - Stochastic Resonances, September 12, 1988.

Michael Holzscheiter (Los Alamos National Laboratory) - The Gravitational Acceleration of the Antiproton, September 28, 1988.

Cool Stars Seminars

Karel Schrijver (JILA) - Are Basal Fluxes Real, October 28, 1987.

Joe Pesce (CASA) - The Search For the Elusive Companion of EG And., November 4, 1987.

Jay Bookbinder (JILA) - The Latest From the Beach, Recent Results From Arecibo, December 9, 1987.

Bob Stencel (CASA) - The UV Shell of Alpha Ori, December 16, 1987.

Jeff Linsky (JILA) - Dainis Dravins Video on Fixed Pattern Noise in IUE Data, January 20, 1988.

Jim Neff (JILA) - Highlights of the Austin AAS Meeting, January 27, 1988.

Karel Schrijver (JILA) - What H Alpha Absorption and Emission Are Telling Us About M Dwarf Chromospheres, February 3, 1988.

Tom Fleming (Arizona) - The Relation Between X-Ray Emission and Rotation in Late-Type Stars From the Perspective of X-Ray Selection, February 10, 1988.

Web Cash (CASA) - NASA UV/IR MOWG Meeting and Rocket Program, February 17, 1988.

Ivan Hubeny (JILA Visiting Fellow, Astronomical Institute, Czechoslovak Academy of Sciences) How the Lyman Alpha and Lyman Beta Lines Are Actually Formed in the Solar Chromosphere, March 16, 1988.

Francoise Praderie (Observatory de Paris, Meudon) - The OI IR Triplet: A Tracer of the Wind in Herbig (PMS) Stars, April 7, 1988.

Mark Monday (Oxford University, England) - Work on 56 Peg, April 20, 1988.

Karel Schrijver (JILA) - Supergranulation and the Decay of Plages, April 27, 1988.

Philip Judge (JILA) - Recent Work and Future Plans for Spectral Diagnostics for Cool Stars, May 4, 1988.

Jay Bookbinder (JILA) - Thoughts on Scatter of Solar Radio Emission, May 20, 1988.

Karel Schrijver (JILA) - Nonlinearity of Flux-Flux Relations, May 25, 1988.

Bill Boyd (CASA) - Transition Region Activity in F Dwarfs, June 1, 1988.

Tom Ayres (CASA) - NLTE CO Revisited, Part I, June 8, 1988.

Tom Ayres (CASA) - NLTE CO Revisited, Part II, June 15, 1988.

Philip Judge (JILA) - Chromospheres of the Reddest Giant Stars, June 22, 1988.

Ed Sion (Vilanova) - V471 TAURI, June 29, 1988.

Dana Backman (NOAO) - Thermal Models of the Beta Pic Disk, July 20, 1988.

Ake Norlund (JILA Visiting Fellow, Copenhagen University Observatory, Denmark) - Talk on his Recent Work, July 26, 1988.

Irene Little-Martin, Steve Little, and Bob Stencel - The Recent IAU Colloquium on the Evolution of Red Giants, August 3, 1988.

Jeff Linsky (JILA) - The HST GTO Observing Programs, August 10, 1988.

Steve Skinner (JILA/CASA) - Herbig Ae/Be Stars, September 7, 1988.

Chemical Physics Colloquia

Steven Colson (Yale University) - Mechanisms of UV Multiphoton Fragmentation of Molecules and Ions, October 2, 1987.

Chuck Wight (University of Utah) - Laser-Induced Reactions of Free Radicals in Low Temperature Solids, October 9, 1987.

Jim Cowin (University of California at Santa Barbara) - Laser Photochemistry on a Metal Surface, October 16, 1987

Tom Taylor (Los Alamos National Laboratory) - The Silver/Copper (110) Interface: Surface Properties and Their Relationship to Second Harmonic Generation, October 23, 1987.

Mark Child, Condon Lecture (Oxford University) - Predissociation and Unimolecular Reactions, October 30, 1987.

Emily Carter (University of California - Los Angeles) - Accurate Energetics From Quantum Chemistry for Transition Metal-Catalyzed Reactions, November 6, 1987.

Bill Engelhoff, Jr. (NIST) - November 13, 1987.

Ara Apkarian (University of California at Irvine) - Photodynamics in Condensed Media, November 20, 1987.

Jim Sloan (NRC Canada) - The Use of Fast Time-Resolved Fourier Transform Infrared Spectroscopy to Measure the Dynamics of 0 (^{1}D) Reactions, December 4, 1987.

Hai-Lung Dai (University of Pennsylvania) - Dynamics and Spectroscopy of Vibrationally Excited Molecules and Complexes: From the Bottom of the Potential Surface to the Dissociation Limit, January 22, 1988.

Michael Duncan (University of Georgia) - Bimetallic Clusters in the Gas Phase, January 29, 1988.

Horia Metiu (University of California at Santa Barbara) - Time Dependent Quantum Mechanics of Photodissociation, February 5, 1988.

Ned Sibert (University of Wisconsin) - Vibrational Spectroscopy and Effective Hamiltonians, February 12, 1988.

Randy Creighton (Sandia) - Selectivity Loss During Tungsten CVD, February 19, 1988.

Jeffrey Hudgens (NIST) - Studies of Electronic Structure and Reactivity of Free Radicals Using Multiphoton Ionization Spectroscopy, February 26, 1988.

Matti Maricq (Brown University) - Vibrational Relaxation of Ions and Molecules at Low Collision Energy, March 4, 1988.

Mark Johnston (Yale University) - March 11, 1988.

Bob Coombe (Denver University) - Excited State Chemistry of Nazides and Isocyanates, March 18, 1988.

Michael Van Hove - Surface Chemistry Through Surface Structure, March 25, 1988.

Philip Pechukas (Columbia University) - Frequency Locking and Dragging, April 15, 1988.

Raymond Kapral (Toronto) - Noise-Induced Reactions Far From Chemical Equilibrium, April 22, 1988.

Gary McClelland (IBM - San Jose) - The Atomic Dynamics of Friction: Theory and Experiment, April 29, 1988.

J. L. Beauchamp (California Institute of Technology) - Produce Kinetic Energy Release Distribution as a Probe of the Energetics and Mechanisms of Organometallic Reactions in the Gas Phase, May 20, 1988.

Bertrand Rowe (Laboratoire d'Aerothemique du Centre National de la Recherche Scientifique, Meudon, France) - Recent Results on Ion-Molecule Reactions at Very Low Temperatures: Astrochemistry Implications, June 3. 1988.

Chemical Physics After Dark Seminars

C. P. Schulz (JILA) - Sodium-Water Clusters, October 21, 1987.

Bernard Bourguignon - Interaction of GA Atoms With Si(100): Scattering and Growth Mechanism Studied by LIF, LEED and Auger Electron Spectroscopy, October 28, 1987.

Steve Sapers (University of Colorado) - Photodissociation of Methyl Iodide as Probed by Multiphoton Ionization, November 4, 1987.

Rick Fletcher (JILA) - Photodissociation Studies of Some Large Molecules Using Time-Resolved FTIR Emission Spectroscopy, November 11, 1987.

Steve Penn (JILA) - The Photodissociation of Methyl Iodide at 230 nm, November 18, 1987.

Dave Sonnenfroh (JILA) - Product Rotational Distributions of Some Basic Thermal Energy Ion-Molecule Reactions, December 2, 1987.

Julian Coutts (JILA) - The Effect of Collisions on Forbidden Lines, December 9, 1987.

Hans Beijers (JILA) - Laser Probing of Ion Velocity Distributions of Ba^+ Drifting in He, December 16, 1987.

Aleksandra Borysow (JILA) - Collision-Induced Spectroscopy: Possible Applications to Planetary and Stellar Atmospheres, January 13, 1988.

Tom Wickham-Jones (University of Colorado) - Photoelectron Spectroscopy of BH_3 and BD_3, January 27, 1988.

Greg Schinn (JILA) - Alignment to Orientation Conversion in Sodium, February 3, 1988.

Dominic Zichi - A Dynamical Theory of Unimolecular Ionic Dissociation Reactions in Polar Solvents, March 9, 1988.

Elfi Kraka (Institut f. Organische Chemie, University of Koln, Argonne National Laboratory) - New Insights to Chemical Reactions: The Reaction Path Hamiltonian Model, March 23, 1988.

Jamie Donaldson (JILA) - Surface Crossings and Predissociation Dynamics of CH_3I, April 6, 1988.

Stephen Angel (University of Colorado) - Picosecond Spectroscopic Studies of the Intrinsic Rate of Intermolecular Electron Transfer in Solution, April 13, 1988.

Aram Schiffman (JILA) - Infrared Transition Moments for OH(v=1) 0): Some High Resolution Spectroscopy and Some Theory to Back It Up, April 27, 1988.

Andy **McIlroy** (JILA) - Vibrational State Mixing in Hydrocarbons at the CH Stretch Level of Excitation, May 4, 1988.

Lisa **Cousins** (JILA) - Kinetic Energy Distributions of Hyperthermal Molecules From Excimer Laser Desorption of Cryogenic Films, May 11, 1988.

Chris **Lovejoy** (JILA) - Spectroscopy and Structure - Is There a Discernible Connection for van der Waals Molecules? The Lessons of N_2O/HF, May 18, 1988.

Doug **Ray** (JILA) - Spectroscopy and Dynamics of Large Cluster Ions, May 25, 1988.

Mark **Polak** (University of California, Berkeley) - Velocity Modulation Spectroscopy of Negative Ions, August 16, 1988.

INVITED TALKS

Quantum Physics Division

P. L. Bender, "Laser Gravitational Wave Observations in Space," Gravitational Physics Seminar, Princeton University, Princeton, New Jersey, November 10, 1987.

P. L. Bender, "Sources and Sensitivities for Laser Gravitational-Wave Observations in Space," Physics Department Colloquium, Rutgers University, New Brunswick, New Jersey, November 11, 1987.

P. L. Bender, "Atmospheric Refraction Uncertainties," Session on Geodesy in the Year 2000, American Geophysical Union Meeting, San Francisco, California, December 9, 1987.

P. L. Bender, "Optical Interferometer In Space," Workshop on Relativistic Gravitation Experiments in Space," Annapolis, Maryland, June 28, 1988.

P. L. Bender, "Distance Measurements In Space: Gravitational Physics Tests and A Proposed Laser Gravitational Wave Antenna," Eleventh International Conference on Atomic Physics, Paris, France, July 8, 1988.

P. L. Bender, "Conceptual Design for a Mercury Relativity Satellite," COSPAR Symposium on Relativistic Gravitation," Helsinki, Finland, July 21, 1988.

P. L. Bender, "Preliminary Optical Design for a Laser Gravitational Wave Antenna in Space," Space Optics for Astrophysics and Earth and Planetary Remote Sensing, Optical Society of America Topical Meeting, North Falmouth, Massachusetts, September 27, 1988.

P. L. Bender, "Observational Accuracy For Lunar Laser Ranging," IAU Joint Commission Meeting #1, Baltimore, Maryland, August 3, 1988.

G. H. Dunn, "Some Recent Results in Electron-Ion Collisions," Physics Department Colloquium, University of Giessen, West Germany, November 2, 1987.

G. H. Dunn, "Resonances in Electron-Ion Collisions," Colloquium, Institute of Physics, Belgrade, Yugoslavia, November 20, 1987.

G. H. Dunn, "Dielectronic Processes in Electron-Ion Collisions," Physics Department Colloquium, University of Nebraska, Lincoln, Nebraska, April 28, 1988.

G. H. Dunn, "Physics With Ion Traps at JILA," Physics Division Colloquium, Argonne National Laboratory, Argonne, Illinois, May 12, 1988.

G. H. **Dunn**, "Dielectronic Capture, Stabilization and Decay," 1988 Joint Congress of the American Physical Society and the Canadian Association of Physics, Montreal, Canada, June 22, 1988.

G. H. **Dunn**, "Dielectronic Processes in Electron-Ion Collisions," International Symposium on Atoms in Strong Fields, Grainau, West Germany, September 5, 1988.

J. E. **Faller**, "Two Precision Gravity Experiments: Tests of the 5th Force Hypothesis," Department of Physics, Purdue University, West Lafayette, Indiana, December 10, 1987.

A. C. **Gallagher**, "Diagnostics of Discharge Production of a-Si:H and a-Si:Ge:H Films," at Eighth Photovoltaic R&D Review Meeting, Golden, Colorado, November 17, 1987.

A. C. **Gallagher**, "Amorphous-Silicon Plasma and Surface Chemistry," Materials Research Department, Universify of Illinois, Urbana, Illinois, May 5, 1988.

A. C. **Gallagher**, "Gas and Surface Processes and Their Effect on Film Quality," at European Conference on Silane-based CVD, Palaiseau, France, November 27, 1988.

J. L. **Hall**, "Toward the Ultimate Laser Spectroscopic Resolution," Davisson-Germer Award Lecture, American Physical Society Meeting, Baltimore, Maryland, April 19, 1988.

J. L. **Hall**, "Towards the Ultimate Laser Spectroscopic Resolution," Plenary Lecture, 1988 International Conference on Quantum Electronics, Tokyo, Japan, July 1988.

J. L. **Hall**, "The Proscpects for Optical Frequency Standards Using Ramsey Fringes in an Atomic Fountain," 4th International Symposium on Frequency Standards and Metrology, Ancona, Italy, September 5-9, 1988.

J. L. **Hall**, "Narrow-Line Lasers with Sub-Hertz Linewidths," 4th International Symposium on Frequency Standards and Metrology, Ancona, Italy, September 5-9, 1988 (with Dieter Hils).

J. L. **Hall**, "A New Measurement of the Anisotropy of the Speed of Light Using Laser Spectroscopy of a Fast Ne Beam," 4th International Symposium on Frequency Standards and Metrology, Ancona, Italy, September 5-9, 1988 (with N. Bjerne, O. Poulsen, S. A. Lee, L-U Anderson, E. Riis).

D. G. **Hummer**, "The Atomic Internal Partition Function," Sixth Topical APS Conference on Atomic Processes in High-Teperature Plasmas, Santa Fe, New Mexico, September 20, 1987.

S. R. **Leone**, "Alignment Effects in Electronic Energy Transfer and Reactive Events," NATO Advanced Research Workshop on Selectivity in Chemical Reactions," Bowness, England, September 1987.

S. R. Leone, "Laser Probing of Product State Distributions in Thermal-Energy Ion-Molecule Reactions," Faraday Discussion No. 84 on Dynamics of Elementary Gas Phase Reactions, Birmingham, England, September 1987.

S. R. Leone, "Laser Probing of Alignment and Velocity Effects in Collision Dynamics," Chemistry Department, University of Minnesota, Minneapolis, Minnesota, October 5, 1987.

S. R. Leone, "Time-Resolved FTIR Studies of Laser Photofragmentation," FACSS Meeting, Detroit, Michigan, October 1987.

S. R. Leone, "Orbital Alignment Effects in Atomic Collision Physics," Physics Department, Wesleyan University, Middletown, Connecticut, October 1987.

S. R. Leone, "Time-Resolved FTIR Emission Studies of Laser Photofragmentation," Chemistry Department Colloquium, University of Pennsylvania, Philadelphia, Pennsylvania, December 1987.

S. R. Leone, "Time-Resolved FTIR Studies of Polyatomic Molecule Photodissociation Dynamics," Argonne National Laboratory, Argonne, Illinois, March 1988.

S. R. Leone, "Laser Probing of Alignment and Velocity Effects in Atomic Collision Physics," Emory University, Atlanta, Georgia, March 1988.

S. R. Leone, "Laser Probing of Alignment and Velocity Effects in Atomic Collision Physics," Georgia Institute of Technology, Atlanta, Georgia, March 1988.

S. R. Leone, "Orbital Alignment Effects in Chemical Dynamics," Department of Chemistry, University of Nevada-Reno, May 1988.

S. R. Leone, "Laser Photofragmentation: Time-Resolved FTIR Studies," Chemical Physics Seminar, University of California at Los Angeles, May 1988.

S. R. Leone, "Alignment Effects in Electronic Energy Transfer," Gordon Conference on Atomic and Molecular Interactions, Plymouth, New Hampshire, August 3, 1988.

S. R. Leone, "Frederick Kaufman Memorial Lectures," University of Pittsburgh, Pittsburgh, Pennsylvania, September 1988, Lecture Series.

S. R. Leone, "Laser Probing of Ga Atom Interactions on Si(100)," AT&T Bell Laboratories, Murray Hill, New Jersey, September 1988.

S. R. Leone, "Laser Photofragmentation Dynamics With Time Resolved FTIR," International Laser Science Meeting, Atlanta, Georgia, October 4, 1988.

J. L. **Linsky**, "Magnetic Activity In Cool Stars," Astronomical Institute, University of Amsterdam, Amsterdam, The Netherlands, October 9, 1987.

J. L. **Linsky**, "Magnetic Activity In Cool Stars," Institute for Theoretical Astrophysics, Heidelberg University, Heidelberg, Germany, November 9, 1987.

J. L. **Linsky**, "Magnetic Activity In Cool Stars," University Center De Uithof, Laboratory for Experimental Physics, Utrecht, The Netherlands, November 10, 1987.

J. L. **Linsky**, "Infering the Spatial Structure of Stars," Laboratory for Astronomy and Solar Physics, Goddard Space Flight Center, Greenbelt, Maryland, December 4, 1987.

J. L. **Linsky**, "The Spatial Structure and Magnetic Fields on Late-Type Stars," High Altitude Obervatory, National Center for Atmospheric Research, December 17, 1987.

J. L. **Linsky**, "Magnetic Activity In Cool Stars," Max-Planck Institute fur Extraterrestrische Physik, Garching bei Muenchen, Germany, February 19, 1988.

J. L. **Linsky**, "Magnetic Activity In Cool Stars," Center for Astrophysics and Space Sciences, University of California at San Diego, San Diego, California, April 28, 1988.

J. L. **Linsky**, "Spectral Diagnostics From X-Ray to Radio Wavelength," Fourth Institute d'Astrophysics Meeting on the topic Modelling the Stellar Environment: How and Why?, Paris, France, June 29, 1988.

J. L. **Linsky**, "Solar and Stellar Magnetic Fields and Atmospheric Structures: Observations," International Astronomical Union, Colloquium No. 104, Solar and Stellar Flares, Stanford University, Palo Alto, California, August 15, 1988.

J. L. **Linsky**, "High Resolution X-Ray Spectroscopy of Stellar Coronae," International Astronomical Union Colloquium No. 115, High Resolution X-Ray Spectroscopy of Cosmic Plasmas, Harvard University, Cambridge, Massachusetts, August 23, 1988.

J. L. **Linsky**, "Magnetic Activity on Solar-Type Stars," Physics and Astronomy Departments, University of Indiana, Bloomington, Indiana, September 28, 1988.

D. J. **Nesbitt**, "IR Spectroscopy of Weakly Bound Clusters: Molecular Pinballs, Hinges and Helicopters," Department of Chemistry, Colorado State University, Fort Collins, Colorado, December 1, 1987.

D. J. **Nesbitt**, "The Spectroscopic Signatures of Floppiness in Molecular Complexes," International Workshop on Structure of Small Molecules and Ions, Neve Ilan, Israel, December 14, 1987.

D. J. Nesbitt, "Rovibrational Intramolecular Dynamics in Small Gas Phase Clusters," Department of Chemistry, University of Georgia, Athens, Georgia, January 19, 1988.

D. J. Nesbitt, "Rovibrational Intramolecular Dynamics in Small Gas Phase Clusters," Department of Physics, Georgia Institute of Technology, Atlanta, Georgia, January 20, 1988.

D. J. Nesbitt, "Rovibrational Intramolecular Dynamics in Small Gas Phase Clusters," Department of Chemistry, University of Virginia, Charlottesville, Virginia, January 22, 1988.

D. J. Nesbitt, "Dynamics of Jet Cooled Molecules via High Resolution IR Laser Spectroscopy," Department of Chemistry, University of Illinois, Champaign-Urbana, Illinois, April 27, 1988.

D. J. Nesbitt, "IR Laser Studies of Spectroscopy and Dynamics in Slit Jet Cooled Molecules," Institute for Molecular Spectroscopy, Okazaki, Japan, July 22, 1988.

D. J. Nesbitt, "Sub-Doppler IR Laser Studies of Nonlinear Vibrational Dynamics in Jet-Cooled Molecules," ACS New England Regional Meeting '88, University of Maine, Orono, Maine, August 1, 1988.

D. J. Nesbitt, "Sub-Doppler Infrared Spectroscopy in Slit Supersonic Jets: A Study of All Three van der Waals Modes in vi Excited ArHCl," Faraday Discussions 86, University of Exeter, Exeter, England, September 13, 1988.

D. J. Nesbitt, "IR Spectroscopy of Complexes in Supersonic Jets: An Experimental and Theoretical Playground," Department of Theoretical Chemistry, Cambridge University, Cambridge, England, September 16, 1988.

D. J. Nesbitt, "Difference Frequency and Diode IR Laser Studies of Vibrational Dynamics in Supersonic Jets: Molecular Gymnastics and IVR," American Chemical Society, Los Angeles, California, September 26, 1988.

D. J. Nesbitt, "Chemical Dynamics via IR Laser Spectroscopy: Clusters and Radicals," Aerospace Corporation, El Segundo, California, September 28, 1988.

D. W. Norcross, "Theory of Electron-Molecule Collisions," 40th Annual Gaseous Electronics Conference, Georgia Institute of Technology, Atlanta, Georgia, October 13, 1987.

A. V. Phelps, "Applications of Electron Cross Section Data," 40th Annual Gaseous Electronics Conference, Georgia Institute of Technology, Atlanta, Georgia, October 16, 1987.

TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Quantum Physics Division (577)

P. L. Bender, Chairman, LAEOS-3 Science Advisory Group, NASA.

P. L. Bender, Member, Ultraviolet/Visible/Relativity Management and Operations Working Group, NASA.

P. L. Bender, Member, Technical Working Group on Imaging Interferometry in Space, NASA.

P. L. Bender, Member, Geostationary Platform Earth Science Steering Committee, NASA.

P. L. Bender, Member, Crustal Dynamics Working Group, NASA.

G. H. Dunn, Member, Executive Committee, Division of Atomic, Molecular and Optical Physics (DAMOP) of the American Physical Society.

G. H. Dunn, Chairman Elect of DAMOP.

G. H. Dunn, Chairman, Public Education Committee of DAMOP.

G. H. Dunn, Member, DAMOP Committee to Recommend Prize Structure in the Field of AMO Physics.

G. H. Dunn, Member, NSF Panels (Chairman of one) to Examine and Recommend Top Contestants for NSF Science and Technology Centers.

J. E. Faller, Member, Working Group II of the International Gravity Commission.

J. E. Faller, Member, Special Study Group 3.86, "Estimation of Absolute Gravimetric Determinations," of the International Gravity Commission.

J. E. Faller, Member, Special Study Group 3.87, "Development of WorldWide Absolute Gravity Net," of the International Gravity Commission.

J. E. Faller, Member, U. S. Interagency Gravity Standards Committee.

J. E. Faller, Member, Management Operations Working Group on Lunar Ranging.

J. E. Faller, Member, Physics Departments' "Graduate Committee".

J. E. Faller, Member, Directing Board of IGC (International Gravity Commission).

J. L. Hall, Delegate, Consultative Committee for the Definition of the Meter (BIPM), Sχvres, France, 1970 - present.

J. L. **Hall**, Chairman, International Steering Committee for Conferences on Laser Spectroscopy.

J. L. **Hall**, Member, NBS Committee for NBS Precision Measurement Grants.

J. L. **Hall**, Member, Nominating Committee, Optical Society of America.

J. L. **Hall**, Member, Advisory Committee to the Global Oscillation Group, National Solar Observatory.

J. L. **Hall**, Member, AMO Subcommittee of Physics Division, Academy of Science.

D. G. **Hummer**, Member, Editorial Board, Computer Physics Communications.

D. G. **Hummer**, Member, Steering Committee of the United Kingdom Collaborative Computational Project on Stellar Atmospheres.

D. G. **Hummer**, Co-Director, International Stellar Opacity Project.

S. R. **Leone**, Chairman, Division of Chemical Physics, American Physical Society, 1987-1988.

S. R. **Leone**, Editorial Advisory Board, Chemical Reviews, 1982-1988.

S. R. **Leone**, Committee on Atomic and Molecular Science, National Research Council, 1986-1989.

S. R. **Leone**, Editorial Advisory Board, Journal of Physical Chemistry, 1984-1990.

S. R. **Leone**, Editorial Board, Progress in Reaction Kinetics, 1987-1989.

S. R. **Leone**, Editorial Board, Molecular Physics, 1988-1991.

S. R. **Leone**, Advisory Editorial Board, Chemical Physics Letters, 1987-1989.

J. L. **Linsky**, Member, Users' Committee, International Ultraviolet Explorer Satellite.

J. L. **Linsky**, Co-Investigator, High Resolution Spectrograph, Space Telescope.

J. L. **Linsky**, Member, Lyman Far Ultraviolet Spectrograph Explorer Phase A Science Team.

J. L. **Linsky**, Member, Scientific Organizing Committee for the International Conference "A Decade of Ultraviolet Astronomy with the IUE Satellite," Greenbelt, Maryland, April 12-15, 1988.

J. L. **Linsky**, Member, International Ultraviolet Explorer (IUE) Proposal Review Panel.

J. L. **Linsky**, Member, Infrared Astronomy Satellite (IRAS) Proposal Review Committee.

J. L. **Linsky**, Member, Science Advisory Council, Mount Wilson Institute.

J. L. **Linsky**, Interdisciplinary Scientist on the Advanced X-Ray Astrophysical Facility (AXAF) and Member of the AXAF Science Working Group, NASA.

J. L. **Linsky**, Member, Astrophysics Council, NASA.

J. L. **Linsky**, Member, IUE Long Range Planning Committee.

J. L. **Linsky**, Chairman, Steering Committee, Synoptic High Resolution Spectroscopic Observing Group.

J. L. **Linsky**, Member, Scientists on Spaceborne Interferometry, NASA.

J. L. **Linsky**, Chairman, Infrared Astronomy Project Concepts Evaluation Panel, NASA.

J. L. **Linsky**, Member, Astrophysics Data Operations Study Committee, Goddard Space Flight Center, NASA.

J. L. **Linsky**, Co-Investigator, Space Telescope Imaging Spectrograph, NASA.

J. L. **Linsky**, Chairman, Management Operations Working Group, Science Operations Branch, NASA.

J. L. **Linsky**, Chairman, US Scientific and Technical Working Group for the Large Earth-Based Solar Telescope, High Altitude Observatory, NCAR.

J. L. **Linsky**, Chairman, Senior Review of the Astrophysics Data Program, NASA.

J. L. **Linsky**, Chairman, Workshop on Signal-to-Noise Enhancement of IUE Data, NASA.

J. L. **Linsky**, Member, Joint Evaluation Committee for Proposals for the SOHO/Cluster Mission, NASA and ESA.

D. J. **Nesbitt**, Member, Organizing Subcommittee for IQEC '88, "Fundamental Laser Spectroscopy and Physics."

D. W. **Norcross**, Member, Working Group Supervising Collaborative Computational Project 2 (Continuum States of Atoms and Molecules) of the U.K. Science and Engineering Research Council, 1983 - present.

CONSULTING

A. C. Gallagher

Dr. Gallagher is consulting with the Lamp Division and Corporate Research Division of General Electric Corporation.

J. L. Hall

Dr. Hall is consulting with the Theoretical Astrophysics Group at Caltech in the area of laser techniques for gravity wave detection, and informally with colleagues in industry involved with stable laser design and application, and also consults with: Excel Precision Corporation, Santa Clara, California.

Advisory Committee to the Global Oscillation Network Group, National Solar Laboratory.

S. R. Leone

Dr. Leone does consulting with Spectra Technology on laser chemical physics.

J. L. Linsky

Dr. Linsky consults with NASA concerning (1) future programs in the area of ultraviolet X-ray and infrared astronomy, (2) future programs in solar and heliospheric physics, (3) operations and long range planning for the International Ultraviolet Explorer satellite, (4) definition of the proposed LYMAN Far Ultraviolet Spectroscopic Explorer satellite, (5) definition of the proposed Advanced X-ray Astronomical Facility, (6) calibration and initial operations of the Space Telescope High Resolution Spectrograph, (7) data operations for future missions, (8) interferometry from space, and (9) future infrared astronomy missions.

Dr. Linsky consults with the National Optical Astronomy Observatory (NOAO) and the Association of Universities for Research in Astronomy (AURA) concerning (1) operation of the National Solar Observatory and Sacramento Peak Observatory, (2) planning for coordinated ground-based and space observations, (3) potential need for a large-aperature ground-based solar telescope, (4) planning for synoptic high resolution spectroscopic observations, and (5) the long term goals of the NOAO.

D. W. Norcross

Dr. Norcross is consulting with the Theoretical Atomic and Molecular Physics Group at the **Lawrence Livermore Laboratory** on problems related to laser modeling, and is a Visiting Scientist (consultant) to Division T-4 of the **Los Alamos Laboratory** on problems related to electron collisions with atoms, ions, and molecules.

A. V. Phelps

Dr. Phelps does informal consulting and advising with DoD and DoE laboratories and their industrial and university contractors in the area of atomic and molecular processes in high power switches, laser induced breakdown and charged particle beam propagation. For the Lawrence Livermore National Laboratory this has been formalized by the granting of support for a postdoc.

OTHER AGENCY RESEARCH

Quantum Physics Division

P. L. Bender	NASA	Determination of worldwide tectonic plate motions and large scale intra-plate distortions.
P. L. Bender	NASA	Integrated water vapor calibrator measurements.
P. L. Bender & **J. E. Faller**	NASA	Laser gravitational wave observations in space.
P. L. Bender	NSF	Crustal dynamics in the S.W. Pacific using G.P.S.
G. H. Dunn	DOE	Cross sections and rates describing electron collisions with atoms and ions.
G. H. Dunn	DOE	Determine atomic, molecular, and nuclear data pertinent to the magnetic fusion energy program.
J. E. Faller	AFGL	Absolute gravity studies.
J. E. Faller	DMA	Gravimeter equipment support.
J. E. Faller	DMA-N	Absolute "G" co-op program.
J. E. Faller	MERADCOM	Fabrication of two gravity gradiometers for subsequent field testing and evaluation.
J. E. Faller	NASA	Examination and evaluation of the laser lunar ranging multi-lens telescope.
J. E. Faller	NGS	Routine maintenance of the absolute instrument during fiscal year 1988.
J. E. Faller & **P. L. Bender**	NSF	Development of very low frequency isolation systems for ground-based gravitational-wave interferometers.
A. C. Gallagher	DOE	Spectroscopic diagnostics of electron-atom collisions.
A. C. Gallagher	SERI	Diagnostics of glow discharges used to produce hydrogenated amorphous silicon films.

J. L. Hall	ONR	Precision atomic beam spectroscopy using stabilized lasers.
D. G. Hummer	NASA	High resolution spectrograph observing program.
D. G. Hummer & 9 Co-Investigators	NASA	Theory of Spectrum Formation in Astrophysical Systems.
D. G. Hummer & B. Bohannan	NSF	Optically-thick stellar winds and photospheres of hot stars.
S. R. Leone	AFOSR	Laser measurements of state-resolved Ga and atom scattering, sticking, and desorption on metal and semiconductor surfaces.
S. R. Leone	AFOSR	State-resolved dynamics of ion-molecule reactions in a flowing afterglow.
S. R. Leone	AFWL	Diode laser probing of iodine atoms; optically pumped SO laser.
S. R. Leone	ARO	Surface deposition and etching interactions of laser-generated translationally hot atoms and radicals.
S. R. Leone	DOE	Fourier transform infrared spectroscopy and dynamics of combustion.
S. R. Leone	DOE	Time-resolved FTIR emission studies of laser photofragmentation and chain reactions.
S. R. Leone	NSF	State-resolved molecular dynamics.
J. L. Linsky	NASA	Interdisciplinary scientist on the Advanced X-ray Astrophysical Facility (AXAF).
J. L. Linsky	NASA	Hubble Space Telescope Imaging Spectrograph
J. L. Linsky & T. Fleming	NASA	X-ray Observations of late-type stars using the Rosat all-sky survey.
J. L. Linsky	NASA	International Ultraviolet Explorer studies of astronomical sources.
J. L. Linsky & J. Bookbinder	NASA	International Ultraviolet Explorer studies of astronomical sources.
J. L. Linsky & A. Brown	NASA	Ultraviolet observations of selected astronomical sources.

J. L. Linsky	NASA	Basic research in solar physics.
J. L. Linsky	NASA	Hubble Space Telescope High Resolution Spectrograph (2 grants).
J. L. Linsky **K. Schrijver**	NASA	Coronal temperature cool stars.
D. J. Nesbitt	AFOSR	Infrared transition moments and collisional dynamics.
D. J. Nesbitt	NSF	Direct IR laser absorption spectroscopy in linear jets: Vibrational dynamics of van der Waals molecules.
D. J. Nesbitt	SLOAN	SLOAN Research Fellowship.
D. W. Norcross	DOE	Atomic and molecular collision processes.
D. W. Norcross	DOE	Electron impact excitation of atomic ions.
A. V. Phelps	AFWAL	Detection of excited states by laser induced fluorescence.
A. V. Phelps	LLL	Non-equilibrium electrons in gases.

TRIPS SPONSORED BY OTHERS

Quantum Physics Division (577)

P. L. Bender

October 19-23, 1987 - Washington, D.C.
Attended meetings of the NASA Crustal Dynamics Working Group and Lunar Laser Ranging Working Group at Goddard Space Flight Center.
Sponsor: NASA Goddard.

November 9-13, 1987 - New Brunswick, New Jersey.
Presented a Physics Colloquium on "Sources and Sensitivities for Laser Gravitational Wave Observations in Space," at Rutgers University.
Sponsor: Rutgers, The State University.

December 6-11, 1987 - San Francisco, California.
Attended a Meeting of the American Geophysical Union and presented an invited talk.
Sponsor: NASA Goddard.

January 10-15, 1988 - Austin, Texas.
Attended the Geodynamics Laser Ranging System Workshop, and presented a talk on "Geostationary Platform Laser Ranging System";
Attended the American Astronomical Society meeting;
Attended the meeting of the NASA Technical Working Group on Optical Imaging Interferometry in Space.
Sponsor: NASA Goddard.

March 20-24, 1988 - Los Angeles, California.
Attended the NASA Global Positioning System Workshop at the Jet Propulsion Laboratory.
Attended the Crustal Dynamics Working Group Meeting.
Attended the Lunar Laser Ranging Working Group Meeting.
Sponsor: NASA-Goddard.

April 17-25, 1988 - Baltimore, Maryland.
Attended the meeting of the NASA Lageos-3 Working Group;
Attended the meeting of the NASA Water Vapor Radiometer Working Group at the Goddard Space Flight Center.
Sponsor: NASA Goddard.

July 4-8, 1988 - Paris, France.
Attended the Eleventh International Conference on Atomic Physics.
Sponsor: Eleventh International Conference on Atomic Physics.

Bender (cont.)

August 2-3, 1988 - Baltimore, Maryland.
Attended the International Astronomical Union Meeting.
Sponsor: NASA-Goddard.

September 6-8, 1988 - Austin, Texas.
Attended a meeting of the NASA LAGEOS-3 Study Advisory Committee at the University of Texas in Austin.
Sponsor: NASA Goddard.

October 10-22, 1988 - Grasse, France, and Munich, West Germany.
Consulted with scientists in Grasse concerning lunar laser ranging (Grasse);
Attended the Principal Investigators Meeting for the NASA Crustal Dynamics Project (Munich).
Sponsor: NASA Goddard.

G. H. Dunn

September 27 - October 3, 1987 - Santa Fe, New Mexico.
Attended the Conference on Atomic Processes in High Temperature Plasmas.
Sponsor: Department of Energy.

November 1 - December 1, 1987 - Giessen, West Germany; Belgrade, Yugoslavia.
Worked with E. Salzborn and A. Muller on electron-ion collision experiments as per NATO Exchange Agreement (Giessen);
Worked with Drs. D. Belic and J. Kurepa on research related to atomic processes as per U.S. - Yugoslavia Joint Fund for Science and Technology (Belgrade)
Sponsors: Department of Energy; U. S. Embassy, Belgrade, and NATO Agreement; U.S. - Yugoslavia Joint Fund; and NATO (West Germany).

March 26-29, 1988 - Washington, D. C.
Chairman of a committee to evaluate Science and Technology Research Center proposals for the National Science Foundation.
Sponsor: National Science Foundation.

April 17-21, 1988 - Baltimore, Maryland.
Attended the DAMOP Meeting and gave a paper.
Sponsor: Department of Energy.

April 28-29, 1988 - Lincoln, Nebraska.
Gave a colloquium at the University of Nebraska.
Sponsors: Department of Energy and the State of Nebraska.

Dunn (cont.)

May 11-12, 1988 - Argonne, Illinois.
Gave a colloquium at Argonne National Labs.
Sponsors: Argonne National Laboratory and the Department of Energy.

J. E. Faller

October 19-21, 1987- Washington, D. C.
Attended the NASA LLR M/OWG Meeting held in conjunction with the Crustal Dynamics Program Meeting.
Sponsor: NOAA - National Geodetic Survey.

December 9-11, 1987 - West Lafayette, Indiana.
Presented an invited colloquium for the Department of Physics at Purdue University.
Sponsor: AF Geophysics Laboratory.

January 19 - February 1, 1988 - Hannover, West Germany; Paris, France; Les ARcs, Savoie, France.
Consulted with Drs. Torge and Schnull at the Institute fur Erdmessung on their gravimeter (Hannover);
Met with Dr. Speake of BIPM (Paris);
Attended the VIIth MORIOND Workshop (Les ARcs).
Sponsor: AG Geophysics Laboratory.

February 19, 1988 - Colorado Springs, Colorado.
Presented a talk at Colorado College.
Sponsor: University of Colorado.

March 23-24, 1988 - Pasadena, California.
Attended the Crustal Dynamics Workshop at the Jet Propulsion Lab.
Sponsor: AF Geophysics Laboratory.

March 25-26, 1988 - Washington, D. C.
Presented a talk at the Cosmos Club.
Sponsor: Defense Mapping Agency.

June 5-12, 1988 - Tsukuba, Japan.
Attended the '88 Conference on Precision Electromagnetic Measurements and gave an invited paper during the 5th Force Symposium. Visited Japanese labs.
Sponsor: Conference on Precision Electromagnetic Measurements.

June 28-29, 1988 - Annapolis, Maryland.
Attended NASA workshop on Relativistic Gravitational Experiments in Space and gave an invited talk.
Sponsor: NASA.

A. C. Gallagher

October 12-16, 1987 - Atlanta, Georgia.
Attended the Gaseous Electronics Conference and gave a talk.
Sponsor: Solar Energy Research Institute.

November 21 - December 1, 1987 - Paris, France.
Visited labs and consulted with colleagues at Meudon, Saclay, and attended and gave presentation at the EEC Research Program on Amorphous Silicon Based Photovoltaic Workshop, focusing on depositing good amorphous silicon and related alloys and fabricating devices.
Sponsor: European Economic Community Research Program on Amorphous Silicon.

April 19-23, 1988 - Urbana, Illinois; Cleveland, Ohio.
Gave a talk at the University of Illinois, Department of Applied Physics.
Sponsor: University of Illinois.

August 30 - September 1, 1988 - Bethesda, Maryland.
Attended the Department of Energy Contractor's meeting.
Sponsor: University of Colorado.

J. L. Hall

January 14-19, 1988 - Palo Alto, California.
Visited Coherent, Incorporated, to discuss state-of-the-art laser technology (Palo Alto);
Visited Coherent, Incorporated, to discuss state-of-the-art laser technology (Sacramento).
Sponsor: Coherent, Incorporated.

March 24-26, 1988 - New York, New York.
Met with Dr. K. Sugimoto of NHK Public Broadcasting (Tokyo) and Officials of Ore, Incorporated (Denver) regarding proposed U.S./Japanese cooperation in development of large screen laser display systems.
Sponsor: Ore, Incorporated.

June 15-19, 1988 - Stanford and Santa Clara, California.
Consulted with Spectra Physics (Stanford);
Interaction with staff at Excel Precision (Santa Clara).
Sponsor: Excel Precision.

Hall (cont.)

July 7-24, 1988 - Tokyo, Japan.
Interacted with scientists at the Institute for Laser Science regarding scientific and technical problems of mutual interest;
Attended International Conference on Quantum Electronics.
Sponsor: Institute for Laser Science.

September 3-9, 1988 - Ancona, Italy.
Attended the 4th International Symposium on Frequency Standards and Metrology (Ancona).
Sponsor: Italian Symposium.

D. G. Hummer

September 27 - October 2, 1987 - Santa Fe, New Mexico.
Attended the "Sixth Topical APS Conference on Atomic Processes in High-Temperature Plasmas," and presented an invited review paper on "Atomic Internal Partition Functions."
Sponsor: NASA Goddard.

January 18-29, 1988 - Boston, Massachusetts.
Collaboration with Professor G. B. Rybicki of Harvard-Smithsonian Center for Astrophysics on further development of accelerated-lambda-iteration method for solution of multilevel radiative transfer problems. Assisted Professor Alec Dalgarno in setting up and running the collisional-radiative recombination program developed by Pete Storey and myself, for application by Professor Dalgarno to OI and NII.
Sponsor: Smithsonian Institution.

June 15 - July 3, 1988 - London, England; Munich, West Germany; Belfast, N. Ireland.
Worked with Dr. P. J. Storey, University College London, on helium collisional-radiative recombination (London);
Worked with Professor R. Kudritzki, Institute for Astronomy and Astrophysics, University of Muncih (Munich);
Attended Opacity Project Meeting (Belfast).
Sponsor: NATO Grants.

August 14-19, 1988 - Montreal, Canada.
Attended IAU Colloquium #113, "Physics of Luminous Blue Variables."
Sponsor: NASA Goddard.

Hummer (cont.)

December 1988 - September 30, 1989 - Munich, West Germany.
Work at the Institute for Astronomy and Astrophysics, University of Munich on continuing collaborative projects.
Sponsors: The von Humboldt Foundation, and the Department of Physics, University of Munich.

S. R. Leone

October 4-7, 1987 - Minneapolis, Minnesota; Detroit, Michigan.
Presented an invited talk at the University of Minnesota (Minneapolis, Minnesota);
Attended the FACSS (Analytical Chemistry) Meeting (Detroit, Michigan).
Sponsors: University of Minnesota, Coblentz Society, and The Federation of Analytical Chemistry & Spectroscopy Society.

October 15-23, 1987 - Washington, D. C.; Hartford, Connecticut.
Attended the CAMS Meeting of NRC and presented an invited talk (Washington, D. C.):
Presented a seminar, "Orbital Alignment Effects in Atomic Collision Physics," at Wesleyan University (Hartford, Connecticut).
Sponsors: National Academy of Science, Wesleyan University, and Brookhaven National Laboratories.

December 9-11, 1987 - Philadelphia, Pennsylvania.
Presented a Chemistry Department colloquium at the University of Pennsylvania.
Sponsor: The University of Pennsylvania.

May 12-17, 1988 - Reno, Nevada; Los Angeles, California.
Attended seminar on "Orbital Alignment Effects in Chemical Dynamics," at the University of Nevada Reno (Reno);
Attended the seminar on "Laser Photo Fragmentation," at UCLA (Los Angeles).
Sponsor: University of Nevada Reno.

J. L. Linsky

October 4-10 1987 - Amsterdam, Netherlands.
Attended a meeting of the Science Assessment Panel for the SOHO/Cluster Mission.
Sponsor: EER Systems Corporation.

October 18-20, 1987 - Baltimore, Maryland.
Chairman of the Workshop on Signal-to-Noise Enhancement of IUE.
Sponsor: Creative Management Associates Inc.

October 28-29, 1987 - Huntsville, Alabama.
Attended an AXAF Science Working Group meeting at Marshall Space Flight Center.
Sponsor: NASA George C. Marshall Space Flight Center.

November 3-4, 1987 - Amsterdam, Netherlands.
Attended meetings of the Joint Evaluation Committee for the SOHO/Cluster Mission.
Sponsor: EER Systems Corporation.

November 30 - December 4, 1987 - Baltimore, Maryland.
Attended a meeting of the Space Telescope Imaging Spectrograph Instrument Development Team; discussions with Dr. S. Drake, Dr. Y. Kondo, and Dr. M. Hansen, and other colleagues at Goddard Space Flight Center.
Gave a colloquium at Goddard Space Flight Center.
Sponsor: NASA Goddard.

January 14-16, 1988 - San Diego, California.
Attended a meeting of the Space Telescope High Resolution Spectrograph Team at the University of California at San Diego.
Sponsor: NASA Goddard.

February 15-20, 1988 - Amsterdam, Netherlands.
Attended a meeting of the Joint Evaluation Committee for the SOHO/Cluster Mission.
Sponsor: EER Systems Corporation.

February 22-24, 1988 - Greenbelt, Maryland.
Attended a meeting of the IUE Proposal Peer Review at Goddard Space Flight Center.
Sponsor: Creative Management Associates Inc.

February 28 - March 1, 1988 - Huntsville, Alabama.
Attended a meeting of the Science Working Group of the Advanced X-ray Astrophysical Facility at Marshall Space Flight Center.
Sponsor: NASA George C. Marshall Space Flight Center.

March 14-16, 1988 - Baltimore, Maryland.
Received NASA's Exceptional Scientific Achievement Metal at NASA's Annual Honor Awards Ceremony, and discussed future space satellites (in particular, LYMAN and AXAF) with NASA Headquarters personnel and congressional staffers.
Sponsor: NASA George C. Marshall Space Flight Center.

Linsky (cont.)

March 20-30, 1988 - Greenbelt, Maryland; Belfast, Northern Ireland.
Attended a review of the NASA Astrophysics Data Program (Greenbelt);
Attended a meeting of scientific collaborators working on studies of stellar flares and active regions with the IUE satellite (Belfast).
Sponsor: The BDM Corporation, Armagh Observatory, and NASA Goddard.

April 4-5, 1988 - Tucson, Arizona.
Attended a meeting of the U.S. Scientific and Technical Working Group for LEST of which Dr. Linsky is Chairman.
Sponsor: University Corporation For Atmospheric Research.

April 9-15, 1988 - Greenbelt, Maryland.
Attended a meeting of the Space Telescope Imaging Spectrograph Team;
Attended an IUE Users Committee Meeting;
Attended a Conference on "A Decade of UV Astronomy with the IUE Satellite."
Sponsor: Creative Management Associates Inc. and NASA Goddard.

April 18-21, 1988 - Greenbelt, Maryland.
Attended a meeting of the Lyman Phase A Science Team at Goddard Space Flight Center.
Sponsor: ORI, Inc.

April 25-26, 1988 - San Diego, California.
Gave a colloquium at the Center for Astrophysics and Space Sciences of the University of California.
Sponsor: University of California.

April 27-29, 1988 - Baltimore, Maryland.
Attended a meeting of the AXAF Science Working Group and had discussions with Dr. Guenter Riegler and Charles Pellerin at NASA Headquarters.
Sponsors: The BDM Corporation and NASA George C. Marshall Space Flight Center.

May 16-18, 1988 - Baltimore, Maryland.
Chairman at a meeting of the IUE Signal-to-Noise Improvement Committee;
Presented the results of the Senior Review of the Astrophysics Data Program to Dr. Len Fisk, Associate Administrator of NASA.
Sponsor: Birch & Davis Associates, Inc.

Linsky (cont.)

June 2-4, 1988 - Estes Park, Colorado.
Attended a meeting of the Space Telescope GHRS Instrument Definition Team.
Sponsor: NASA Goddard.

June 28-30, 1988 - Paris, France.
Attended the "Colloquium on Modeling the Stellar Environment: How and Why," at the Institute d'Astrophysique in Paris and presented an invited review paper on the topic "Spectral Diagnostics from X-rays to Radio Wavelengths."
Sponsor: NASA George C. Marshall Space Flight Center.

July 12-14, 1988 - Washington, D. C.
Attended a meeting of the NASA Astrophysics Science Operations Management Working Group.
Sponsor: NASA Goddard.

July 26-28, 1988 - Berkeley, California.
Attended a meeting of LYMAN Science Working Group Subcommittee on EUV Spectroscopy.
Sponsor: The Johns Hopkins University.

August 14-20, 1988 - San Francisco, California.
Attended the IAU Colloquium No. 104 on the topic Solar and Stellar Flares;
Participated in a meeting of colleagues to plan future observations of flare stars using the IUE and Hubble Space Telescope.
Sponsor: NASA.

August 21-25, 1988 - Boston, Massachusetts.
Attended the International Astronomical Union Colloquium No. 115, High Resolution X-ray Spectroscopy of Cosmic Plasmas.
Sponsors: NASA Goddard and International Astronomical Union.

September 3-9, 1988 - Rome, Italy and Washington, D. C.
Presented the plans of the NASA Science Working Group studying the proposed LYMAN for UV Spectrograph Explorer mission to a meeting of Italian Astronomers potentially interested in a collaborative spacecraft.
Chairman at a meeting of the IUE Signal-to-Noise Committee at Goddard Space Flight Center.
Sponsor: NASA Goddard

David J. Nesbitt

December 12-27, 1987 - Rehovot, Israel.
Attended the International Conference on Structure of Small Molecules and Ions, Weizman Institute, and gave an invited talk.

Sponsor: International Conference on Structure of Small Molecules and Ions, Weizman Institute.

January 18-22, 1988 - Athens, Atlanta, Georgia; Charlottesville, Virginia.
Presented a talk at the University of Georgia (Athens);
Presented a talk at Georgia Tech (Atlanta);
Presented a talk at the University of Virginia (Charlottesville).
Sponsors: University of Georgia, Georgia Tech, and the University of Virginia.

April 25-28, 1988 - Champaign, Illinois.
Presented an invited talk at the University of Illinois.
Sponsor: University of Illinois.

July 15-24, 1988 - Tokyo, Okazaki, Japan.
Attended the International Quantum Electronics Conference and gave a talk at the University of Tokyo (Tokyo);
Presented a talk at the Institute for Molecular Science (Okazaki).
Sponsor: Optical Society of America.

July 30 - August 5, 1988 - Orono, Maine and Plymouth, New Hampshire.
Presented a talk at Northeastern Regional ACS meeting (Orono);
Attended the Gordon Conference on Atomic and Molecular Interactions (Plymouth).
Sponsor: American Chemical Society.

D. W. Norcross

October 13-16, 1987 - Atlanta, Georgia.
Attended the Gaseous Electronics Conference.
Sponsor: Department of Energy.

A. V. Phelps

October 12-20, 1987 - Atlanta, Georgia.
Attended the Gaseous Electronics Conference.
Sponsor: AFWAL, Wright-Patterson AFB.

April 18 - May 1, 1988 - Boston, Massachusetts.
Gave seminar on "Role of Ionization by Fast Ions and Atoms in Electrical Breakdown at Low Pressures and High Voltages," and worked on a paper with L. C. Pitchford at GTE Laboratories.
Visited MIT and discussed models of ion mition in discharges with Professor H. W. Swain.
Sponsor: GTE Laboratories.

UNIVERSITY AND DEPARTMENT COMMITTEE MEMEBERSHIPS

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P. L. Bender	Thesis Committees for: M. J. Bergoffen Physics Department, University of Colorado D. N. de Vries Physics Department, University of Colorado T. M. Niebauer Physics Department, University of Colorado C. Roecken Geological Sciences Department, University of Colorado A. S. Trupin Physics Department, University of Colorado T. M. Van Dam Geological Sciences Department, University of Colorado S. J. Walter Physics Department, University of Colorado
G. H. Dunn	Chairman of JILA Member, several Ph.D. examinations committees Thesis Committees for: S. Jefferts Physics Department, University of Colorado S. Morgan Chemistry Department, University of Colorado M. Schauer Physics Department, University of Colorado G. Schinn Physics Department, University of Colorado C. Timmer Physics Department, University of Colorado

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Physics Department, University of Colorado

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Member, JILA Shops Committee

JILA Building Project Coordinator

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Physics Department, University of Colorado

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JILA Space Committee

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Physics Department, University of Colorado

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D. G. Hummer	Thesis Committees for: J. Doggett Astrophysical, Planetary, and Atmospheric Sciences Department, University of Colorado A. Hayden Astrophysical, Planetary, and Atmospheric Sciences Department, University of Colorado S. McCandliss Astrophysical, Planetary, and Atmospheric Sciences Department, University of Colorado S. Voels Astrophysical, Planetary, and Atmospheric Sciences Department, University of Colorado
S. R. Leone	Final Ph.D. Defense Committee for: M. Alexander Chemistry Department, University of Colorado K. Carleton Chemistry Department, University of Colorado K. Lykke Chemistry Department, University of Colorado J. Smedley Chemistry Department, University of Colorado JILA Visiting Scientists Office.

J. L. Linsky

University Space Science and Policy Task Force

Search Committee for a faculty position in Theoretical Astrophysics, Department of Astrophysical, Planetary, and Atmospheric Sciences

Thesis Committees for:

- J. Neff
  Astrophysical, Planetary, and Atmospheric Sciences Department, University of Colorado

- S. Saar
  Astrophysical, Planetary, and Atmospheric Sciences Department, University of Colorado

- S. Skinner
  Physics Department, University of Colorado

- A. Veale
  Astrophysical, Planetary, and Atmospheric Sciences Department, University of Colorado

D. J. Nesbitt

Co-Chairman, JILA Colloquium Committee

JILA Data Center Advisory Committee

Library Committee, Department of Chemistry

Chairman, Chemical Physics After Dark Seminar Series

D. W. Norcross

Chair, JILA Computing Committee

Chair, JILA Building Committee

Graduate Committee, Department of Physics

JILA Data Center Advisory Committee.

Thesis Committee for:

- T. Gorczyca
  Physics Department, University of Colorado

- H.-L. Zhou
  Physics Department, University of Colorado

A. V. Phelps Thesis Committees for

J. Doyle
Physics Department, University of Colorado

M. O'Callaghan
Physics Department, University of Colorado

G. Schinn
Physics Department, University of Colorado

GRADUATE STUDENTS AND POSTDOCTORAL RESEARCH ASSOCIATES SUPERVISED

Quantum Physics Division (577)

	Graduate Students	Postdoctoral Research Associates
P. L. Bender	D. B. Newell	D. Hils
	S. J. Walter	
	X. Wu	
G. H. Dunn	A. Cachelin	J. L. Forand
	S. Jefferts	K. Rinn
	M. Schauer	D. Swenson
	K. Timmer	
	E. Wahlin	
	B. Adrian (Undergrad)	
J. E. Faller	H. Godwin	
	M. McHugh	
A. C. Gallagher	D. Atkins	M. Harris
	J. Doyle	G. Lin
	K. Gibble	H. Werij
	X. Han	
	G. Schinn	
	M. Troyer	
J. L. Hall	H. Jin	P. Busch
	M. Eickhoff	J. M. Chartier
	C. Oates	M. C. Noecker
	M. Wintersr	
	M. Zhu	
D. G. Hummer	A. Hayden	D. C. Abbott
	S. McCandliss	W. Schmutz
	S. Voels	
S. R. Leone	L. Cousins	H. Beijers
	K. Knutsen	V. Bierbaum (25%)
	L. Kovalenko	J. Cline
	S. Rogers	R. Dressler
	R. Smilgys	R. Fletcher
	C. Taatjes	P. Miller (NRC)
	E. Woodbridge	D. Oostra
		S. Penn (NRC)
		R. Robinson
		D. Sonnenfroh (NRC)
		K. Yamasaki

	Graduate Students	Postdoctoral Research Associates
J. L. Linsky	J. Neff S. Saar S. Skinner A. Veale	C. Ambruster J. Bookbinder A. Brown J. P. Caillault T. Fleming P. Judge D. Luttermoser K. Schrijver
D. J. Nesbitt	R. Lascola C. Lovejoy A. McIlroy M. Robinson A. Schiffman M. Schuder	D. Nelson (NRC)
D. W. Norcross	T. Gorczyca H.-L. Zhou	J. Mitroy A. Pradhan G. Snitchler
A. V. Phelps		J. Borysow V. T. Gylys

COURSES TAUGHT AT UNIVERSITY OF COLORADO

Quantum Physics Division

S. R. Leone	Physical Chemistry Laboratory Course - Development and Construction of New Experiments
	Chemistry 550 - Chemical Dynamics (Spring 88)
J. L. Linsky	Special Topics in APAS: Stellar Atmospheres - APAS 650 (Fall 1987)
D. J. Nesbitt	Chemistry 452 - Quantum Chemistry (Fall 1987)
	Chemistry 558 - Quantum Chemistry (Fall 1988)
A. V. Phelps	Physics 3330 - Junior Laboratory (Fall 1988)

PUBLICATIONS

Division 577

D. C. Abbott and P. S. Conti, "Wolf-Rayet stars," *Ann. Rev. Astron. Astrophys.* 25, 113-150 (1987).

S. Alston, "Limiting behaviors of off-shell scattering wave functions and T matrices for centrally modified Coulomb potentials," *Phys. Rev. A* **38**, 636-644 (1988).

C. W. Ambruster, (S. Sciortino and L. Golub), "Rapid, low-level X-ray variability in active late-type dwarfs," *Astrophys. J. Suppl.* **65**, 273-305 (1987).

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J. A. Bookbinder and (F. M. Walter), "A VLA survey of an X-ray selected sample of F dwarfs," in *Cool Stars, Stellar Systems and the Sun*, Proceedings, Boulder, Colorado, 1987 (J. L. Linsky and R. E. Stencel, Eds., Springer-Verlag, 1987), pp. 260-261.

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A. Brown, "Chromospheric variability mechanisms affecting pre-main sequence stars," in *Cool Stars, Stellar Systems and the Sun*, Proceedings, Boulder, Colorado, 1987 (J. L. Linsky and R. E. Stencel, Eds., Springer-Verlag, 1987), pp. 466-468.

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*D. C. Griffin, (M. S. Pindzola and C. Bottcher), "Distorted-wave calculations of the electron-impact ionization of highly ionized Na-like ions," *Phys. Rev. A* **36**, 3642-3653 (1987).

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J. Huovelin, S. H. Saar and (I. Tuominen), "Relations between broad-band linear polarization and Ca II H and K emission in late-type dwarf stars," *Astrophys. J.* **329**, 882-893 (1988).

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