NBSIR 86-3470

Technical Activities 1986

Center for Chemical Physics

December 1986

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

NBSIR 86-3470

Technical Activities 1986

Center for Chemical Physics

Pierre J. Ausloos, Director

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Measurement Laboratory
Center for Chemical Physics
Gaithersburg, MD 20899

December 1986

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary
National Bureau of Standards, Ernest Ambler, Director

INTRODUCTION

This book is a summary of the technical activities of the NBS Center for Chemical Physics (CCP) for the period October 1, 1985 to September 30, 1986. The Center which is one of four units in the National Measurement Laboratory consists of four divisions with a total permanent staff of about one hundred which is augmented by approximately seventy guest scientists.

The Center for Chemical Physics (CCP), (1) develops and maintains the scientific competences and experimental facilities necessary to provide the nation with measurement methodologies and measurement services in the areas of thermochemistry, chemical kinetics, surface science and molecular spectroscopy; (2) measures, compiles, critically evaluates, and disseminates reference data to the industrial, government, and academic communities nationally and internationally; (3) develops theoretical methods and concepts, predictive equations and models; (4) develops standards and techniques of measurement; (5) provides federal, state and local governments, industry and the academic community with essential standards and certified standard reference materials needed to maintain the integrity of the measurement system; (6) provides consultative services and participates in collaboration efforts with other NBS Centers and the outside community.

The summary of activities is organized by division: Surface Science, Chemical Kinetics, Chemical Thermodynamics and Molecular Spectroscopy. The report of each division is divided into: (1) an introductory discussion of the objectives and programs of the division; (2) a review of all projects which includes accomplishments and future plans; (3) lists of outputs and actions which indicate in a quantitative way the activity and accomplishments of the division.

A detailed table of contents has been provided. It will permit the reader to find those activities of greatest interest. More information about particular work may be desired. To obtain this, the reader should address the individual scientists or their division, c/o Center for Chemical Physics, Chemistry Building, B-162, National Bureau of Standards, Gaithersburg, MD 20899.

NOTE: Certain commercial equipment, instruments, or materials are identified in this report in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table of Contents

SURFACE SCIENCE - - DIVISION 541

CHEMICAL KINETICS - - DIVISION 542

CHEMICAL THERMODYNAMICS - - DIVISION 543

MOLECULAR SPECTROSCOPY - - DIVISION 545

SURFACE SCIENCE DIVISION

C.J. Powell, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1986

1. Introduction

A. Background

Over the last ten years, 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 1990s" (National Academy Press, Washington, D.C., 1986).

The Pimentel report identifies chemical catalysis as one of five research frontiers in chemistry. A major recommendation was that modern chemical techniques be applied to obtain a molecular-level and coherent understanding of catalysis that encompasses heterogeneous, homogeneous, photo-, electron-, and artificial enzyme catalysis. For heterogeneous catalysis, in particular, surface science methods can be applied to identify reaction mechanisms and rates important in molecular sieve synthesis and catalysis and in catalysis by metals and oxides. These methods also enable evaluations to be made of the direct effects of catalytic poisons and promoters and can be used to develop new conversion catalysts, catalytic substitutes for precious metals, and catalysts to improve the quality of air and water. In addition, chemistry at solid surfaces is discussed at some length as a prominent example of the intellectual frontiers associated with the national well-being and surface science instrumentation is similarly identified as a significant example of instrumentation needed for modern chemical analysis and research. Other opportunities identified in the Pimentel report include understanding molecular dynamics for the control of chemical reactions, understanding the properties of clusters and of reactions on their surfaces, and the role of surface chemistry in diverse areas ranging from the synthesis of novel materials to energy production, reduction of environmental pollution, increased national security, and improved economic competitiveness.

The Brinkman report identifies surfaces and interfaces as a key area of condensed-matter physics in one of the volumes of the report. Specific topics discussed are the determination of surface-atomic structure, spectroscopy of elementary excitations at surfaces, interactions of atoms and molecules with surfaces, characterization of the interfaces between a solid and either a solid, liquid, or gas phase, and surface theory. Numerous opportunities in these areas were specified including experiments and theory to define the dynamical processes when atoms and molecules interact with surfaces, critical phenomena at surfaces, and measurements of the kinetics of surface processes. Extensive connections of surface and interface science were identified with information processing, speech and data communications, energy generation, transportation, space technology, national security, and medical applications. The significant role of surface and interface characterization was also identified in sections of the volume on Scientific Interfaces and Technological Applications dealing with the physics-chemistry interface, materials science, and microelectronics. Finally, a number of key questions and opportunities in the general area of atomic physics, particularly those dealing with atomic and molecular excitations and dynamics, state-to-state chemistry, laser spectroscopy, and clusters, were described in the volume on atomic, molecular, and optical physics; these issues are also important in surface science and in fully utilizing a number of the surface spectroscopies.

In a third recent report "Research Briefings 1986" (National Academy Press, Washington, D.C., 1986), the science of interfaces and thin films is one of four areas of science and technology identified as having "high-leverage research opportunities." Topics discussed in this report include characterization of "buried" interfaces, the production and characterization of smooth, defect-free epitaxial films, reactivity and catalytic activity of ultrathin films, characterization of processes occurring at biomaterial-tissue interface, mechanical properties of fiber-reinforced composites, and improvement of thin films for corrosion prevention, amongst many others. These topics are vital in the development of improved microelectronic devices, biomaterials, new structural materials, and coatings as well as technologies for new materials and processes.

A large number of techniques are utilized for surface and interface characterization. A choice of one of 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). 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.

The techniques utilized in surface science have generally been applied to characterize surfaces in an ultrahigh vacuum environment. The solution of many scientific and technical problems often requires removal of liquid- or gas-phase material prior to surface examination and/or the removal of solid-phase material to expose a region of interest. While this approach has often been successful, artifacts of many different types can arise during the removal of one or more phases. There is therefore a growing need for improved measurement methods that can be used for the *in situ* characterization of solid-solid, solid-liquid and solid-gas interfaces with the sensitivity, elemental specificity, and spatial resolution comparable to those attained with the current surface-characterization methods.

B. Goal, Objectives and Division Program

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 standard procedures, calibration data, and reference materials in cooperation with national and international standards organizations; and

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

Objectives (1) through (3) are met organizationally through an NBS task titled "Surface Science-Standards and Measurements" (program codes 155, 156, and 272). The Division's program for this task is divided into two principal activities, a Surface Standards Program and a Surface Measurements Program. Work performed during the year in these two area is reported in Sections 2 and 3, respectively.

Objective (4) is met through the Surface Competence Program (program code 261). This task was established in October, 1984 and represents a new focus by the Division in two areas, "Novel Two-Dimensional Materials" and "State Characterization of Energetic Species Ejected from Surfaces". A separate report on these activities is given in Section 4.

The Division's program is supported financially by other NBS offices and by other Federal Agencies (in addition to the base support allocated by NBS, the National Measurement Laboratory and the Center for Chemical Physics). These arrangements enable the Division to meet NBS objectives and standards needs and also to contribute its expertise and facilities to important national programs. During FY86, support was received from the following offices and agencies:

Office of Standard Reference Data
- Surface Science: Sputtering Yield Data
- Workshop on Quantitative Surface Analysis

Office of Standard Reference Materials
- Characterization of Additional Lots of SRM2135
- Workshop on Quantitative Surface Analysis

NBS Brookhaven Project Coordinator
- Travel to Brookhaven National Synchrotron Light Source

Department of Energy
- Structure and Reactivity of Chemisorbed Species and Reaction Intermediates
- Structure and Reactivity: Applications of Neutron Inelastic Scattering and of Negative-Ion ESDIAD
- Laser Studies of Chemical Dynamics at the Gas-Solid Interface (joint with Molecular Spectroscopy Division)

Air Force Office of Scientific Research
- Laser Studies of Chemical Dynamics at the Gas-Solid Interface (joint with Molecular Spectroscopy Division)

Office of Naval Research
- Use of Synchrotron Radiation to Characterize Oxide Surfaces

U.S.-Spain Joint Committee for Scientific and Technological Cooperation
- Structure and Reactivity in Catalysis by Metals and Oxides

C. Technical Output and Professional Interactions

Sections 5 and 6 of this report contain listings of the publications and talks, respectively, for the past year by Surface Science Division staff and for projects supported by the Division.

Many members of the Division staff hold leadership positions in professional societies and groups, as listed in Section 8. These interactions not only reflect the professional esteem in which these staff members are held but provide useful mechanisms for both disseminating the results of NBS work and for learning of significant measurement problems being faced by those using surface-characterization equipment.

Interest in surface science and surface characterization at NBS continues to grow. The Division has had an active Seminar program, as indicated in Section 7, and these seminars have been attended by other NBS staff. The Division staff also participates in an informal weekly lunch meeting, attended by scientists from a number of NBS organizational units, at which developments in surface science are discussed. Members of the Division staff are frequently consulted on a wide range of NBS problems.

Much of the Division's work is carried out in collaboration with other scientists within the Center for Chemical Physics, within NBS, within the U.S.A., and internationally. The nature of these collaborations is shown in Section 9. These collaborations are considered important because they enable a relatively small Division staff to work synergistically with other experts, they enable us to have access to unique facilities or expertise, and they enable our expertise to be extended to a larger range of important scientific and technical problems.

The Division has been fortunate in having seventeen visiting scientists work at NBS for varying periods during the past year, as indicated in Section 10. These scientists enrich our staff and our projects. A further enrichment of our programs comes from Postdoctoral Research Associates who typically hold two-year appointments; five Postdoctoral Research Associates worked in the Division during FY 1986.

2. SURFACE STANDARDS PROGRAM

G. P. Chambers, W. F. Egelhoff, Jr., N. E. Erickson, J. Fine,
Y. Hashiguchi, R. D. Kelley, R. L. Kurtz, T. E. Madey,
D. Marton, C. J. Powell, R. Stockbauer, and S. Tanuma

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 standard practices, 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.

A. Reference Data

We describe here results of projects in which needed reference data are being generated. Section 2.C includes recent review articles by Division Staff that summarize and evaluate data required in a number of surface spectroscopies.

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 NBS 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 Physics 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.

Two interactive data-base management programs were previously developed to handle the specific needs of the data compilation. The structure developed allows easy data entry into one of these data bases; information can then be transferred to the second data base for rapid access and searching. Additional software has been written to sort and tabulate the searched data in a format suitable for publication. In this past year extensive use was made of our 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. Work has begun on abstracting certain experimental parameters which will be used to evaluate the reliability of the sputtering yield data.

In the coming year, we intend to make an evaluation of the sputtering yield data available for elemental targets. These data are to be assigned a "quality rating" which will be determined from an evaluation of the measurement method and the conditions under which the measurements were made. This evaluation will include an assessment based on the combined effect of ambient vacuum condition, target reactivity, and rate of sputtering. We will compile this evaluated data in both tabular and graphical form for those parameters of interest to the surface-analysis and sputter-depth-profiling community.

2. Reference Data for the Calibration of the Energy Scales of X-Ray Photoelectron Spectrometers and Auger-Electron Spectrometers

(N. E. Erickson, S. Tanuma, 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 NBS 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.

Several years ago, we made preliminary measurements of the BEs by XPS for the principal core levels of Cu, Ag, and Au and of the Auger-electron KEs from the same metals. It was hoped that data of this type would be convenient and satisfactory for the calibration of individual instruments. Unfortunately, the electronics on our instrument were not then as stable as we desired so we have replaced critical power supplies with high-precision programmable power supplies (PPSs) whose outputs can be monitored with high-precision digital voltmeters (DVMs). 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 NBS are important to ensure maximum user confidence, particularly since there are still some discrepancies in some recent high-accuracy measurements.

We give below two reports that summarize work over the past year. First, we have compared the outputs of several high-precision PPSs in our laboratory with several high-precision DVMs. These comparisons indicate that artifacts can occur in these instruments. Artifacts of the type we have found may in fact make an energy-scale calibration of an XPS or AES instrument at a limited number of points (such as with reference data for Cu, Ag, and Au) of doubtful validity since there could be nonlinearities at intermediate energies. If measurements of high accuracy are required, it may be necessary for a user to characterize the performance of the PPS or DVM in more detail. Reference data for Cu, Ag, and Au (and eventually other materials) will then be useful benchmark values. Second, we have analyzed algorithms for locating peak maxima in XPS. Our analysis provides a means for a user to select the conditions for data acquisition so that peaks can be located with a desired accuracy.

We have recently completed the calibration of one PPS and one DVM in collaboration with Mr. T. E. Kiess of the NBS Electricity Division. There were a number of technical problems to be overcome, particularly in extending the calibration to voltages above 1000 volts. These instruments have now been calibrated with an uncertainty of better than 10 mV at voltages close to those to which we will make the BE and KE measurements for Cu, Ag, and Au. We expect to make these measurements soon.

(a) Investigation of Errors in Programmable Power Supplies and Digital Voltmeters

The determination of XPS BEs and AES KEs is usually based on the assumption that the analyzer energy has been incremented uniformly through the energy region selected and that the actual analyzer energy is a continuous and linear function of the programmed value. We checked this assumption in the course of making our new BE and KE measurements. A programmable power supply was used to step the analyzer over the spectral region of interest while a precision digital voltmeter sampled the voltages to verify that no transmission errors had occurred. In the course of checking this agreement with a number of different instruments, a variety of both digital and analog faults were uncovered which are believed to be of a generic nature and hence are likely to be found to greater or lesser degree in virtually all extant instruments.

Fig. 2.1 shows a plot of the voltage difference between a DVM output and the input voltage to a PPS observed for a particular pair of instruments for a sequence of voltages between 10 and 1000 V. Instead of there being a strictly linear deviation between the instruments, which is what might be expected for instruments that had not recently been calibrated, one sees that there are eight discontinuous regions (octades) with a progressively increasing discrepancy between the programmed and measured voltages. This particular set of data indicates, via the steps, that there are bit errors in the resistor decoding network that drives the power supply such that, as one octade is incremented, the supply does not transfer smoothly over into the next higher octade. The number of such discontinuous regions depends on the particular sequencing arrangement that the manufacturer has chosen to use so the number and exact voltages where such discontinuities are apt to occur cannot generally be predicted. It can be predicted, however, that transition regions will occur. In this particular example all the major deviations are of the same sign, but the deviations could be rather variable in both magnitude and sign.

The progressively increasing discrepancy with increasing voltage in Fig. 2.1 is suggestive of a power heating effect in a resistor divider network such that the resistor value increases with the square of the applied voltage. This type of problem can be expected in virtually all high voltage power supplies and can be difficult to detect since many analyzer power supplies have a high impedance and cannot be checked with an ordinary voltmeter because the supply will be loaded. Checking the voltage across the feedback resistor segment of the divider network will, of course, not reveal this particular problem.

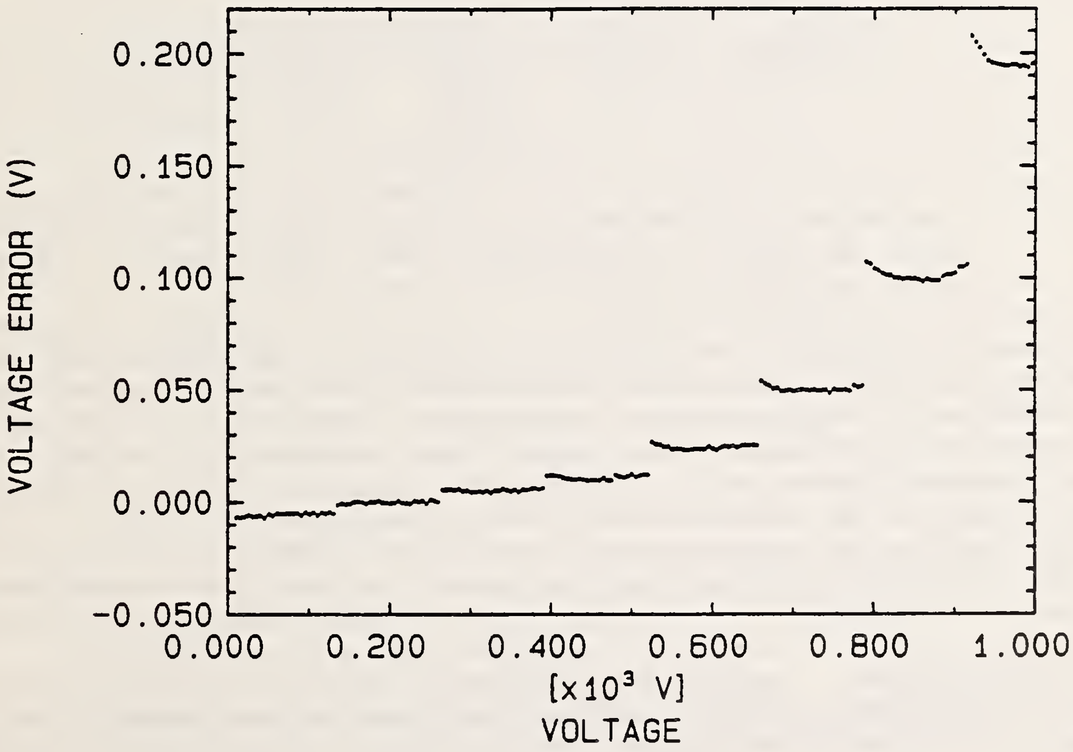


Fig. 2.1 Plot of deviation between a digital voltmeter output and the input voltage to a programmable power supply for a sequence of voltages between 10 and 1000 V.

In other comparisons, we have found appreciable deviations (up to 150 mV) that have occurred over a one volt interval, as illustrated in Fig. 2.2. This fault, which was identified as occurring in a particular voltmeter, is most likely due to a bit decoding error in the circuitry providing communication between an internal counter and the applied voltage. This type of error is expected to be repeated as the same sequence of low- or medium-order bits is repeated at other voltage levels.

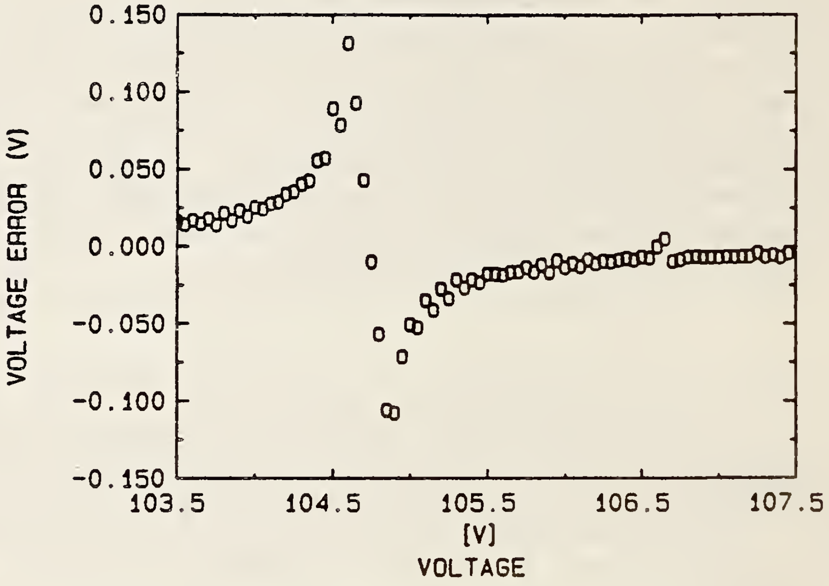


Fig. 2.2 Plot of deviation between a digital voltmeter output and the input voltage to a programmable power supply over a 4 V range of output voltage.

These problems can be extremely difficult for the manufacturer or user to locate since more than a million different combinations of values are possible with high-precision instruments. Fortunately, a modeling and test-point selection method has recently been developed in the NBS Electrosystems Division and it is hoped that analyzer manufacturers will avail themselves of this methodology as it becomes known. This methodology greatly decreases the number of test points that have to be sampled since most logic elements are used in a repetitive fashion as values are incremented. It is also hoped that more complete calibration procedures will be developed by instrument manufacturers for their specific equipment. The errors indicated in the two figures would reflect themselves as shifts in peak positions and possible peak distortions depending upon the relative position of the peak and the transition regions.

(b) Analysis of Peak Location Algorithms

The assertion that a particular electron peak has a certain binding or kinetic energy implies that it is known how to determine the location of the peak. The peak location is usually defined as the position of the peak maximum but a procedure for determining this position is rarely specified. The practical problem is that most real peaks are not symmetric about their center and the location of the maximum is sometimes a matter of subjective evaluation. There are, however, at least two procedures that can be found in the literature although neither seems to have been subjected to any validation checks. The first involves fitting, via a least-squares procedure, a quadratic equation to the top 5% of the peak. The problem with this method is that, in order to get a good fit, one should have a sufficient number of points and good counting statistics since the curvature close to the maximum is not very large. Many electron analyzers, especially older ones, can only step with fairly large energy increments, say 0.05 or even 0.1 eV. With a reasonably narrow peak one may then have only 5 to 10 points to determine the three parameters which describe a quadratic equation. This lack of redundancy in the presence of a small curvature and possibly poor statistics can lead to a fairly large uncertainty in the peak location.

The second procedure is to locate the centers of a sequence of fractional peak heights and to extrapolate these to the top of the peak. The accuracy of this method is limited by the precision with which the centers of the chords can be located.

To study this problem, we have generated a series of synthetic XPS spectra using broadened Doniac-Sunjic line shapes of different widths and with various values of the asymmetry parameter covering the range of values normally encountered. The exact peak maximum location is known from the generating function. We have then determined the accuracy and precision with which least-squares quadratic and quartic fits locate the peak maximum in the presence of various amounts of generated random noise and for various fractions of the peak height in the fit.

It is difficult to summarize this multiparameter space succinctly. In general, a quadratic curve will give good results only if the very top of the curve, say the top 5% to 10%, is analyzed. The difficulty is that noise combined with a small number of data points can make this analysis very unreliable. A quadratic fit over a larger fraction of the peak height leads to a systematic position shift if the asymmetry parameter is substantial. The best solution seems to be to use as small a step size as possible so as to maximize the number of data points, use the top 25% to 30% percent of the peak so that the sides are reasonably well defined even if the data are fairly noisy, and use a fourth order polynomial fit to account for peak asymmetries.

An additional method is also being investigated. This involves applying a Savitzky-Golay smooth to the data and then taking the derivative. Preliminary results indicate that this procedure is competitive in accuracy to the quartic fit method.

3. Reference Data for X-Ray Photoelectron Spectroscopy and Auger-Electron Spectroscopy

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

A project was initiated in FY 82 with funding by the NBS Office of Standard Reference Data 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 NBS, and the Surface Science Division is providing technical review.

To date, over 800 references have been examined and more than 11,000 line positions included. The database can be searched for reference, compound, element, spectral line, and physical state of the compound. Work will be completed in the next few months. The reference data will be included in a report for the Journal of Physical and Chemical Reference Data.

4. Comparison of L_3-Shell Binding Energies in Six 3d Metals Measured by X-Ray Photoelectron Spectroscopy, Appearance-Potential Spectroscopy, and Electron Energy-Loss Spectroscopy

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

The binding energies (BEs) of core electrons in solids are of importance in a number of electron-spectroscopic methods of surface or thin-film characterization such as x-ray photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES), appearance-potential spectroscopy (APS), and electron energy-loss spectroscopy (EELS). A frequently made assumption is that BEs measured by one technique are identical to those measured by another (within the common measurement uncertainties), but there have been some indications of systematic differences. The extent to which significant differences occur, however, has been obscured by uncertainties in BE values associated with the particular measurement method, with possible errors in voltage measurements, and with possible specimen impurities.

We have measured L_3-shell BEs for Ti, V, Cr, Fe, Co, and Ni by XPS, APS, and EELS. In order to avoid the more obvious sources of error, we have used the same specimens for each of the three BE measurements and the same reference power supply (whose output is believed accurate to 0.01 V). Our work also differs from most previous comparisons in the following three respects. First, the electron energy scales for the XPS and EELS measurements were calibrated by a method in which electrons from a thermionic source were accelerated to a selected energy, scattered elastically by the specimen, and detected at an energy close to that of the XPS or EELS feature or interest. These calibrations were performed with an uncertainty of about ± 0.1 eV, and the XPS and EELS BEs were determined with a total estimated uncertainty of ± 0.2 eV. Second, we have found that the one-electron model previously used in the analysis of APS data for the 3d metals is invalid for Ti and V (see section 3.H) and is only marginally valid for Fe and Cr. An improved model has been developed that allows us to extract more reliable BEs for these metals. The AFS BEs have an uncertainty of about ± 0.3 eV except for Cr for which the uncertainty is estimated to be ± 0.4 eV. Finally, we have made EELS measurements as a function of incident electron ranging from about 50 eV above the threshold for core-level excitation (i.e., the L_3-level BE) to about 1500 eV. These measurements were made to investigate the extent to which the EELS spectral data and the derived BEs changed as the excitation varied from near-adiabatic (as for the APS measurements) to sudden (as for the XPS measurements).

Our BE results are summarized in Fig. 2.3 where we show BE values as a function of excess energy in the excitation. APS is a threshold-excitation method so all APS BEs are shown at zero excess energy. For EELS, the excess energy is the incident energy minus the BE while for XPS, the excess energy is the photoelectron kinetic energy.

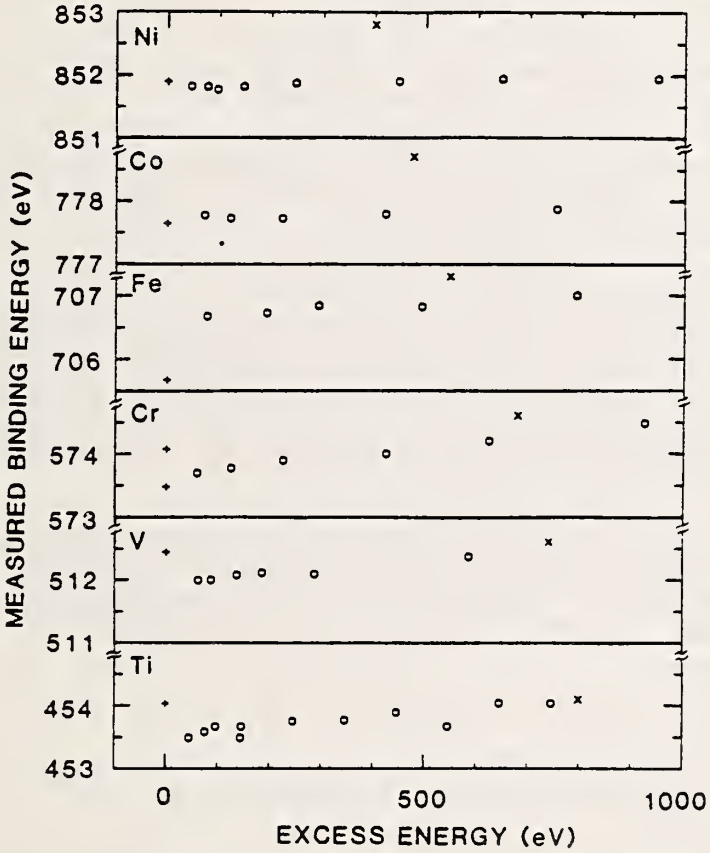


Fig. 2.3 Values of L_3-level binding energies for Ti, V, Cr, Fe, Co, and Ni as determined by three techniques: +, APS; o, EELS; x, XPS. The BE values are shown as a function of excess energy in the measurement, as defined in the text.

The BEs measured by the three methods for Ti and V are very similar although the EELS BEs for both metals appear to be systematically lower than the APS and XPS BEs. The EELS BE values at high excess energies agree with the other values but the non-dipole final states excited at low incident electron energies exhibit lower BEs. For both Co and Ni, the EELS and APS BEs are in good agreement and are appreciably lower than the XPS BEs. The difference between the XPS and APS BE values is 0.9 eV for Ni and 1.1 eV for Co. For Fe, we find a 1.7 eV difference between the XPS and APS BEs, and EELS BEs that are intermediate. For Cr, it was more difficult to determine an APS BE and two values are shown in Fig. 2.3 that represent reasonable limits in our analysis. The average difference between the XPS and APS BEs is then 0.8 eV and the EELS BEs are intermediate between the XPS and APS values, as for Fe.

Our results clearly show that BEs measured by different methods can have significant differences; for the L_3-levels of the 3d metals, these differences were up to 1.7 eV. The larger differences occurred to the right of the series where the XPS BEs of Fe, Co, and Ni exceeded the APS BEs by 0.9-1.7 eV. The reasons for the differences are not known in detail but are believed to be associated with the different relaxation and screening responses of each metal for each type of spectroscopy. For APS, a core hole is created adiabatically together with two slow electrons, while for XPS a core hole is created suddenly with a relatively fast (400-800 eV) photoelectron in our experiments. In the EELS experiments, a core hole is generated together with an excited electron above the Fermi level (which may be localized in the presence of the core hole) together with another electron with energy here of ≈ 50-1000 eV. It is therefore not considered surprising that BEs determined by spectroscopies with different excitation mechanisms are different. Only for chromium, however, do the EELS BEs interpolate approximately between the APS and XPS BEs, the limits for adiabatic and sudden excitations, as might naively be expected. Finally, our work clearly indicates that BEs determined by one spectroscopic method should not be used for the energy calibration of another type of instrument unless the extent of systematic differences is known.

We plan to explore the origins of the BE differences by making similar measurements with other materials (e.g., non-transition metals), alloys, adsorbates, and for implants (e.g., of rare-gas ions) into different solids.

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

(W. F. Egelhoff, Jr., R. L. Kurtz, C. J. Powell, and R. Stockbauer)

Values of inelastic mean free paths (IMFPs) and attenuation lengths (ALs) of low-energy 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.

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 30Å 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). Finally, knowledge is needed of the extent to which concepts (and data) developed for polycrystalline or amorphous materials break down in single-crystal materials.

Our accomplishments of the past year have been in the following three areas.

(a) Energy Dependence of Electron Inelastic Mean Free Paths

Comparisons of the AL and IMFP data are often made through plots of AL and/or IMFP values versus electron energy. While these plots are very useful for assessing the relative magnitudes of AL and IMFP values and their trends as a function of energy, they are not well suited to a detailed examination of the energy dependence. A particularly convenient and appropriate method of examining the dependence of AL or IMFP values on electron energy is the Fano plot. The product of a particular inelastic cross section (which in the simplest cases could be for a discrete excitation, ionization, or total inelastic scattering in a gas) and electron energy is plotted versus electron energy on a logarithmic scale. At sufficiently high electron energies, this plot is expected to be linear with a slope that can be derived from appropriate optical data. Such behavior is expected quite generally from the Bethe theory for inelastic electron scattering in matter. Since the Bethe theory is well established, use of the Fano plot is a simple and effective means for analyzing the internal consistency of experimental cross-section data with optical adsorption measurements, and for determining the minimum incident electron energy for which the Bethe theory is valid.

An analysis has been made of the energy dependences of calculated IMFPs for Al, Cu, Ag, and Au from four recent sources of data. Linear Fano plots were obtained for each metal using data from the calculations of Ashley _et al_. and Powell but the Fano plots with the data of Szajman _et al_. had distinct curvature. Fano plots with the data of Penn showed linearity over two separate energy ranges, typically from 80 to 500 or 1000 eV and from 1000 or 1500 eV to 10000 eV. These variations were attributed to different treatments in the calculations of exchange and correlation and of the dependence of the differential inelastic scattering cross section on momentum transfer.

There were significant variations in the slopes of the Fano plots for each material using the four sources of IMFP calculations. The expected slope of the Fano plot can be calculated from optical absorption data and thus can be used as a guide in selecting a preferred data set. Values of the Fano-plot slopes from three of the data sets generally agreed well with the optical values but the slope values based on the data of Szajman _et al_. exceeded the optical values by 9 to 40%.

It was found that the slopes of Fano plots using AL data for Al, Cu, and Au, were larger than the optical values by 29 to 54%. A similar result has been obtained in other analyses of inelastic-scattering cross-section data and is believed due to the electron energies not being high enough to be in the asymptotic Bethe region. A separate analysis of the optical data showed that the minimum electron energy for which linear Fano plots can be expected is about 400 eV for Al and about 1000 eV for Cu, Ag, and Au. Experimental AL measurements in different types of materials over a wide electron energy range are required to define more clearly the energies where the Fano plots attain their asymptotic slopes.

Calculations are in progress of IMFPs from experimental optical data using an algorithm developed recently by Dr. D. R. Penn of the NBS Electron Physics Group. Since optical data are available over a sufficiently wide photon-energy range for a limited number of materials, it is of interest to compute IMFPs and to search for possible systematics in the dependences on electron energy and material parameters.

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

During the past year we expanded our efforts to measure electron attenuation lengths in condensed molecular solids by performing experiments on the X-24C beam-line (a joint effort of NBS and the Naval Research Laboratory) at the Brookhaven National Synchrotron Light Source. The goal of this experiment is to measure electron attenuation lengths over a wider electron energy range than is possible at the NBS SURF-II storage ring. Films of molecular solids of variable thickness are condensed on a cooled copper substrate and the intensity of substrate valence-band photoemission measured as a function of film thickness. These experiments were conducted with different photon energies and attenuation lengths measured for corresponding photoelectron energies. At Brookhaven, we can make the attenuation-length measurements over the range of about 50 to about 1200 eV which is the range of practical interest for Auger-electron spectroscopy and x-ray photoelectron spectroscopy. Furthermore, careful attenuation-length measurements over a wide electron energy range should enable more accurate determination of the energy dependence.

Films of the molecular solids are prepared by the technique of microcapillary-array dosing, the method we developed in our previous experiments at SURF-II. The Brookhaven surface science chamber was modified to include an in-situ photon intensity monitor, the microcapillary array dosing system (with gas-handling manifold), and an additional cryopumping block for reduced operating pressure. Preliminary measurements were made with water at an electron kinetic energy of 155 eV; however, several experimental snags developed. These complications, coupled with erratic machine operations, precluded the completion of these measurements. Most problematic was that the grating installed in the extended-range monochromator had been manufactured with an improper blaze angle; this mistake resulted in usable photon flux with a maximum photon energy near 160 eV. This grating is being replaced and beryl crystal diffracting elements are presently being prepared also. These elements should be in place for the next run.

The electron attenuation-length measurements will continue in the next available time-slot and will include measurements on condensed films of water, methanol, and cyclohexane (materials for which attenuation-length measurements were made earlier in the energy range 18-68 eV).

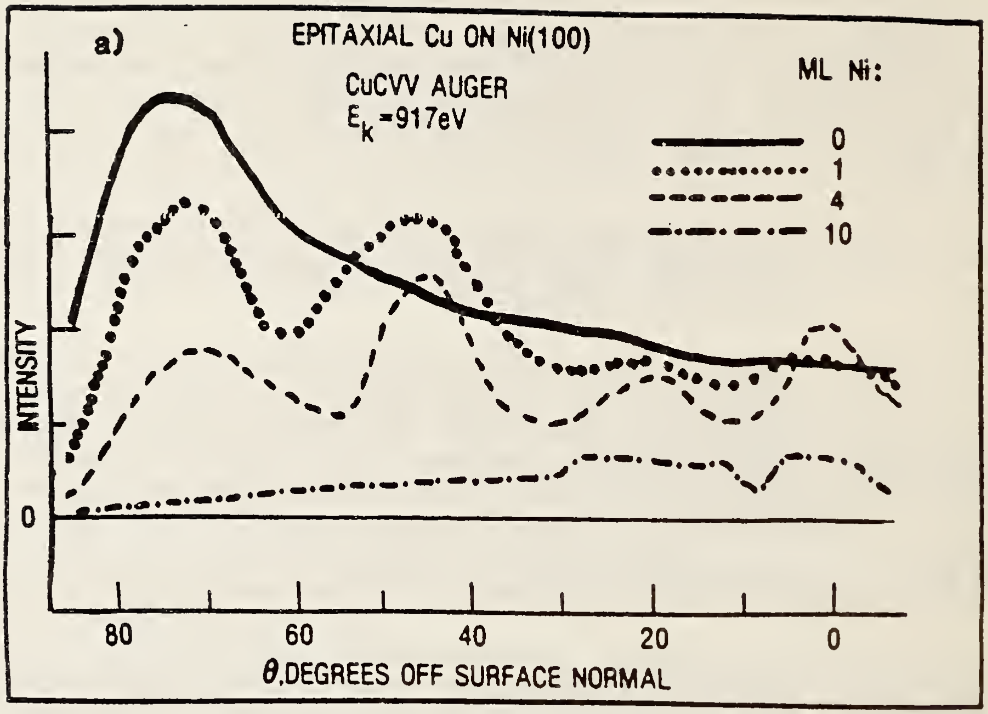
(c) Layer-By-Layer Analysis of the Effects of Forward Scattering of Electrons in Attenuation Length Measurements with Single Crystals

Attenuation lengths have been frequently measured from the characteristic decay of an AES and XPS signal as a film of increasing thickness is deposited on a substrate. This decay is generally monotonic for amorphous or polycrystalline samples. For single- crystal samples, however, a fundamental complication for such measurements is the enhancement of an AES or XPS peak intensity along crystal axes. These enhancements along nearest-neighbor directions are due to forward scattering of the emitted electrons by lattice atoms (see Fig. 2.4(b)).

As part of an effort to characterize and elucidate the influences of forward scattering on AL measurements, several simple model systems have been studied. Figure 2.4(a) presents data on such a system. The substrate consists of a monolayer (ML) of Cu epitaxially grown on Ni(100). The attenuation of the Cu AES signal is measured as epitaxial layers of Ni are grown on the Cu. Extreme departures from monotonic decay are observed. At the angles at which the strongest forward scattering is expected, 45° and 0°, the Cu AES signal is actually increased by overlayers and is not reduced to below the clean-Cu levels until more than 4 ML of Ni has been deposited.

Certain types of electron analyzers (e.g., the cylindrical-mirror analyzer) may integrate XPS and AES signals over a wide range of angles and still recover a monotonic decay. Other types of analyzers (e.g., the hemispherical analyzer) often select small solid angles and in such cases, as here, it is clear that the simple concept of exponential electron attenuation breaks down in single-crystal materials. In such cases, quantitative surface analysis by XPS and AES will have large uncertainties unless corrections can be made for the effects of forward scattering. Data of the type shown in Fig. 2.4(a) can be used to select the polar angles and solid angles for which the current simple models for quantitative AES and XPS are more likely to be valid.

Figure 2.4 also provides insight into the layerwise breakdown of the angular distribution of pure Cu(100). Summing the spectra shown in Fig. 2.4 from 0 to ~ ∞ ML of Ni (including those not shown) produces a result essentially identical to the pure Cu(100) angular distribution. This result is reasonable since Ni overlayers scatter electrons in very nearly the same manner as Cu overlayers. Thus, Fig. 2.4(a) makes it possible to see the layerwise contributions to the angular distribution of the Cu AES signal from pure Cu(100).



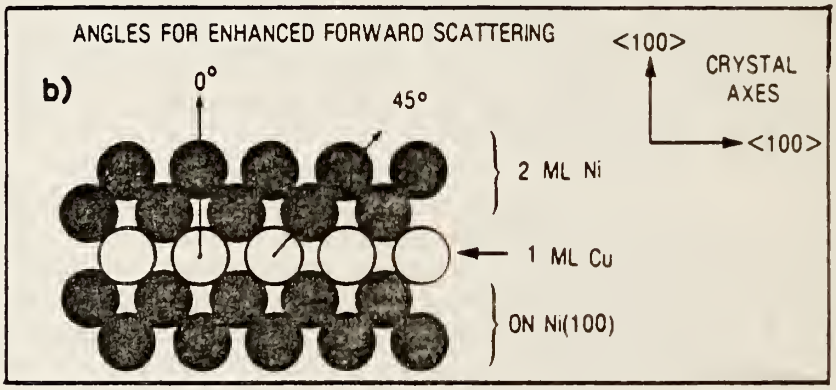


Fig. 2.4(a) Changes in the angular distributions of Auger electrons from an epitaxial Cu monolayer for the indicated number of nickel overlayers.

(b) Illustration of the atomic geometry for these sandwich structures

6. Algorithm for Fitting Sputter-Depth Profiles at Interfaces (J. Fine, G. P. Chambers, and D. Marton)

The determination of interface widths from sputter-depth-profiles is presently accomplished by means of graphical methods. Since the shapes of such interface profiles are generally not symmetric and since there is no accepted method of measuring interface widths, accurate width determination as well as intercomparison of results is often difficult to accomplish. One solution to this problem is to fit numerically the interface profile shape to an appropriate analytical expression from which one can obtain a factor proportional to different definitions of the interface width.

In collaboration with Dr. W. H. Kirchhoff of the NBS Chemical Thermodynamics Division, a fitting analysis for Auger-electron sputter-depth profiles has been developed using a logistic function of the form:

$$I = [A + a(T-T_0)]/(1 + e^{-t}) + [B + b(T-T_0)]/(1 + e^{t})$$

where I is the peak intensity of the Auger spectrum of the sputtered atom as a function of the time T. A is the intensity from a totally covered surface, B is the background intensity from a completely uncovered surface, and a and b empirical parameters which can account for additional time dependence or instrumental effects. T_0 is the apparent midpoint of the transition region and t is a dimensionless, reduced time defined as $(T-T_0)/D$. The scaling factor, D, is the characteristic time for sputtering through the interface region. Asymmetry in the depth profile can be accommodated by allowing D to vary with time.

A least-squares fitting program has previously been written to fit measured Auger spectral intensities to the above equation for completely resolved interfaces (i.e., where component X goes from 100 to 0% and component Y goes from 0 to 100%). We showed that this logistic function could be fitted to Auger data for the NBS multilayered Ni/Cr thin-film structure SRM2135 to within the experimental error of a few percent.

This past year, extension was made of this fitting using the logistic function to interfaces which are not fully resolved. This situation occurs when sputter profiling a very thin layer of material (less than, say, 5 nm) in between two thick layers of another material. By making use of the derivative of the above equation, we have shown that remarkably good fits can be made to high-resolution sputter profiles obtained in our laboratory. The fits were made to depth profiles of a multilayer Ni/Ag thin-film structure which had thin Ag layers (≈ 4 nm) and thick Ni layers (≈ 50 nm). These fits to the analytical logistic function give functional parameters from which we have been able to make quantitative determinations of layer thickness for such very thin films.

A limited distribution has been made during the year of the fitting program and its documentation. The program has been written in Fortran 77 and can be run on IBM-compatible personal computers. Packages containing the program on a floppy disc, a program listing, a detailed description of the program, and examples of its use (with corresponding test data on the disc) were distributed at the spring meeting of ASTM Committee E-42 on Surface Analysis and at the Applied Surface Analysis Symposium in Dayton. At the latter meeting, a demonstration was also given of the program. The purpose of the distribution was to enable further tests and evaluations of the program to be made. We are currently exploring mechanisms for wider dissemination of the program that will enable a larger number of people to make use of this software.

7. Adsorbate Surface Coverage Measurements

(T. E. Madey)

An important parameter in surface science measurements is the coverage (surface density in atoms/unit area) of atoms or molecules which are adsorbed on a given surface. In many instances, there is a factor of two or three uncertainty in measurements of coverage. Such large uncertainties provide major problems in data interpretation, modelling of surface structures, determination of surface kinetics, etc. During the last few years, several experimental methods have been developed which have the potential for providing absolute measures of surface coverage, with a substantially smaller uncertainty (~ ± 25%). Such methods include molecular-beam reflection techniques, high-energy ion backscattering, radiotracer measurements, and nuclear reactions induced by ion bombardment. We expect shortly to initiate a comparative study of these methods with the goal of preparing a critical review of absolute coverage data and of relevant measurement methods.

B. Reference Materials

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

(J. Fine, Y. Hashiguchi, and D. Marton)

The objective of this project is to develop standard reference materials (SRM's) 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 densities 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.

Prototype thin-film structures were initially fabricated in order to evaluate their usefulness as depth profiling SRM's and to develop appropriate characterization techniques. These structures were made by sputter deposition as part of a joint US/Yugoslavia program between NBS and Dr. B. Navinsek at the J. Stefan Institute in Ljubljana. Analyses of these prototype materials at NBS and by members of ASTM Committee E-42 on Surface Analysis were done using Auger-electron spectroscopy (AES), x-ray fluorescence, secondary-ion mass spectroscopy (SIMS), Rutherford backscattering spectroscopy, and proton-induced x-ray emission. The results were satisfactory and a stock of similar thin-film SRM's were fabricated in 1982 using the sputter deposition facility at the J. Stefan Institute in Ljubljana. Production and characterization of the Ni-Cr thin-film SRM was supported by the NBS Office of Standard Reference Materials.

Preliminary analyses obtained on the nickel-chromium multilayered thin-film structures indicated that this material should be of considerable benefit as a depth-profiling SRM. It has been characterized and calibrated in order to determine the uniformity and periodicity of the thin-film layers, absolute film thicknesses, sputtered interface depth resolution, and structural stability. The results of these measurements indicated that this Ni/Cr structure could be accurately calibrated for depth profile analysis; it was issued as NBS Standard Reference Material 2135 in the fall of 1985.

Sales of the SRM through the NBS Office of Standard Reference Materials were greater than we anticipated and by the spring of 1986 our initial stock of 80 specimens was sold. An additional stock of 25 specimens, which we had previously calibrated, was issued as NBS SRM 2135a and these, too, were sold by the summer of 1986.

Two additional batches of Ni/Cu structures (about 200 specimens) were characterized by Auger sputter-depth profiling and by neutron activation analysis. These should be ready for issue in the fall of 1986 and should be sufficient to maintain our stock of SRM 2135 for about another year. We are now making arrangements with Dr. Navinsek for the fabrication of about 600 Ni/Cr structures.

Future work includes characterizing and certifying "marker" layer-type sputter-depth-profile SRM which we have recently fabricated in production quantities. This material also was fabricated in Dr. Navinsek's laboratory and consists of eight Cr layers (~ 40 nm each) separated by about 2 monolayers of Cr_2O_3. Preliminary experiments have been carried out to characterize these structures by Auger depth profiling. This is a difficult test since the Cr_2O_3 marker layers are very thin and since the oxygen Auger peaks nearly overlap those of chromium. We have been able to detect the oxygen Auger signal after developing a special background subtraction program. In some experiments, we were able to detect all seven oxide layers in a structure (even the one that was 280 nm deep) after very careful instrumental alignment and with a low-energy (1 keV) argon ion beam. Accurate determination of the position of the marker could be achieved by fitting a theoretical curve to each of the seven oxygen peaks in the depth profile. The theoretical curve was the same as that used to describe the Ag/Ni depth profiles (section 2.A.6) and had terms that described surface-roughness development and radiation-enhanced diffusion occurring during the sputtering of the specimen. In other experiments, we were unable to detect the deeper oxide layers, presumably because of the higher interface broadening associated with roughness development and radiation-enhanced diffusion.

We plan to perform additional characterizations of the Cr/Cr_2O_3 structures. We will measure depth profiles for a wider range of experimental conditions and will calibrate the chromium total film thickness by neutron activation analysis. It is possible that the material may not be suitable for routine use in Auger depth profiling (except perhaps as a stringent test of operating conditions). We expect, however, that it will be useful as a depth-profile standard in SIMS since this technique is more sensitive than AES and does not suffer from the problem in AES for Cr and O of peak overlap in energy. We anticipate that this structure can be issued as an SRM next year.

2. Quantitative Sputter Depth Profiling of Interfaces
(J. Fine, D. Marton, Y. Hashiguchi, and G. P. Chambers)

Determination of composition-versus-depth at virgin solid/solid interfaces is at present difficult to achieve with current sputter-depth-profiling techniques. This is due, to a large extent, to a lack of understanding of the effects of the various bombardment conditions (i.e., ion beam energy, species, angle of incidence, current density, and sputtered depth) on interface resolution. A consistent set of measurements obtained for various ion beam parameters, all done on the same material, would significantly enhance our ability to assess the abruptness of interfaces before sputter-profile analysis took place and would be of value in determining optimum sputter-profile conditions.

Our development of multilayer thin-film structures with known layer thickness and periodicity (as described above) makes it both possible and practical to examine systematically the dependence of interface resolution on ion beam parameters. Use of the computer- controlled, sequential-mode N(E) Auger data system which has been previously developed allows us to obtain reliable and accurate Auger measurements while the fitting of this data to particular functions results in quantitative determination of the interface width and the asymmetry of the interface profile.

Our principal objective in the past year has been to investigate interface broadening mechanisms in depth-profile measurements and to define the limits on the use of layered structures as sputtering-rate reference materials. Two important processes occurring during sputtering have been selected for these studies: the development of surface roughness and radiation-enhanced diffusion. Silver/nickel multilayered samples, fabricated in the laboratory of Dr. B. Navinsek (Ljubljana, Yugoslavia) and consisting of five thin (~ 4 nm) Ag layers embedded between six thicker (50 nm) Ni layers and sputter-deposited on Si wafers have been used as test materials for these measurements.

(a) Surface roughness development during sputter-depth profiling

Both theoretical and experimental studies have been carried out. A simple statistical model has been developed to explain the phenomenon of increasing surface topography (roughness) during ion sputtering of solid targets. The square-root depth dependence of the surface roughness, which has been observed in some cases, is explained by assuming that the roughness increase is caused by the differences in sputtering rates obtained on differently oriented crystallographic surfaces, and that the distribution of the sputtering rates is fully random. Deviation from the random distribution of the sputtering rate leads to different types of depth dependences for the surface roughness.

A light-scattering experiment has been set up in conjunction with the Auger depth-profiling apparatus to measure the surface roughness changes in-situ (i.e. without breaking the vacuum). Stylus measurements with a Talystep instrument (in collaboration with Dr. T. Vorburger of the NBS Precision Engineering Division) have been utilized as calibrations. The light source used in this experiment is a 5 mW unpolarized 630 nm He-Ne laser, and the scattered light is collected by an ellipsoidal reflector. The opening angle of the reflector is about 45° which limits the maximum surface wavelength that can be measured to about 1.85 µm. This experiment is far from the ideal arrangement in which the total scattered light intensity could be measured and thus only relative roughness values can be measured here. This is, however, the first known experiment to measure surface roughness changes <u>in situ</u> following sputtering.

Preliminary experiments carried out with this set-up at 1 keV argon ion energy showed that the surface roughness increased from the starting value for the unsputtered surface of 1 nm to about 6 nm at 50 nm depth and to about 12 nm at 250 nm depth. These results are consistent with the assumption of a square-root depth dependence of the roughness increase and with semi-empirical results obtained from the Auger depth profiles described below.

(b) Radiation-enhanced diffusion during sputter-depth profiling.

Earlier studies in this laboratory have shown that ion bombardment of Ag/Ni multilayer thin-film structures similar to those used in the present experiments lead to a segregation of Ag at the same surface. This phenomenon was explained by assuming that radiation-enhanced diffusion (RED) was responsible for the Ag transport. This process has now been investigated in more detail by sputtering through all Ag and Ni layers and by describing all peaks in the Ag Auger depth profiles in terms of a distortion of the initially ideal step-like concentration profile. Such Ag-layer profiles become Gaussian-like as a result of surface roughening and are made asymmetric by the RED. The equation describing this modified Ag profile is:

$$c = \frac{c_o}{(4Dt+\Delta z_R^2/2)^{1/2}} \exp\left[-\frac{(St-z_o)^2}{4Dt+\Delta z_R^2/2}\right]$$

where c is the Ag concentration, t is the diffusion time, D is the RED rate, S is the sputtering rate, c_o is a constant depending on the Ag layer thickness, Δz_R is the RMS surface roughness, and z_o is the propagation range of the sputter-induced defects.

A computer program has been developed for fitting the above equation to the experimental data. One example of such a fit is shown in Fig. 2.5. The fit is excellent, and both diffusion rate and roughness data can be easily obtained. The same approach seems to be useful for the interpretation of oxygen depth profiles in Cr/Cr_2O_3 multilayers (see section 2.B.1).

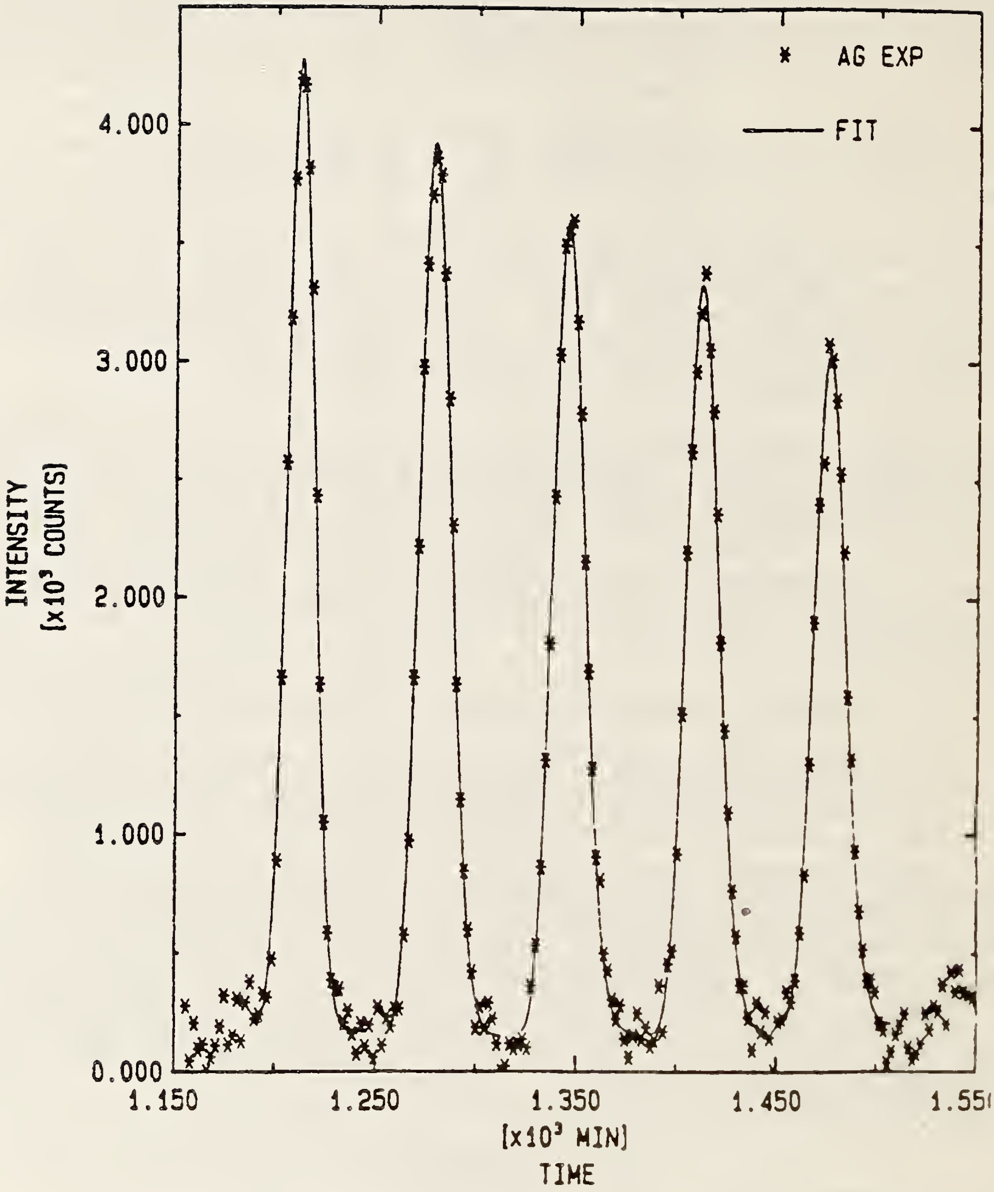


Fig. 2.5 Plot of the Ag Auger-electron signal as a function of sputtering time for an Ag/Ni multilayer thin-film structure consisting of five Ag and six Ni layers on a Si substrate. The points are the experimental intensity measurements and the line is the fit based on the equation given in Section 2.B.2(b).

RED rates have been determined for 1 keV argon ions as a function of current density. It was expected that at low current densities of the ion beam, the sputtering rate would be smaller, the diffusion process would take longer time, and thus wider interfaces would be obtained. This is correct, but the RED rates also decrease for smaller current densities, presumably because of the partial recombination (healing) of the radiation-induced defects. This process decreases the number of defects which then reduces the RED rates. If this process of defect healing is assumed to be exponential, a lifetime or about 250 minutes is obtained. For high sputtering rates, D is found to be 4×10^{-17} cm^2/s for 1 keV ions and around 1×10^{-15} cm^2/s for 4 keV ions. These values for the RED rate are very much larger (by orders of magnitude) than the normal diffusion coefficients for similar systems. The values are strongly dependent on ion energy and therefore appear to be related to defects (probably point defects) caused by the ion bombardment.

These studies of interface layer broadening are to be completed in the next year by obtaining more detailed information on the dependence of these phenomena on the energy of the incident ions. Another important aspect concerns the Ni/Cr standard reference material (see section 2.B.1). Both roughness effects and RED may be applicable to this system; in particular, RED may explain the asymmetry observed in Auger depth profiles of the Ni/Cr multilayers. A rather extensive set of interface measurements obtained on Ni/Cr multilayered structures is now being analyzed to determine the dependence of interface width and asymmetry on the ion bombardment energy and current density as a function of sputtered depth.

C. Review Articles and Books

1. Review Articles

The Division Staff authors 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.

Division staff members have authored 23 review articles recently. The titles and abstracts of review articles published since 1985 are listed below:

(a) "The Thermal Desorption of Adsorbed Species," J. T. Yates, in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds. (Academic Press, N.Y.), 425 (1985).

The experimental and theoretical basis of thermal desorption spectroscopy as a tool for surface characterization is described. Methods of analysis of thermal desorption spectra to obtain kinetic information (desorption energies, desorption order, coverages of adsorbed species) are included, together with numerous examples of desorption on small molecules from single-crystal metal surfaces.

(b) "Experimental Methods in Electron and Photon Stimulated Desorption," T. E. Madey and R. Stockbauer, in Methods of Experimental Physics, Vol. 22, Solid State Physics: Surfaces, R. L. Park and M. G. Lagally, eds. (Academic Press, N.Y.), 465 (1985).

We review experimental techniques and applications of electron stimulated desorption (ESD) and photon stimulated desorption (PSD) of atomic, molecular, and ionic species from surfaces. The physical principles of these methods, as well as details of experimental measurements and data analysis are discussed. We close with a discussion of beam damage in surface analysis.

(c) "Innershell Ionization Cross Sections," C. J. Powell in Electron Impact Ionization, T. D. Märk and G. H. Dunn, eds. (Springer-Verlag, N.Y., 198 (1985).

A review is presented of cross sections for the ionization of inner-shell electrons by electron impact. Calculations, measurements, and empirical formulas are described and compared. Recommendations are given for the selection of cross-section data. Finally, applications of inner-shell ionization cross-section data to materials and surface analysis problems are described.

(d) "The Coordinated Development of Standards for Surface Chemical Analysis", M. P. Seah and C. J. Powell, NBS Internal Report NBSIR 85-3120 (March, 1985).

This report is based on a proposal to the Steering Committee of the Versailles Project on Advanced Materials and Standards (VAMAS) for the coordinated development amongst the VAMAS member states of standards for surface chemical analysis. VAMAS was established following a meeting of the Heads of State or government at Versailles, France in 1982 that agreed on a number of projects relating to technology, growth, and employment. Specifically, VAMAS was organized to promote international coordination in the development of standards in a wide range of advanced material sectors. Surface chemical analysis was approved as a VAMAS Technical Working Area in June, 1984.

The report describes the growth and diversity of surface analysis in the development of advanced materials in modern technologies and the use of surface analysis for improved films and coatings. The principal techniques of surface analysis in common use are identified and the technical limitations to accurate surface analyses pointed out. Accurate surface analyses require: (i) knowledge of the principles of the measurement method, (ii) knowledge of the behavior of the measuring instrument and the (iii) correct interpretation and expression of the final measured result. Standards for the measurement of surface composition with known accuracy and for the reliable determination of chemical state require: (a) a base of principles, definitions of terms, and suitable equations; (b) reference procedures for the measurement of intensities and spectral features, (c) procedures and data for instrument calibrations, (d) reference data for material parameters such as elemental sensitivity factors, matrix terms, chemical state spectra, ion sputtering rates, etc.; and (e) standard methods for specifying an analysis. Specific needs are identified for the common methods of surface analysis, Auger-electron spectroscopy, x-ray photoelectron spectroscopy, and secondary-ion mass spectroscopy together with needs for ion sputtering which is used to obtain composition versus depth information in films and coatings. Existing standards activities in the member countries of VAMAS are reviewed and suggestions are made for additional standards for surface chemical analysis.

(e) "Surface Harpooning", J. W. Gadzuk, Comments on Atomic and Molecular Physics, 16, 219 (1985)

The principles involved in charge transfer/harpooning collisions between atoms or molecules and surfaces are presented in terms of concepts drawn from gas-phase atomic and molecular collision theory. As specific examples, the charge state of atoms and the vibrational excitation or dissociation of molecules which have experienced harpooning while scattering from a surface are considered.

(f) "The Uses and Limitations of ESDIAD for Determining the Structure of Surface Molecules", T. E. Madey, in The Structure of Surfaces, Springer Series in Surface Science 2, M. A. van Hove and S. Y. Tong, eds. (Springer-Verlag, N.Y.), 264 (1985).

The principles and mechanisms of electron-stimulated desorption (ESD) and photon-stimulated desorption (PSD), as well as the utility of the electron stimulated desorption ion angular distributions (ESDIAD) method as a tool for determining the structure of surface molecules, have been described in a recent book and several review articles. The present short paper is intended to provide a guide to the relevant literature, and to describe briefly some recent work relating to the uses and limitations of ESDIAD for determining the structure of surface molecules.

(g) "Recent Advances Using ESDIAD: Applications to Surface Chemistry", T. E. Madey, C. Benndorf, N. D. Shinn, Z. Miskovic, and J. Vukanic, DIET-II, Desorption Induced by Electronic Transitions, Springer Series in Surface Science 4, W. Brenig and D. Menzel, eds. (Springer-Verlag, N.Y.,), 104 (1985).

Recent applications of ESDIAD (electron stimulated desorption ion angular distributions) to surface chemistry are described. Examples include the influence of catalytic promoters and poisons on surface structure and reactivity, the evidence for a new structural form for adsorbed H_2O (i.e., H_2O dimers on Ni(110)), and the characterization of a new bonding mode for CO on Cr(110). Calculations of the perturbing influence of image force and reneutralization effects in ESDIAD are described.

(h) "Recent Developments in Quantitative Surface Analysis by Electron Spectroscopy", C. J. Powell, J. Vac. Sci. Tech. A 4, 1532 (1986)

An overview is given of recent developments in quantitative surface analysis by x-ray photoelectron spectroscopy and Auger-electron spectroscopy. The two major tasks of an analysis are the identification of the surface phases that are present and the determination of the concentrations of particular elements or compounds. Methods for accomplishing both tasks will be described together with the pitfalls and problems that remain. Particular attention is given to the following topics: identification of surface phases and reference data for the calibration of instrumental energy scales; reference data on inelastic mean free paths and attenuation lengths; effects of specimen crystallinity; intensity measurements; measurement of the imaging properties of electron energy analyzers; and the intensity-energy response functions of different instruments.

(i) "Surface Chemical Analysis - Report on the VAMAS Project", C. J. Powell and M. P. Seah, Surf. Interface Anal. 9, 79 (1986)

The VAMAS project on surface chemical analysis is a multi-national cooperation for the provision of standards data and materials for surface chemical analysis measurement and for the provision of the basic understanding necessary for these activities. This project is one of a rapidly growing suite of projects initiated as a result of decisions following the 1982 Versailles Summit Meeting of the Heads of State or Government of Canada, France, Germany, Italy, Japan, UK, USA and the Representatives of the Commission of the European Community. During the past year national representatives to this VAMAS project have been appointed and national committees established. This article summarizes the philosophy, scope, and organization of the project and describes specific activities that have been initiated. Information is given on how individuals, both within and outside the group of member states, may participate.

(j) "Dynamics of Molecular Processes at Surfaces: Vibrational Lineshapes and Spectra", J W. Gadzuk, J. Electron Spectroscopy 38 233 (1986).

Extremely useful connections exist between the dynamics of adsorbed molecule vibrations, as revealed in spectroscopic lineshapes, and the dynamics of molecular processes at surfaces because in both cases, the constituent atoms of a molecule, solid, or combination of the two execute multi-dimensional motion over the same potential energy surfaces, undoubtedly sampling different regions of it.

In this paper, recent insights and advances in surface dynamics will be applied to the problem of vibrational lineshapes. Classical particle and semi-classical wavepacket dynamics will be used to address the issues of energy decay (T_1) vs. pure dephasing ($T_2{}'$) overtones, and non-linear dynamics as they apply to lineshape analysis.

(k) "Electron Stimulated Desorption and its Relation to Molecular Structure at Surfaces", T. E. Madey, J. Vac. Sci. Tech. A 4, 257 (1986).

Recent examples of the use of electron stimulated desorption ion angular distributions (ESDIAD) in determining the structures of molecules on surfaces are discussed. These include the adsorption and decomposition of NH_3 on Fe(100), and the stabilization of H_2O on Ag(110) by impurity O and Br atoms. ESDIAD evidence for "lying down" CO on several surfaces is presented, and the influence of beam damage in producing new surface structures for H_2O on Ni(100) is discussed. Calculations of the influence of the surface image potential and reneutralization effects on ion trajectories are described briefly.

2. Review Articles in Publication

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

(a) "The Chemisorption of Carbon Monoxide by the Transition Metals", J. T. Yates, Jr., T. E. Madey, and J. C. Campuszano, The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis", D. A. King and D. P. Woodruff, eds. (Elsevier, N.Y.)

A comprehensive review of the adsorption of carbon monoxide by transition and noble metals is presented. The systematics of CO adsorption and dissociation are discussed, along with detailed examinations of the surface structures, electronic and vibrational spectra, and kinetic behavior of adsorbed CO.

(b) "Final-State Resolved Studies of Molecule-Surface Interactions", D. S. King and R. R. Cavanagh in New Laser and Optical Investigations of Chemistry and Structures at Interfaces, (Verlag Chemie)

Quantum state-specific diagnostics as applied to surface dynamics are discussed. The NO molecule is used as an illustration of the experimental determination of gas-surface interactions. Topics reviewed included beam-surface scattering, thermal desorption, vibrational accommodation, Doppler profiles, and Fourier-transform infrared emission spectroscopy.

(c) "Core-Level Binding-Energy Shifts in Solids at Surfaces", W. F. Egelhoff, Jr., Surface Sci. Reports.

This review presents an overview of the theory and of various successful approaches to the interpretation of core-level binding-energy shifts observed in photoelectron spectroscopy. The theoretical background is presented at a level readily accessible to the general reader. Particular attention is paid to the relative merits of two basically different conceptual frameworks for interpreting core-level binding-energy shifts, the initial-state--final-state approach and the equivalent-core Born-Haber cycle approach.

(d) "Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces", J. W. Gadzuk, in Vibrational Spectroscopy of Molecules on Surfaces, J. T. Yates, Jr., and T. E. Madey, eds., Vol. 1 of Methods of Surface Characterization (Plenum, N.Y.).

An introduction to the theoretical basis of vibrational excitation mechanisms and processes relevant to vibrational spectroscopy of adsorbed molecules is presented.

(e) "Neutron Inelastic Scattering: Vibrational Spectroscopy of Adsorbed Molecules on Surfaces:, R. R. Cavanagh, J. J. Rush, and R. D. Kelley, in Vibrational Spectroscopy of Molecules on Surfaces, J. T. Yates, Jr., and T. E. Madey, eds., Vol. 1 of Methods of Surface Characterization (Plenum, N. Y.).

An introduction to neutron scattering as a probe of adsorbates at surfaces is presented. Emphasis is placed on experimental aspects of triple-axis and time-of-flight techniques along with a single-phonon model for the spectral features. Wilson FG methods for constructing molecular force fields relevant to the molecular modes of the adsorbate are presented. The applicability of neutron scattering for exploring rotational diffusion and adsorbate torsions is also examined.

(f) "Field Emission Microscopy - Trends and Perspectives", A. J. Melmed, Chemistry and Physics of Solid Surfaces VI, Springer-Verlag

The author's view of the role of surface microscopies, in particular the field emission microscopies, is given. Brief outlines of the historical development and nature of field-electron emission microscopy (FEEM) and field-ion microscopy (FIM) are given and selected examples are presented to illustrate the scope of research in FEEM and FIM. Research trends are described and some projections for the future are made.

(g) "Electron and Photon Stimulated Desorption: Probes of Structure and Bonding at Surfaces", T. E. Madey, Science

Techniques for analyzing the structure and composition of solid surfaces using electron and photon beams often suffer from difficulties due to radiation damage. Damage-producing processes compete with information-producing events during measurements, and beam damage can be a serious perturbation in quantitative surface analysis. However, there are also substantial benefits of electron and photon stimulated damage processes for studying molecules adsorbed on surfaces. Direct information about the geometrical structure of surface molecules can be obtained from measurements of the angular distributions of ions released by electron- or photon-stimulated desorption. The directions of ion emission are determined by the orientation of the surface bonds which are ruptured by beam irradiation. Moreover, photon-stimulated desorption studies using synchrotron radiation are revealing the fundamental electronic excitations which lead to bond-breaking processes at surfaces. These measurements are providing new insights into radiation-damage processes in areas as diverse as x-ray optics and semiconductor electronics.

(n) "Mechanisms and Applications of Electron Stimulated Desorption in Surface Science", T. E. Madey, Vacuum (TAIP)

The principles and mechanisms of electron-stimulated desorption and the utility of the electron-stimulated desorption ion angular distributions (ESDIAD) method as a tool for determining the structure of surface molecules have been described in several recent books and review articles. The present article is intended to provide a guide to the relevant literature, and to outline briefly some recent work relating to the uses of ESDIAD for determining the structure of surface molecules.

(i) "The Interaction of Water with Solid Surfaces", P. A. Thiel and T. T. Madey, Surface Sci. Reports

The purpose of this review is to compare and discuss recent experimental and theoretical results in the field of H_2O-solid interactions. Emphasis is placed upon adsorption studies performed on well-characterized, single-crystal surfaces of metals, semiconductors and oxides. We discuss the factors which influence dissociative vs. associative adsorption pathways. When H_2O adsorbs molecularly, it tends to form three-dimensional hydrogen-bonded clusters, even at fractional-monolayer coverages, because the strength of the attractive interaction between the two molecules is comparable to that of the substrate-H_2O bond. The template effect of the substrate is important in determining both the local and long-range order of H_2O molecules in these clusters. The influence of surface additive atoms (e.g., O, Br, Na, K) on the surface structure and chemistry of H_2O is examined in detail. Results on single crystal substrates are compared with earlier available measurements of H_2O adsorption on high-area materials.

(j) "Core Level Spectroscopy: A Dynamics Perspective", J. W. Gadzuk, Physica Scripta

Various aspects of the dynamics of time-dependent localized potentials and interactions in solids and at surfaces, as they might relate to the fundamental screening and relaxation processes involved in core-level spectroscopies, are explored.

(k) "Dynamics of Molecular Collisions with Surfaces: Excitation, Dissociation, and Diffraction", S. Holloway, M. Karikorpi, and J. W. Gadzuk, Nuclear Instruments and Methods B

Aspects of molecular collisions are discussed which are important in the chemically relevant energy range of ~ 1-10 eV. In particular, the role of charge transfer, potential-energy-surface topology, and intra-molecular ground- and excited-state potential curves are investigated as they pertain to internal vibrational excitation, dissociative adsorption or scattering, and diffractive scattering. The modeling and analysis are based on classical trajectories and semi-classical wavepacket dynamics, both for intra-molecular and translational motion.

(1) "Neutron Scattering Studies of Hydrogen in Catalysts", in Hydrogen in Catalysis: Theoretical and Practical Aspects, Z. Paal and P. G. Menon, eds. (Marcel Dekker, N.Y.).

Neutron scattering studies of hydrogen in catalysis are reviewed. Techniques applicable to catalysis studies (incoherent inelastic neutron scattering (IINS), quasielastic neutron scattering (QNS), and powder neutron diffraction) are introduced. Selected examples are presented with an emphasis on illustrating the utility of these neutron scattering techniques for probing the vibrational, diffusive, chemical, and structural behavior of hydrogen on catalyst surfaces.

3. Books

(S. M. Girvin, C. J. Powell, and T. E. Madey)

Division staff have been active on two book projects during the past year.

(a) The Quantum Hall Effect

The quantum Hall effect is among the most important discoveries in condensed-matter physics in recent years. There has been a great deal of experimental and theoretical activity in the area since its discovery in 1980 by Klaus von Klitzing. Professor von Klitzing received the 1985 Nobel Prize in Physics in recognition of the importance of this phenomenon. While the original experimental discoveries of the integer and fractional effects were quite surprising and unexpected, recent theoretical progress has led to a fairly well-established standard picture of the physical basis of the effects and the field has reached at least the preliminary stages of maturity. However to date, there have not appeared any extensive review articles on the subject. To remedy this, S. M. Girvin in collaboration with Prof. R. E. Prange of the University of Maryland organized a ten-part lecture series on the quantum Hall effect. The lectures were held at the University of Maryland during the 1985 Fall semester. The attendance was extremely gratifying, averaging 70-75 people for the introductory portions and 35 for the last few advanced lectures. In addition to students and faculty members from the University of Maryland, the audience contained people from other local universities and from area industrial and government laboratories. After extensive editing of the notes, we are publishing a book based on these lectures through Springer-Verlag, New York. This will be the first major review of the field to be published and we anticipate that it will be well received. We have already received a request for permission to translate the book into Russian for publication through Mir, Moscow.

(b) Methods of Surface Characterization

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.

Two volumes of the book series will describe the techniques and methods for electron spectroscopy and ion spectroscopy, respectively, which are in widespread use for surface analysis. These volumes will be concerned largely with techniques for which commercial instrumentation is available. Writing for both volumes is close to completion.

A third volume will describe techniques for specimen handling and depth profiling. For specimen handling and treatment, this volume will provide a compilation of methods that have been proven useful. This volume will also address the common artifacts and problems associated with the bombardment of solid surfaces by electrons and ions. Finally, a description will be given of methods for depth profiling. It is hoped that writing for this volume will be completed in 1987.

A fourth volume brings together a description of methods for vibrational spectroscopy of molecules on surfaces. Most of the techniques are currently under active development; commercial instrumentation is available for some techniques but this situation could change in the next few years. Writing of this volume has been completed and manuscripts sent to the publisher.

D. Standards-Committee Activities

Three staff members of the Division hold offices on two ASTM Committees, the E-42 Committee on Surface Analysis and the D-32 Committee on Catalysts, and on the recently established Surface Chemical Analysis Working Party organized under the auspices of the Versailles Project on Advanced Materials and Standards. Participation in the activities of these groups provides an opportunity for leadership, for dissemination of NBS expertise, and to learn of significant measurement problems in relevant areas.

1. ASTM Committee E-42 on Surface Analysis

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

The ASTM Committee E-42 on Surface Analysis, founded in 1976, now has some 120 members; in addition, a larger number of non-members, both within the U.S. and throughout the world, participate in Committee activities. The purpose of the Committee is to advance the field of surface analysis and the quality of surface analyses through the development of appropriate standards, standard practices, reference data, reference materials, round robins, symposia, workshops, and publications.

During the past year, we have drafted a proposed Standard Practice for Determination of the Specimen Area Contributing to the Detected Signal in Photoelectron Spectroscopy and Auger-Electron Spectroscopy for consideration by the ASTM E-42 Committee. This practice describes methods for determining the active specimen area for different conditions of instrument operation, for verifying adequate specimen alignment, and for characterizing the imaging properties of the electron energy analyzer. The practice is restricted to instruments in which the specimen is excited by x-ray or electron beams with widths at the specimen much larger than the specimen dimensions viewed by the analyzer. This draft standard is based in part on recent work at NBS in which extensive measurements were made of the imaging properties of a double-pass cylindrical-mirror analyzer for various operating conditions. The XPS and Auger Subcommittees of the E-42 Committee are currently balloting the proposed standard.

Committee activities of the past year have included development of the following documentary standards (which are at varying stages of review and approval):

- Additional definitions of terms for AES, XPS, SIMS, and Energetic Ion Analysis
- Guide to Depth Profiling in Auger Electron Spectroscopy
- Practice for Reporting Spectra in XPS
- Method for Calculating Data-Gathering Speed in XPS
- Guide to Steady-State Charge-Referencing Techniques in XPS
- Practice for Reporting Sputter Depth Profile Data in SIMS (secondary-ion mass spectroscopy)
- Guide for Specification of Ion Beams for Use in Surface Analysis
- Procedure for Sample Positioning with Cylindrical Mirror Analyzers in ISS (ion-scattering spectroscopy)
- Procedure for Approximate Energy Scale Calibration with Cylindrical Mirror Analyzers Used in ISS
- Proposed Guide for Data Reporting in ISS
- Proposed Guide for the Measurement of X-ray Flux in XPS Instruments
- Proposed Guide for Establishment of Data Bases in Surface Spectroscopies

An E-42 round robin to compare depth-profile measurements of ^{11}B in Si by secondary-ion mass spectroscopy is being concluded. The study was designed to allow participants to compare the accuracy of analysis, background signal levels, detection limits, and artifacts of their instruments and methods. Each participant received three implanted specimens, a standard implanted to a peak concentration of $2.0x10^{20}$ atoms/cm^3 and two other specimens implanted with different, but unreported, concentrations of ^{11}B. Each participant was asked to determine the concentration of ^{11}B in the two unknown specimens. The results determined by 12 participants using 6 different instrument types showed very good agreement. One specimen implanted to $5.0x10^{20}$atoms/cm^3 was determined to have a peak concentration of $4.9x10^{20} \pm 0.3x10^{20}$ atoms/cm^3; and the other specimen implanted to $3.0x10^{19}$ atoms/cm^3 was determined to have $3.4x10^{19} \pm 0.6x10^{19}$ atoms/cm^3. These and other results including values for the dynamic range, detection limit, and sputtering yield of Si for each instrument type will be tabulated in a paper being prepared for publication.

The Committee has prepared a booklet of E-42 surface analysis standards which is about to be published by ASTM. It is believed that many users of surface-analysis equipment will find the booklet to be a convenient compilation of terminology, guides, and recommended practices. The booklet will be updated roughly every two years and should be an effective means of disseminating E-42 standards. Arrangements have also been concluded during the year by which E-42 standards will be republished in the journal "Surface and Interface Analysis" on a timely basis.

The Committee arranges a half-day symposium at the annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy in the spring. The Committee had also been active through 1985 in arranging sessions at the National Symposium of the American Vacuum Society in the fall but this responsibility will now be taken by the newly formed Applied Surface Science Division of the AVS. The E-42 Committee arranges evening workshops at these meetings to discuss common measurement problems. The topic at the 1985 AVS Symposium was "Analysis of Buried Solid-Solid Interfaces".

2. Surface Chemical Analysis Working Party of the Versailles Project on Advanced Materials and Standards (VAMAS)

(C. J. Powell)

The "Versailles Agreement" arose from a meeting of the Heads of State or Government (Economic Summit) of industrialized nations at Versailles in 1982. The participants represented Canada, the Federal Republic of Germany, France, Italy, Japan, the United Kingdom, the United States of America, and the Commission of the European Communities (CEC). A Summit Working Group on Technology, Growth, and Employment was established consisting of government science advisers. This group established international committees in eighteen areas such as photovoltaic solar energy, food technology, advanced robotics, biotechnology, high speed trains, remote sensing from space, and advanced materials and standards.

The Versailles Project on Advanced Materials and Standards (VAMAS) consists of a Steering Committee with representatives from the seven nations above and the CEC. VAMAS supports international trade through projects aimed at providing the technical basis for drafting Codes of Practice and Specifications in Advanced Materials. The scope of the collaboration embraces all agreed aspects of enabling science and technology--data bases, test methods, design methods, materials technology--which are required as a precursor to the drafting of standards in advanced materials. VAMAS activity emphasizes collaboration on prestandards measurement research, intercomparison of test results, and consolidation of existing views on priorities for standardization action. Through this activity, VAMAS fosters the develpment of internationally acceptable standards for advanced materials by the various existing standards agencies.

The overview of VAMAS and the other international committees was concluded recently at the Tokyo meeting of Heads of State. VAMAS will, however, continue as an independent international collaboration through a VAMAS Memorandum of Understanding now being signed by the founding governments.

The Surface Chemical Analysis (SCA) Working Party of VAMAS is one of twelve such groups that have been approved to date. The main objective of the SCA working party is to produce, by coordinated effort, the reference procedures, data, and materials necessary to establish standards for surface chemical analysis. This effort is expected to lead to the international coordination of standards-related activities before national standards are adopted and to the development of standards on an international level.

The SCA Working Party was approved by the VAMAS Steering Committee in June, 1984. National representatives to the SCA Working Party have been appointed with C. J. Powell as Chairman for a three-year period. The most urgent needs for surface analysis pertain to the use of Auger-electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), secondary-ion mass spectroscopy (SIMS) and sputter-depth profiling (SDP). As projects in these areas become established and as other techniques come into greater use, it is expected that the project will broaden. The general requirements are as follows:

- an agreed based of principles, definitions of terms, and equations to relate the techniques and procedures to the measurement;
- reference procedures specifying how to measure intensities and spectral features;
- reference procedures, reference data, and reference materials for calibrating instruments, determining instruments functions, and inter-relating instruments of different designs;

- reference data of elemental sensitivity factors, matrix terms, information depths, libraries of chemical-state spectra, information on ion-sputtering rates, radiation damage, etc.; and

- standard methods of specifying an analysis.

Details of standard needs for AES, XPS, SIMS, and SDP have been identified.

Suitable infrastructures have been developed in most VAMAS states for the SCA project. In the U.S., the ASTM Committee E-42 on Surface Analysis has agreed to participate and cooperate in VAMAS SCA projects. Standards already developed by the E-42 Committee will be disseminated to the other VAMAS states; standards developed later in the other states will be considered for adoption by the E-42 Committee. Suitable projects at NBS and other U.S. laboratories also contribute to the VAMAS SCA activity.

The first meeting of the SCA Working Party national representatives took place in October, 1985 during a conference in The Netherlands. Three international projects were approved at that time and their current status is as follows:

- Development of thin oxide films as reference materials. Work is nearing completion between laboratories in the UK, France, Canada, and Belgium to define the accuracies of different methods for determining the atomic thickness of a tantalum pentoxide on tantalum material developed earlier in the UK. The material is available with two oxide thicknesses and will be useful as standards for calibrating ion-beam fluxes in sputtering experiments and in high-energy ion-beam reaction and scattering experiments.

- Development of calibration data for the energy scales of Auger-electron spectrometers. Traceable calibrations have been established in the UK for Cu, Ag, and Au Auger peaks with an accuracy of ± 0.02 eV. Similar but independent measurements are nearing completion in the USA (at NBS).

- Procedures for quantitative x-ray photoelectron spectroscopy. Test materials prepared in Canada and Germany have been identified as candidates for a proposed round robin to give information on measurements of film thickness and film stoichiometry. A round robin will be designed following test measurements in the USA.

A number of additional international projects have recently been proposed and are currently under review by the national representatives. These projects are listed below together with the countries expected to be interested in participation.

- Correction Methods for Backscattering in Auger-Electron Spectroscopy (FRG, France, Italy, Japan, UK, USA)

- Measurement of Spatial Resolution in Auger-Electron Spectroscopy (Canada, France, UK, USA)
- Tests of Algorithms and Software for Data Processing (Canada, FRG, France, Italy, Japan, UK, USA, CEC)
- Tests of Channeling Effects in Auger-Electron Spectroscopy (Canada, FRG, France, UK, USA, CEC)
- Reference Data for Electron Attenuation Lengths and Inelastic Mean Free Paths (UK, USA)
- Development of Reference Materials Prepared by Ion Implantation (FRG, Italy, UK); this project could be carried out in collaboration with IUPAC Working Group on Surface Analysis
- Development of Reference Materials for the Measurement of Depth Resolution in Depth-Profile Analysis (Canada, FRG, UK, USA)
- Development of Methods for Instrument Alignment and Calibration (Canada, France, Italy, Japan, UK, USA)
- Development of Reference Materials for the Surface Analysis of Polymers (Italy, USA)
- Reference Data for Ion Sputtering Rates in Oxides (FRG, UK, USA)
- Intercomparison to Assess the Reproducibility of Preferential Sputtering in Surface Analysis (UK, CEC)
- Intercomparison to Assess the Reproducibility of Auger-Electron Energy and Intensity Measurements (UK, CEC)
- Multitechnique Characterization of Vacancies in Alumina (France)
- Evaluation of Sensitivity Factors for Secondary-Ion Mass Spectroscopy (Canada, UK, USA)

It is expected that some of these topics will be initiated following discussion at a meeting of the national representatives scheduled for London on November 17, 1986.

The organization of the SCA Working Party has stimulated the initiation of new national activities related to and supportive of the Working Party objectives. Information on these activities is exchanged twice a year and it is anticipated that a number of these will lead naturally to new multilateral activities. Some examples of projects of this type are:

- Development of a standard data transfer format. Initial work has been done in the UK and a draft should be ready for Working Party consideration shortly.
- Calibration of the intensity scale of Auger-electron spectrometers. Methodology is under development in the UK (with CEC support) and it is expected that interlaboratory tests will be conducted in member states next year.
- Development of reference materials by ion implantation. Some research materials have been prepared in the UK and there is interest in calibrating these and other implanted materials in FRG and other countries.

The VAMAS SCA Working Party has aroused a considerable amount of interest and enthusiasm in many of the VAMAS states. Many scientists believe that VAMAS has already provided and will continue to provide a considerable stimulus to the development of standards for surface chemical analysis in each state. Furthermore, through cooperation via VAMAS, national standards will be developed more efficiently and, it is hoped, without conflicts. The specific areas where international cooperation through VAMAS will be most effective are believed to be: (1) the development of data banks and preferred data formats; (2) the development of reference materials; (3) the development of documentary standards for instrument operation and calibration; and (4) the development of recommended procedures for data acquisition, data reduction, and expression of final results.

3. Workshops on Quantitative Surface Analysis

(C.J. Powell)

Two Workshops on Quantitative Surface Analysis will be held in the autumn of 1986. The first Workshop will be held at NBS on October 24 and is co-sponsored by the ASTM Committee E-42 on Surface Analysis, the Surface Chemical Analysis (SCA) Working Party of the Versailles Project on Advanced Materials and Standards (VAMAS), the Applied Surface Science Division of the American Vacuum Society, and NBS (Surface Science Division, Office of Standard Reference Data, and Office of Standard Reference Materials). The second workshop will be held at the National Physical Laboratory (NPL) in London on November 17 and is co-sponsored by NPL and the VAMAS SCA Working Party. Each workshop will precede a major international meeting and will have discussions on reference data, reference materials, reference procedures, and instrument calibration in surface analysis. In a workshop format with ample time for audience participation, it is hoped that recent advances in these areas will become better known, important problem areas and possible solutions will be identified, and opportunities for new national and international (VAMAS) projects will become apparent.

4. ASTM Committee D-32 on Catalysts
(R. A. Haines and R. D. Kelley)

The activities of the ASTM Committee D-32 on Catalysts are concerned with the physical and chemical properties of commercial catalysts and with developing suitable procedures for catalytic activity measurements. The membership of the Committee numbers approximately 130 representatives of the major producers and users of catalysts including a significant international component. The technical activities are carried out in four sub-committees: Physical/Chemical Properties which has 6 task groups; Physical/Mechanical Properties - 6 task groups; Chemical Analysis - 2 task groups; Catalytic Properties - 5 task groups. In general, the work of the Committee has moved into areas that involve complex and often controversial measurements. Examples of these are the measurement of catalyst acidity, of the sensitivity of cracking catalysts to metallic impurities, and of multi-element chemical analysis by atomic absorption.

The Subcommittee on Chemical Analysis is chaired by R. D. Kelley. The precious metals task group continues to be involved with the Standard Test Method for platinum in reforming catalysts which has been submitted for a Main Committee ballot--the final step in establishing a standard. This platinum standard has involved eleven draft procedures, many round-robin analyses and about ten years of effort. An analytical method for palladium--Standard Test Method for Palladium in Molecular Sieve Catalysts--has also been submitted for Main Committee ballot. The palladium procedure is interesting in that it has involved two negative votes on the subcommittee level and at least one on the Main Committee ballot. All of these negative votes are concerned with the fact that commercial contracts call for greater accuracy than has been possible in the several round-robin tests conducted with the participation of a large number of companies. This issue will continue to enliven future task group meetings. The base metals task group is proceding with the development of a satisfactory test method for determining several base metals by optical atomic spectroscopy.

The Office of Standard Reference Materials (OSRM) is finalizing an agreement with ASTM Committee D-32 to distribute catalyst reference materials. R. A. Haines serves as a liaison between the two groups. The Committee has preserved the catalysts, catalyst carriers and feed stocks used in their round robins. The 1986-1987 SRM catalog already lists three high-surface-area powders for which the Committee has extensive round robin data using a static BET technique. Material is at NBS awaiting packaging which has been characterized for particle-size distribution and reactivity via gas-oil conversion microactivity tests. A series of zeolites is also available for which diffraction intensity, unit cell dimensions and zeolite areas have been determined. Other materials for which the Committee has data include supported metal catalysts (metal content) and formed catalysts (crush strength). Demand for these materials, once available, will be used as a guide for NBS catalyst standards work.

3. SURFACE MEASUREMENTS PROGRAM

D. R. Burgess, Jr., R. R. Cavanagh, H.-H. Chen, N. E. Erickson,
J.W. Gadzuk, T. J. Jach, A. L. Johnson, R. D. Kelley, R. L. Kurtz,
C. V. S. Larsson, T. E. Madey, J. M. Nicol, C. J. Powell,
D. E. Ramaker, N. D. Shinn, R. Stockbauer and P. D. Szuromi

A. Reaction Kinetics at High Pressures over Single-Crystal Catalysts (P.D. Szuromi, R. D. Kelley, 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 of the Department of Energy.

Progress during the last year included studies of the hydrogenation activity of single-crystal W catalysts, as well as the poisoning effect of adsorbed sulfur and oxygen on the W substrates. A surprising result involved the poisoning of W by S. In contrast to the poisoning of Ni by S, where a long-range interaction was observed, there is an apparent short range effect of S on W(110). Details are given below.

1. Sulfur Inhibition of Methanation Over W(110)

Sulfur inhibition of methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$) over an active W(110) catalyst has been studied. Reaction rates were measured for realistic conditions ($P = 100$ Torr, $H_2/CO = 100$, 600-750K), while sulfur coverages (θ_S) and carbon and oxygen coverages on the working catalyst were determined by Auger-electron spectroscopy (AES). This work demonstrated that: (1) E_a is not changed by sulfur; (2) For $\theta_S \cong 0.22$ (approximately saturation of the S p(2x2) structure), the rate decreases fourfold, and at higher θ_S decreases slowly by site blocking; (3) Sulfur has almost no effect on postreaction carbon ($\cong 0.3$ ML), but oxygen coverages decrease from $\cong 0.4$ ML at $\theta_S = 0$ to $\cong 0.05$ ML at $\theta_S = 0.4$; (4) Below $\theta_S \cong 0.07$ inhibition is strong ($\cong 40\%$ at $\theta_S = 0.05$) and the effect appears long-range, but at higher θ_S it is weaker and the effect appears short-range. In contrast, earlier work in this laboratory showed that long-range effects dominate for all θ_S for methanation over Ni. Model thermal desorption studies of the decrease in saturation coverages of β-CO and H_2 at 90 K due to sulfur show good agreement with decreases in the methanation rate for $\theta_S \geq 0.22$, but below this θ_S the coverages drop linearly, as for a short-range effect. However, addition of coadsorbed oxygen (0.05-0.10 ML, the average oxygen coverage in excess of carbon for the working catalyst at these values of θ_S) caused β-CO and H_2 coverages to decrease in the same way as the methanation rate, i.e., negative deviations from linearity. Long-range effects of sulfur are seen when oxygen disrupts sulfur clustering. Thus deactivation of methanation by sulfur over W(110) is interpreted in terms of oxygen-induced changes in sulfur cluster formation.

2. Effect of Oxygen on Methanation Over Tungsten

Experiments were performed in which oxygen was added deliberately to the H_2+CO reactant mixture in trace quantities (10^{-4} to 10^{-1} Torr at total pressures of 100 Torr). Addition of 10^{-2} Torr of oxygen caused the disappearance of methanation activity even at 700 K. Auger analysis after reaction demonstrated that surface oxidation had taken place. This resembles the inactvity of classical tungsten catalysts toward methanation, which is due to difficulties in fully reducing the tungsten. The inactivity of the oxidized surface in these studies also shows that the reactor has a low blank activity.

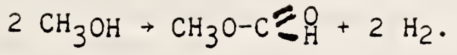
3. Modifications to the Experimental System

Modifications to the sample manipulator used for the near-ambient pressure studies have been completed that will allow low-energy electron diffraction and thermal desorption spectrometry to be used in conjunction with existing capabilities for Auger and ultraviolet photoemission spectroscopies. This manipulator is currently being installed and tested. Also, an x-ray source has become available for our use that will add the capability for x-ray photoelectron spectroscopy (XPS).

During next year, we will expand the scope of our program to different types of reactions (dehydrogenation and partial oxidation) and catalysts (transition metal oxides grown over metals). Such reactions and catalysts are of interest currently for synthesis of important chemical intermediates. Our overall goal remains the same - to understand more clearly fundamental processes in heterogeneous catalysis by: (1) preparing catalysts with well-defined surfaces; (2) studying reaction kinetics under realistic conditions of pressure and temperature; and (3) employing ultra-high vacuum surface science techniques for *in situ* characterization of working catalysts.

Initially, the studies will focus on reactions over copper-based catalysts, for several reasons. Several classes of reactions are catalyzed by copper-based catalysts, so a number of avenues are possible, including rections over metallic copper, copper oxides, and mixed-metal oxide catalysts (examples include methanol synthesis from syngas over copper-zinc oxide catalysts and from methane over copper-molybdenum oxide). In addition, many surface science studies have been conducted for the adsorption of organic molecules on copper surfaces. This body of work will be employed in interpreting our results.

These studies will proceed in two phases. The initial work (during the next year) will focus on the dehydrogenation of methanol to methyl formate over copper. The second phase will concentrate on partial oxidation reactions over cuprous oxide, in this case acrolein synthesis from propylene. Methyl formate synthesis occurs catalytically over copper as



$$2\ CH_3OH \rightarrow CH_3O\text{-}C\begin{smallmatrix} = O \\ - H \end{smallmatrix} + 2\ H_2.$$

Methyl formate has the potential of becoming an important chemical intermediate based on C_1 methanol. Metallic copper is unique in producing both methyl formate and valuable hydrogen using only methanol as a feed. (The other heterogeneous route to methyl formate from methanol involves oxidation and produces water rather than hydrogen as the byproduct.) The Arrhenius and pressure dependence of this reaction over copper will be determined over as wide a range of conditions as possible. The effect of surface geometry on the reaction will be determined by using a Cu(100) crystal in both its well-annealed (cubic close-packed) and sputtered (amorphous) forms, and, for comparison, polycrystalline samples. In addition, the effects of promoters, such as alkali metal oxides, and of inhibitors, which include acidic oxides such as those of Mo and W, will be investigated. The availability of AES and XPS allows the correlation of changes in kinetics with the <u>coverages</u> of such surface modifiers.

Finally, as time and resources permit, other avenues will be explored, including hydrdogenation and hydrogenolysis reactions over model thin-film catalysts (fractional monolayers of metal deposited on crystalline metal or oxide substrates).

B. Molecular Structure and Reactivity on Surfaces as Studied Using ESDIAD AND HREELS

(T. E. Madey, A. L. Johnson, N. D. Shinn, and C. U. S. Larsson)

A continuing challenge in surface science is to determine the structures of molecules on surfaces, particularly in the absence of long-range order. The goals of this project are to provide a <u>direct</u> determination of the structures of adsorbed molecules using the Electron Stimulated Desorption Ion Angular Distribution (ESDIAD) method, and to characterize the structures and reactivity of surface species using High-Resolution Electron Energy Loss Spectroscopy (HREELS). These techniques, both singly and in combination, are powerful tools for surface structural characterization.

The thrusts of this project during the last year were (a) to determine the influence of surface additives (e.g., catalyst promoters and poisons) on the local structure and reactivity of small molecules (CO, NH_3, H_2O) on surfaces, (b) to determine the structures of those molecules on initially-clean surfaces, particularly in controversial cases, and (c) to develop a digital imaging ESDIAD system to improve the measurements of surface molecular structure. This work has been supported, in part, by the Office of Basic Energy Sciences of the Department of Energy.

During the last year, progress has been made in the following areas:

1. Structure of CO on Surfaces of Catalytic Interest: Is it Standing Up, Lying Down, or Inclined?

We have used ESDIAD in combination with HREELS and other surface spectroscopies to study the adsorption of CO on three transition-metal surfaces. In each case, there were indications from our own measurements (as well as from measurements made in other laboratories) that the CO may be strongly inclined or "lying down", rather than the more widely-reported "standing up" configuration. In three cases, CO on Cr(110), CO on Fe(100) and CO on K-dosed Ru(001), it has been found using HREELS that the CO stretching frequencies are abnormally low, in the frequency range 1150 to 1460 cm^{-1}; these stretches are strongly down-shifted from the typical frequency range (~ 1800-2050 cm^{-1}) for CO adsorbed in a standing-up fashion, bonded via the C atom. It has been proposed that the low CO stretching modes are associated with strongly-inclined or lying-down species coordinated to the substrate via both C and O atoms. We performed ESD and ESDIAD studies in all three cases, and confirm that there is little or no O^+ or CO^+ ion emission at any desorption angle from the CO characterized by the low-frequency stretching modes. For CO on the clean Cr(110) and Fe(100) surfaces, this is the expected result for strongly inclined or lying-down CO, and confirms the structural assignments. For CO + K on Ru(001), the influence of reneutralization effects on ion yields is highly probable due to the CO-K interaction, and the configuration of CO (standing up or lying down) remains controversial.

2. Evidence for Molecular O_2(ads): Chemisorption of Oxygen on Cr(110)

In most studies of oxygen interacting with transition metals, it is reported that oxygen dissociates rapidly to form a monolayer of atomic oxygen; subsequently, an oxide layer forms. We have found a strikingly different behavior for the adsorption of oxygen on Cr(110) at 120 K. At low coverages, dissociative oxygen adsorption dominates, while at higher coverages, HREELS and ESDIAD data provide evidence for a co-existing minority <u>molecular O_2 state</u>. An O_2(ads) vibrational frequency of 1020 cm^{-1} and a six-beam ESDIAD pattern are suggestive of super-oxo O_2(ads) bonding at local sites, each with the O-O molecular axis tilted away from the surface normal. Molecular O_2(ads) has been seen previously on less reactive surfaces (Ag, Cu, Pt, Pd), but this is the first time that O_2(ads) has been reported on such a reactive surface having a high heat of oxygen adsorption.

3. New Digital ESDIAD System

Up to the present time, all of our ESDIAD data have been obtained by photographing the two-dimensional patterns displayed on a fluorescent screen. In order to permit more quantitative determination of ion angular distributions, desorption angles (and, by inference, surface bond angles), we have constructed a new digital imaging system based on a high-sensitivity video camera for detecting the ESDIAD images on the fluorescent screen.

The digital imaging system is composed of a laboratory computer with a hard disk, a color monitor, a video camera and hardware boards for video data acquisition and arithmetic processing. The hardware allows the acquisition of live images or the digitization of photographs, the formation of histograms and contour plots, digital image manipulation (such as background subtraction, smoothing, and feature recognition/-enhancement/removal), and plotting. We have demonstrated the ability to do single-ion counting as well as image integration to form ESDIAD patterns. These abilities are crucial for allowing the ESDIAD pattern to be quantified, and for when angle and time-resolved spectra (i.e., negative ion spectra) are acquired. Several digitized ESDIAD patterns obtained using this system are shown in Fig. 3.1; these are described in the following paragraphs.

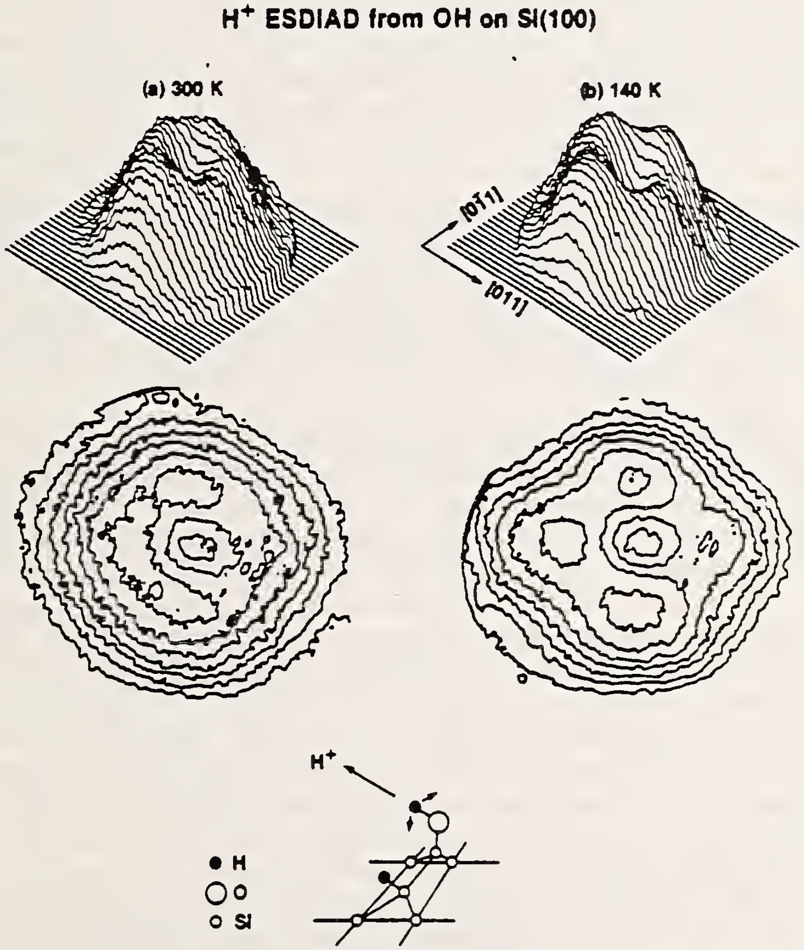


Fig. 3.1 H^+ ESDIAD and schematic model illustrating the bonding of OH to a Si(100) surface. The data were obtained using the new digital ESDIAD system. Column (a): H^+ ESDIAD (perspective and contour plots) for T = 300K; column (b): H^+ ESDIAD at 140K. A schematic bonding model in which H and OH are bound to both ends of a Si(100) dimmer is shown below. The four H^+ beams resolved in column (b) are due to ESD from degenerate dimer configurations. The decrease in resolution of ESDIAD at 300K is due to increased vibrational motion of the OH.

4. Structure of H_2O Adsorption on Planar and Stepped Surfaces of Silicon

Despite the extensive interest in the surface chemistry of H_2O, there have been relatively few structural studies of H_2O on surfaces having high heats of M-O bond formation where dissociation is likely to occur. We have recently applied the new digital imaging ESDIAD system to the study of H_2O on surfaces of Si; this is the first ESDIAD study ever reported for adsorption on a semiconductor surface!

The adsorption of water on the reconstructed planar (100)2x1 and single domain-stepped (100) 2x1 (cut 5° towards (011)) surfaces of silicon was studied using LEED and digital-imaging ESDIAD as a function of temperature (160-650 K) and coverage. Water has been shown by Chabal and Christman to chemisorb dissociatively to form surface OH groups. At 300K, the H^+ ESDIAD pattern for the planar surface is a nearly symmetric halo (see Fig. 3.1), indicating that OH is oriented with its bond vector inclined away from the surface normal, while at low temperature ($\lesssim$200K) a four-lobed pattern preserving substrate symmetry is observed. This reversible temperature dependence is related to librations and rotations of the OH complexes. ESDIAD from the stepped surface exhibits two-fold symmetry, with enhanced emission towards the steps, consistent with bonding of OH to single-domain terrace sites. An interpretation based on the dimer model of the Si(100) reconstruction has been formulated.

Plans for next year are centered on three areas. First, a major new thrust is to develop the technology for measuring ESDIAD of negative ions, and to apply the new methodology to challenging problems in surface chemistry of adsorbed molecules. There are several reasons for these proposed experiments. First, ESDIAD of positive ions has proven so useful in surface chemistry that we anticipate new structural information about adsorbed molecules whose ion fragments include negative ions. Certain classes of molecules (e.g. halogen-containing species) generate high yields of atomic negative ions (F^-, Cl^-) under electron bombardment. Other candidates include H^- and O^- from H_2O, CO, etc. Second, these studies will provide new insights into the basic mechanisms of ion fragmentation and the influence of surface parameters on ion trajectories, etc. In a few special cases, we expect to compare directly negative- and positive-ion ESDIAD from the same surface species (e.g. H^+ and H^- from NH_3, H_2O). Third, this is a new scientific and technical challenge. Such measurements have never been made before, and there may be unanticipated benefits; e.g., the technology necessary for negative ion detection will permit the first mass-resolved, two-dimensional ESDIAD measurements.

Test molecules for ESDIAD of negative ions include HF, F_2, PF_3, the completely fluorinated analogue of acetone [$(CF_3)_2CO$], di(trifluoromethyl) ether [$(CF_3)_2$ O], and fluorine-substituted pyridine. In all cases, we will combine kinetic measurements with measurements of local structure. Strong repulsive interactions between the electron-rich fluorine-containing portions of the adsorbed molecules may well lead to a rich assortment of local structures. Of particular interest will be the search for adsorbate/substrate systems where ESDIAD of both positive and negative ions can provide complementary structural information.

Second, we will continue our studies of the structure of small molecules on clean metal surfaces, and the influence of surface additives (such as catalyst promoters and poisons) on the structure and chemistry of adsorbed molecules. Examples will include several controversial cases, e.g., the structure of acetylene on Cu(100), and the effect of impurity O and Br on the structure and chemistry of H_2O on Cu(110).

Finally, we will expand our effort in the surface chemistry of electronic materials by applying ESDIAD to the study of semiconductor surfaces, in particular, to characterize the surface structures formed on Si surfaces during adsorption and reaction of small molecules. Despite the technological importance of semiconductors in catalysis and electronics, there have been no published studies of adsorbate structures on semiconductors using ESDIAD.

We intend to characterize the surface chemistry of atomically stepped and planar Si surfaces interacting with small molecules (H_2O, H_2O_2, CH_3OH, NH_3, CH_3OH, HF, F_2) of importance in semiconductor device processing (wet oxidation, plasma etching, reactive ion etching, etc.). A promising new area is the adsorption and decomposition of transition metal carbonyls ($Fe(CO)_5$, $Cr(CO)_6$, etc.) on Si. A study of thermal desorption, electron beam-induced desorption, ESDIAD and HREELS of adsorbed carbonyls will provide valuable insights into the physics and chemistry of metal deposition and silicide formation on Si surfaces.

C. Neutron Scattering Studies of Catalysts

(J. M. Nicol, R. R. Cavanagh, and R. D. Kelley)

Neutron scattering techniques applied to adsorbate systems on high-area catalytic surfaces are providing new insights into catalytic science. NBS has played a lead role in this effort having a unique combination of neutron physicists and surface chemists with an interest in catalysis. During the past year, work has focused on inelastic incoherent neutron scattering (IINS) studies of the interaction of hydrogen with palladium and quasielastic scattering (QNS) studies of the ammonium ion in zeolite rho. This work has been carried out at the NBS research reactor with support, in part, from the Chemical Sciences Division of the Office of Basic Energy Sciences, Department of Energy.

1. Adsorbate Dynamics in Zeolites

Quasieleastic neutron scattering has been used to characterize the diffusive motions of NH_4^+ in zeolite rho. This work reflects a collaborataive effort between the Surface Science Division (R. R. Cavanagh and J. M. Nicol) and the Reactor Radiation Division (T. J. Udovic and J. J. Rush) at NBS, and E. I. DuPont de Nemours (D. R. Corbin), W. R. Grace (M. J. Wax), and the University of California at Santa Barbara (G. D.

Stucky). By measuring the influence of neutron momentum transfer on the elastic incoherent structure factor (EISF), it has been possible to determine the reorientational motions of the ammonium. We have been able to demonstrate that the NH_4^+ groups undergo essentially three-fold reorientational motions. However, the fourth (and "anchoring") proton periodically changes roles with one of the rotating protons. Figure 3.2

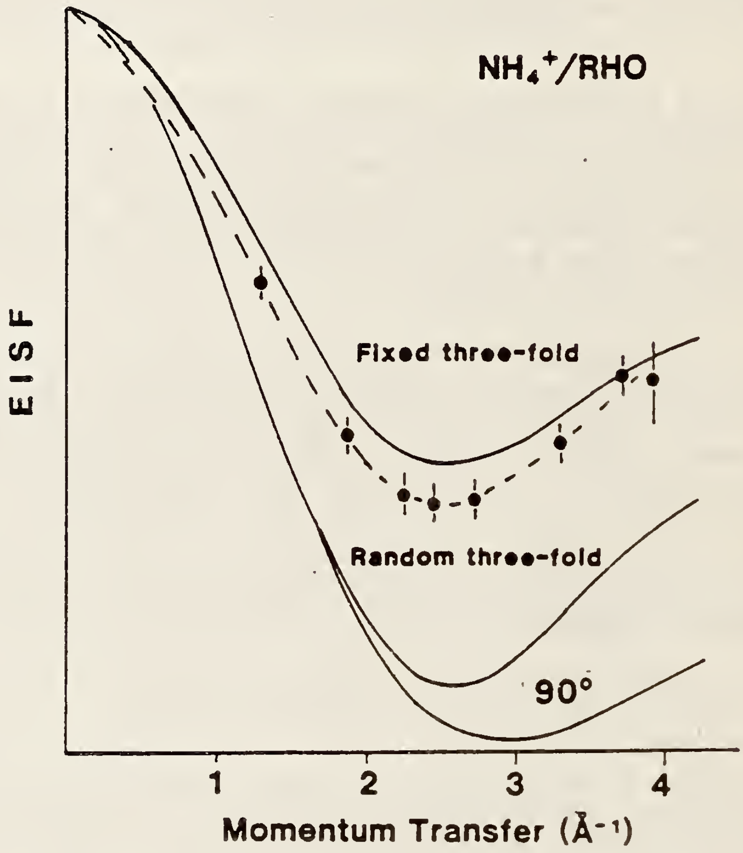


Fig. 3.2 Elastic incoherent structure factor as a function of neutron momentum transfer (Q) between 1 and 4 Å^{-1}. The points correspond to data taken at the NBS reactor on NH_4^+ in zeolite rho. Three models of the reorientational motion are indicated: Fixed three-fold (120° rotations about a single fixed 3-fold axis), random three-fold (120° rotations at random about all four 3-fold axes), and 90° (90° rotation about a two-fold axis with each proton sampling four different positions).

shows the data recorded at the NBS reactor along with the predictions of three different reorientational models (120° rotation about a single fixed 3-fold axis, 120° rotations at random about all four 3-fold axes, and rotation about a two-fold axis). Two points should be made regarding these data. The value of Q where the minimum in the EISF is observed provides a measure of the applicability of any model to the observed data. Clearly, one of the models predicts a Q_{min} value (~3 Å^{-1}) which is inconsistent with the data (2.3 Å^{-1}). The second point is related to the depth of the modulation in the EISF. Since deammoniation of the NH_4/rho generates the protonated form of the zeolite (H-rho), there will be a non-zero contribution to the EISF at all Q from the H-rho in the specimen. Thus, the observation of a deeper minimum in the EISF than predicted by an anchored 3-fold rotor (despite the intensity contributed from H-rho) clearly establishes the random 120° model as the best model for the reorientational motion.

The activation energy for this mode has also been estimated from the temperature dependence of the Lorentzian component of the quasielastic scattering signal. An exceptionally low activation energy (~20 meV) is obtained. This barrier is comparable to the lowest observed activation energies for NH_4^+ in molecular solids, and represents the first direct measurement of such dynamics in zeolites.

Futher work is in progress to examine the reammoniation of zeolite H-rho, starting with an ammonia loading equivalent to one NH_4^+ ion per unit cell. In addition to characterizing the diffusive motions of the NH_4^+ ions by quasi-elastic scattering, vibrational spectroscopy of the ammonium modes in the 5 to 20 meV range is being investigated by inelastic neutron scattering. By collecting data over the temperature range 4 to 300 K, a more detailed picture of site geometries and bonding interactions will be obtained.

2. Interaction of Hydrogen with Palladium

IINS is being used to characterize the adsorption and absorption of hydrogen by small particles of palladium (Pd black), with particular emphasis on the identification of subsurface hydrogen. This work is a collaborative effort between the Surface Science Division (J. M. Nicol, R. D. Kelley, and T. E. Madey) and the Reactor Radiation Division (J. J. Rush). The data indicate that bulk β-hydride forms readily following high doses of hydrogen at temperatures as low as 77 K. At lower hydrogen doses, spectral features have been associated with vibrational modes of both surface and subsurface hydrogen. The subsurface species appears to be associated with a vibrational mode at ca. 58 meV, consistent with hydrogen bonded in octahedral sites in the Pd lattice. Evidence for the subsurface hydrdogen is the broad lineshape which is quite distinct from the more narrow linewidth of the β-hydride, and the reactivity with chemisorbed oxygen (measured in oxygen-titration experiments).

Experiments are underway to generate and characterize a hydrogen-free Pd sample and to examine the dynamics of the surface-subsurface equilibrium. Force-constant calculations and other experimental work is being undertaken to try to establish site geometries for the H-Pd system.

In the next year, in addition to the continuing work with zeolites and with palladium black, we will prepare a Raney nickel sample using ^{60}Ni. The low incoherent cross-section of this isotope makes the substrate nearly invisible and provides an unusual opportunity to study the structure and dynamics of an adsorbed hydrogeneous species in great detail.

D. Surface Characterization Using Synchrotron Radiation

(R. Stockbauer, R. L. Kurtz, N. D. Shinn, H.-H. Chen, D. E. Ramaker, and T. E. Madey)

Major goals of this effort are (a) to determine the electronic structure of surfaces and adsorbates using variable-wavelength synchrotron radiation and ultraviolet photoelectron spectroscopy (UPS), and (b) to identify the electronic excitations which result in the photon-stimulated desorption (PSD) of ions form molecules adsorbed on surfaces as well as from condensed molecular films. When possible, PSD ion yields are correlated with UPS of both valence states and core-electronic states of the surface species. These measurements provide tests of recent theoretical models of electron- and photon-stimulated desorption, and provide new insights into the bond-breaking processes induced by ionizing radiation incident on surfaces. The work has been supported in part by the Office of Naval Research.

Accomplishments during the past year were in six areas: (1) electron- and photon-stimulated desorption on ions from oxide surfaces; (2) electronic structure of molecules adsorbed on surfaces; (3) instrumentation of a new beamline at the NBS synchrotron radiation facility SURF-II; (4) construction of a new display analyzer; (5) progress at the Brookhaven National Synchrotron Light Source (NSLS); and (6) theory of stimulated desorption.

1. Electron and Photon-Stimulated Desorption of Ions from Oxide Surfaces

Recent efforts in our laboratory to understand the mechanisms involved in stimulated desorption have forced a re-evaluation of the factors that influence surface stability under ionizing radiation. Our experimental results in desorption from different surfaces of TiO_2 have shown that the local surface atomic arrangements can be as important in determining ion desorption probability as the electronic structure. To expand our efforts in further elucidating the fundamental processes involved in desorption induced by electronic transitions (DIET), we have begun to study different materials and (using synchrotron radiation) to probe deeper core levels.

During the past year, we pursued these two efforts on BL-1 of the NBS SURF-II synchrotron storage ring as well as at the Deutsches Electronen Synchrotronen (DESY) in Hamburg by studying DIET from single-crystal surfaces of MgO. At DESY we used the wiggler beam-line coupled to the Flipper monochromator to measure ion emission from MgO with photon energies spanning <u>all</u> of the electronic energy levels. Excitations spanning the O 1s level produced striking results.

These measurements are the first observation of a fundamentally new excitation producing desorption: core-exciton production whose subsequent decay induces the desorption of O^+ and H^+. The H^+ signal originates from surface contamination on the MgO from the ambient vacuum. We found evidence for the contribution of several excitonic states to the desorption of O^+ and the data show that these states are different from those giving rise to H^+ desorption. Electron yield data from partially oxidized Mg imply that these excitations are localized in the near-surface region.

Core excitons consist of a bound conduction-electron/core-hole pair and, with a deep core-hole such as the O 1s, are localized on a single atomic site. The obvious signature of an excitonic state is the observation of excitations that result from photon absorption at energies below the binding energy. In the case of an insulator such as MgO, this corresponds to absorption of a photon that places the photo-excited electron at an energy in the bulk band-gap.

In Fig. 3.3 the O^+ and H^+ ion yield curves are shown near the onset in O 1s excitation. The onset in O 1s core excitation to unoccupied

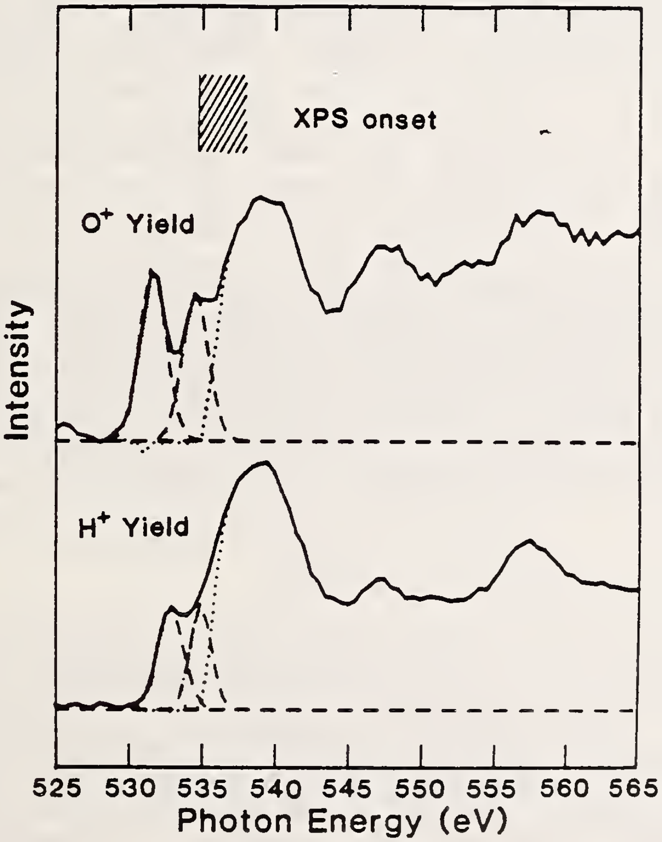


Fig. 3.3 O^+ and H^+ ion yields from MgO(100) versus incident photon energy. The spectra are decomposed into the excitonic desorption contribution given by the Gaussian peaks. When the Gaussians, given by the dashed curves, are subtracted from the spectrum, the dotted curve is obtained.

conduction band states in the bulk is indicated by the shaded bar. Clearly, the excitation producing O^+ desorption at 531.6 eV involves photon energies that place the photoelectron in the 7.8 eV bulk band-gap, an excitonic state. When the ion yield curves are compared with fluorescence and electron energy-loss (ELS) measurements, one finds structure essentially identical to that for photon energies above 535 eV in Fig. 3.3. Using the usual dipole-selection rules, we therefore identify the two Gaussian peaks in the O^+ desorption as $1s^1 2s^2 2p^6 3p^1$ and $1s^1 2s^2 2p^6 4p^1$ excitons and the feature in the H^+ desorption at 532.9 eV as due to a $1s^1 2s^2 2p^6 3p^1$ exciton of OH^-. The observation of H^+ desorption at the O 1s level is not surprising since hydrogen is stable on MgO surfaces in the form of OH^- radicals.

In the decay of these excitonic excitations, the excited electron is less likely to be a participant (which would result in a 1h final state) than it is to remain as a spectator to the decay. A 2h1e state will result from the $1s^1 2s^2 2p^6 3p^1 \dashrightarrow 1s^2 2s^2 2p^4 3p^1$ decay. Since the radial extent of the 3p wavefunction is large, incomplete screening of the O core by the 3p electron will produce a state that is nonbonding and will influence the stability of the O on the surface. Should the 3p electron escape (and this is assisted by the loss of the exciton binding energy after the Auger decay), the O^+ will clearly be in a repulsive surface Madelung potential.

We plan to continue these studies of ion desorption by expanding our recent work on MgO and TiO_2 to include studies of other isostructural oxide surfaces with varying electronic configurations. An example of such a comparison would be that of $TiO_2(001)$ and $Ti_2O_3(10\bar{1}2)$. We will also begin work on partially-oxidized transition-metal surfaces. These surfaces will allow the application of standard synchrotron radiation techniques that are often unsuccessful when applied to insulating oxides.

2. Electronic Structure of Molecules Adsorbed on Surfaces: Relation to Geometric Structure

Synchrotron ultraviolet photoemission studies of carbon monoxide chemisorption on Cr(110) at 90 K confirm the sequential population of two structurally different molecular binding states. The first state (α_1CO) consists of molecules with <u>both</u> the carbon and oxygen atoms coordinated to the chromium surface; a previously proposed model locates these molecules in the two-fold symmetric surface hollow sites with the intramolecular axis aligned roughly along the $[1\bar{1}0]$ direction. The measured photon energy dependence and limited angular dependence of the α_1CO photoemission peak intensities strongly support this model and are consistent with the proposed local binding site. Only after this binding mode saturates at 1/4 monolayer does the α_2CO binding state appear. For this latter state, the CO molecules are terminally bound to the surface with the C-O axis aligned approximately along the [110] surface normal. A comparison of spectral differences for α_1CO and α_2CO reveals previously unseen binding-mode-dependent effects in the adsorbed CO electronic structure, highlighted by an increase in the CO 4σ orbital binding energy for the lying-down state. These data have been related to previously reported vibrational and stimulated desorption results for Cr(110)/CO.

In parallel experiments in our SURF-II apparatus, electron-stimulated desorption (ESD) experiments using a time-of-flight pulse-counting method were performed for molecular CO chemisorbed on the Cr(110) surface at 80 K. Consistent with previous qualitative observations, negligible CO^+ and O^+ desorption signals were measured from the α_1CO overlayer which saturates at 1/4 monolayer. For $\theta_{CO} > 0.25$, a terminally-bonded (α_2CO) binding mode is populated in addition to the existing α_1CO binding mode and the ion yield sharply increases. For α_2CO, both O^+ and CO^+ ions are observed; the CO^+ ions desorb with characteristically lower kinetic energies than O^+ ions. Near saturation coverages of CO(ads), an observed decrease in the O^+ yield is attributed to adsorbate-adsorbate interactions which reduce the ion desorption probability, as seen in ESD studies of terminally-bonded CO on other metals. These results have been considered in the context of two possible models proposed for the α_1CO binding state, and related ESD observations for CO chemisorbed on potassium-promoted Ru(001) and Fe(001).

3. New Laminar Grating Installed at SURF

A laminar-profile toroidal-grating monochromator has been installed on our dedicated beamline at the NBS SURF-II synchrotron storage ring. This grating is expected to reduce significantly the vexing problem of higher-order contributions to the diffracted light and yet result in good transmission over the 20-100 eV range. Instead of the usual ruled-grating profile, the grooves in this grating have been ion-etched to produce a square-wave profile. The groove-depth has been produced so that destructive interference occurs between the top and bottom faces for all the even orders. Measurements of the relative contributions of all orders through 4th order is presently underway; however preliminary results show significant attenuation of 2nd and 4th order light.

PSD data as well as total secondary-electron emission to which the PSD data are compared are adversely affected by this higher-order radiation. In both experiments, the signals from the different-order radiation are indistinguishable which necessitates removal of the higher-order contribution. By reducing the higher-order radiation from the monochromator, these corrections become smaller allowing us to examine weaker PSD signals and to determine thresholds more accurately.

4. Construction of Angle-Resolving Display Analyzer

A new ellipsoidal-mirror angle-resolving electron- and ion-energy analyzer has been assembled and is undergoing initial testing. This outstanding instrument was designed and constructed at NBS (based on an instrument constructed at IBM by D. Eastman). It is ideally suited for angle-resolved PSD, and will be the only such analyzer in North America used for these measurements. Details and scientific plans are given in section 4.B.3.

5. Resonant Photoemission from Cu Measured at Brookhaven NSLS

During our run this spring at the Brookhaven National Synchrotron Light Source, we were able to make measurements of resonant photoemission from sputtered Cu(100) over the photon energy range spanning the Cu 3p excitation onsets. Photoemission measurements reveal two distinct 3d shake-up satellites at 12 to 14.6 eV apparent binding energy. Interference between these satellites and the Auger decay channels that open up when the photon energy exceeds the 3p excitation onset produce resonances in the satellite intensity. There are two resonant energies (75.5 and 78.5 eV) that correpond to resonances with excitations from $3p_{1/2}$ and $3p_{3/2}$ states. The two distinct satellites are believed to arise from the multiplet splitting of the Cu $3d^8$ configuration. These experiments demonstrate the versatility of the NBS-NRL X24C beam-line with the extended energy range and good resolution of the grating/crystal monochromator.

We also attempted during this run to measure electron attenuation lengths in condensed molecular solids. This work is described in section 2.A.5(b).

6. Theory of Stimulated Desorption

Our work during the last year has addressed an important issue related to the photon-stimulated desorption (PSD) of ions from surfaces. What are the relative roles of direct photoexcitation and indirect excitation via secondary electrons in PSD ion yields? The question of the magnitude of indirect, secondary-electron processes in PSD is an extremely important one. If the ion yield is dominated by such indirect effects, the utility of PSD for the determination of surface structure is severely limited.

Recent reports on the magnitude of secondary-electron contributions in electron/photon-stimulated desorption (ESD/PSD) appear to be contradictory. It has been reported that secondary electrons provide the dominant contribution to the H^+ yield from NH_3/Ni at energies above the N 1s core excitation and this process is called X-ray-induced ESD (XESD). Others have concluded that the XESD process is the dominant mechanism in the PSD of N^+ and O^+ ions from mixed condensed gases such as N_2 and O_2 and in the PSD of H^+ ions from OH/YbO-Sm. On the other hand, large differences are often found between the secondary-electron yield and the PSD ion yield (e.g., O^+ from O/Cr and O/W, H^+ from OH/Ti and Cr, and H^+ from H/diamond) providing strong evidence for the dominance of a direct photon-excitation mechanism. The total absence of ion yield contributions at certain core levels (e.g., the O^+ yields from NO/Pt(110) and CO/Ru(0001) reveal no structure at the N, Ru, or Pt core levels) also indicates that the XESD process is not dominant. Finally, a semiquantitative determination of the secondary-electron contribution to the ESD OH^* yield from OH/TiO_2, where large contributions are expected, indicates that backscattered electrons are responsible for only about 30% of the OH^* desorption.

In this work, we have re-examined the three systems mentioned above, in which dominant XESD effects have been postulated. ESD ion angular distribution (ESDIAD) data on the NH_3/Ni system and a detailed determination of the mechanisms involved in H^+ desorption indicated that all of the features attributed to the XESD effect may, in effect, arise from direct core-level processes. A re-examination of the PSD N^+ and O^+ yields from condensed N_2 and O_2 reveals that the indirect XESD mechanism contributes just one-third of the N^+ yield, but dominates the O^+ yield. This arises because the direct Auger-stimulated desorption (ASD) process following core-hole excitation is inactive for O^+ desorption, but remains active for the N^+. This differences is believed to arise because of $2\pi^*$ electron transfer in condensed O_2 (i.e., electron hopping between neighboring O_2 molecules); the $2\pi^*$ band is, of course, empty in condensed N_2. Finally, a detailed interpretation of H^+ desorption from OH/Ti and Cr, and comparison with the system OH/YbO-Sm indicate that the direct ASD process is also inactive in the latter case. Thus we show for these three systems that either alternate interpretations of the data are possible, indicating that the XESD effect is small, or that the XESD process dominates only because the direct mechanism is suppressed. This makes the results on these three systems consistent with the significantly larger number of papers which indicate that the XESD effect is generally not a major problem.

Plans for the next year include an examination of recent PSD data for MgO (section 3.D.1). The O^+ and H^+ ion yields spectra reveal large excitonic-like features which are not completely understood. Detailed interpretation of these data may also provide information about the role of secondary electrons and the XESD effect in ionic insulators. The extent of these effects in the alkali halides, e.g., LiF and NaCl, has been somewhat controversial. The MgO system is an excellent model system for such studies, since it is more stable than the alkali halides and the electronic processes appear to be simpler. A theoretical examination of the PSD ion yields from condensed and chemisorbed hydrocarbons, and an examination of hydrogen bonding effects, may also be attempted as the data become available.

E. Dynamical Effects Associated with Core-Level Ionization

(T. J. Jach)

The NBS Quantum Metrology Group under the direction of Dr. R. D. Deslattes has developed a program to study the electronic effects associated with core-level ionization in atoms, molecules and at surfaces. Specific effects which are being studied include dynamical effects in inner-shell vacancy production, relaxation of the extra-atomic environment, and production of multiple vacancies, with or without ionization. One member of the Surface Science Division Staff has been working half-time on this project.

For the past four years, this team has designed and built the X-24A Beamline at the National Synchrotron Light Source (Brookhaven National Laboratory). During 1986, the beamline, which is optimized for soft x-ray production in the energy range 800-2000 eV, finished its first full year of operation. The X-24A soft x-ray beamline at Brookhaven has been functioning extremely well, producing the highest flux in the world ($>4\times10^{11}$ photons/sec) with an energy resolution of 0.4 eV.

The first round of experiments has been on gas targets, both monatomic and polyatomic; the model systems we are studying will shed light on solids we intend to study in the future. Argon is the "hydrogen atom" of multi-electron atoms since its one-electron excited states are the easiest to calculate using Hartree-Fock-type procedures. Theorists are therefore actively interested in experiments at this level.

An experimental chamber has been built in which the gas is confined to a cell with thin beryllium windows transparent to x-rays entering at the energy range of current interest (about 3 keV) as well as to fluorescent x-rays produced by radiative decays. The emitted x-rays are analyzed by a highly efficient spectrometer consisting of a crystal bent along a Rowland circle and a position-sensitive proportional counter. This state-of-the-art combination allows whole line spectra to be taken simultaneously.

The NSLS x-ray ring is due to shut down for 6-8 months starting in December, 1986 for extensive modifications. As a result, we have concentrated on taking the maximum amount of data, with next year to be devoted to interpretation of the results and preparation of reports. The following experiments have been performed during the past year.

1. X-ray Raman Threshold Behavior Near the Ar K-edge

It is possible to induce fluorescence from the Ar Kα (2p-1s) and Kβ (3p-1s) transitions at incident energies which are too low to excite the 1s electron into the lowest empty bound state. This is accomplished by a Raman process in which an electron is promoted from a virtual state near the 1s state which is then filled by radiative decay of a 2p or 3p state. Using a high-intensity monochromatic x-ray beam and a high-resolution crystal spectrometer, we have been able to directly excite such transitions and measure the amplitudes for fluorescent decay from these states. Theoretical calculations have existed for some time for these amplitudes, but the difficulty in observing the effect with statistically significant count rates has made them difficult to evaluate. We have already obtained data of sufficient quality to allow us to separate out resonant and non-resonant Raman contributions.

2. Energy Dependence of Shake-up Satellites in the Ar Kα and Kβ Lines

The adsorption spectrum of argon (and of more complicated molecules) contains a number of features only resolvable with a highly monochromatic beam above the threshold K-edge. These features are attributed to excitations of one core and one or more valence electrons which are excited by a shakeup process. Similarly, there are satellite lines observed at energies above the fluorescent emission of Kα or Kβ radiation which show an energy dependence near threshold. Because of the high resolution of our monochromator and spectrometer, we have been able to obtain extensive data on the threshold at which these satellites turn on and relate them to specific features in the absorption spectrum. This was possible because of the excellent energy stability of our monochromator over long periods of time. The data allow us to discriminate between various theoretical assignments which have been made for the quantum numbers of the absorption and satellite features.

3. Relative Coherent Elastic and Resonant Elastic X-ray Cross Sections at the Ar K-edge

We have measured the x-rays elastically scattered from argon atoms at energies all through the K-edge, with sensitivity to their polarization. This allows us to separate out the resonant and coherent components and determine cross-sections for each. We hope that this work will be accurate enough to produce absolute cross sections.

4. The Chlorine Fluorescence Spectrum as a Function of Bonding in Multi-atomic (Freon) Molecules

As a start on more complicated molecular spectra, we have observed the K fluorescence lines from chlorine atoms in freon. The chlorine atom is only one electron removed from argon, and can be present as one, two, or three neighboring atoms in freon. This system is therefore appropriate to study the effects of bonding.

5. Photoemission Spectrum of Ar Near the K Edge

In addition to studying the x-ray fluorescence spectra of gases and solids, we need to examine their non-radiative decays and their photoemission spectra. This is important in studies such as of covalent bonding and of post-collisional interactions of the outgoing particles. We are extending the work we have done with gas targets in cells to windowless gas-jet targets. As a step in this direction, we have taken preliminary data with a differentially pumped gas cell connected to a hemispherical electron analyzer. We have measured the photoemission spectrum from argon and hope to extend these measurements in the coming year.

The above experiments were performed in collaboration with Drs. P. Cowan, S. Brennan, and R. LaVilla of the NBS Quantum Metrology Group. The chlorine fluorescence experiment was a collaboration with Dr. Perera of Lawrence Berkeley Laboratory and the photoemission experiment was a collaboration with Dr. S. Banna of Vanderbilt University.

F. Development of Silicon Diode Radiation Detectors for Synchrotron Radiation Research

(T. Jach)

Scientists using x-rays from synchrotron radiation light sources have been traditionally conservative in selecting detection schemes such as gas ion chambers, scintillation counters, film, or Si(Li) detectors. We have developed a new technology over the past four years in which silicon PIN photodiodes, both as-is and with special modifications, have been employed as radiation detectors in experiments. These diodes are manufactured as detectors of radiation, but in fact they are excellent detectors of x-rays over an energy range of 500 eV to 20 keV. Their efficiencies exceed those of ion chambers by an order of magnitude and they offer additional advantages of small size, compatability with ultra-high vacuum systems, and lack of a need for power supplies.

Two experiments were performed during the past year on the Naval Research Laboratory Beamline X-23B. These experiments are part of a continuing (and unique) effort to provide data for synchrotron users on the characteristics of silicon PIN diodes in the x-ray region. As a result of our previous publications, three of the beamlines which use double-crystal monochromators at NSLS now use diode feedback loops which offer much-improved performance. The following measurements have been made recently.

1. Spectral and Spatial Response of Various PIN Photodiodes from 2-7 keV

We have improved upon our earlier measurements by determining the spectral sensitivity and spatial resolution of several commercially available PIN diodes. These measurements were made at the output of a beamline using x-ray mirror optics and a double-crystal x-ray monochromator. The system offered a wider energy range than the tube source used in the previous measurements and allowed us to eliminate corrections for the harmonic and fluorescence contributions which were potential sources of error.

2. Harmonic Rejection in Feedback Loops for Double-crystal Monochromators

Diffraction and EXAFS (extended x-ray absorption fine structure) measurements, among others, are subject to errors due to the fact that crystal monochromators reflect x-rays not only at the fundamental Bragg condition but at higher-order harmonics. One way of eliminating this error is to overlap the rocking curves of the two crystals in the monochromator in such a way as to pass the radiation of the first-order Bragg reflection but not higher orders. This scheme has never been successfully incorporated into the AC feedback loop circuitry which is the best way of electromechanically maintaining the two crystals at the Bragg condition while the energy is scanned. Using PIN diode detectors of differing sensitivity, we have demonstrated a means of solving this problem in a most satisfactory manner. It permits the AC feedback loop to be maintained on the side of the rocking curve in a way which discriminates against the harmonic component to any degree that is arbitrarily selected. The method allows scanning the monochromator through an energy range of 1 keV or more and should prove superior to the DC method which has been used up to this time.

This work was performed in collaboration with Dr. J. Kirkland of NRL and Dr. P. Wolf of Virginia Polytechnic Institute and State University.

G. Production and Characterization of Ultrasmooth Surfaces
(T. J. Jach)

Previous surface science experiments have indicated a need for surfaces which are extremely flat and smooth on an atomic scale. An example of this need is the desire to study photoemission from a metallic thin film at grazing incidence to obtain maximum surface sensitivity. There are also obvious reasons for wanting to make smooth detect-free substrates and thin film such as in the semiconductor industry where device widths of 100 Å are being approached. We have initiated an effort to (a) characterize substrates and thin films for roughness down to a scale of 3 Å; and (b) push the limit of surface smoothness attainable to 10 Å or better for a variety of materials.

Studies are progressing on interpreting gold thin-film deposition on amorphous glass surfaces, as observed by scanning reflection electron microscopy. A wide body of previously unconnected data on the reflectivity, surface roughness, resistivity, etc. of thin films of gold (and other metals) appears to be related to surface growth of microcrystals during deposition. We have observed new whisker growth modes which occur because diffusion kinetics are limited to certain crystal faces by substrate temperature. These results, based on electron microscopy data taken last year, are presently being prepared for publication. This work is being done in collaboration with Dr. L. Holdeman of Comsat and Dr. G. Hembree of the NBS Precision Engineering Division.

H. Electron Spectroscopy of Surfaces
(C. J. Powell, N. E. Erickson and D. E. Ramaker)

A number of electron-spectroscopic techniques are in widespread use for the determination of surface composition, surface vibrational modes, and surface electronic structure. Techniques such as Auger-electron spectroscopy, x-ray photoelectron spectroscopy, and electron energy-loss spectroscopy are useful but the observed spectral lineshapes are often complex. These lineshapes reflect the many processes often involved when electron beams interact with surfaces and when electronic excitations occur. The factors influencing observed lineshapes need to be understood in order that the spectroscopic techniques can be fully utilized and, in particular, so that quantitative intensity measurements can be made (e.g., for quantitative surface analysis).

As part of a project to measure the L_3-shell binding energies of 3d transition metals by different spectroscopic techniques (see section 2.A.4), we have made a detailed examination of the L_3 appearance-potential spectra (APS) of six 3d metals. We measured the so-called Auger-electron APS in which electrons of variable energy bombard the target material and a measurement is made of the derivative of the target current as a function of electron energy in the vicinity of the core-level BEs. Our APS data for Ti, V, Cr, Fe, Co, and Ni are similar to those reported previously but we have established our electron energy scale with greater accuracy and made a more extensive analysis of the data.

In order to determine an APS BE, it is necessary to compare a measured spectrum with one calculated from a model. In the past, APS data have been interpreted in terms of a simple one-electron model in which both the excited core electron and the incident electron have final states near the Fermi level of the target. According to this model, a self-convolution is made of the empty density of states (DOS), obtained from published calculations, and this is convolved with a Lorentizian function to represent core-hole lifetime broadening. A derivative is then taken for comparison with experiment. While this model has long been known to be oversimplified, it has been employed successfully for a number of materials including some 3d metals. We found that this approach gave satisfactory results for the APS data of Co and Ni but there were significant inconsistencies for Ti and V and inconsistencies of a lesser degree for Cr and Fe.

We have interpreted the inconsistencies between measured and calculated APS data in terms of a new Initial-State, Final-State rule in which intensities reflect the initial state, lineshapes reflect the final one-electron DOS in the presence of the core hole, and multiplets reflect electron coupling for the lighter elements of the transition series and hole coupling for the heavier elements. The DOS in the presence of the core hole has been modelled using an expression due to Cini which has been found useful in analogous studies of Auger-electron lineshapes. The modified DOS is given by:

$$N_{\mathrm{mod}}(E) = \frac{N(E)}{[1-UI(E)]^2 + [U\pi N(E)]^2}$$

where N(E) is the DOS from the literature for each metal, I(E) is the Hilbert transform of N(E), and U is the effective core-hole, valence-electron attractive energy. Figure 3.4 shows our AP spectrum for vanadium at the bottom and a series of calculated spectra based on $N_{\mathrm{mod}}(E)$ for various values of U. As U is increased, the calculated curves become closer in agreement with experiment; although the measured spectrum does not show two clear peaks, there is a weak shoulder at 515 eV. Similar results have been obtained for Ti. Better agreement between experiment and calculation could be obtained by adding more broadening in the calculated spectra (which could be ascribed to the lifetime of the excited two-electron state).

In addition to obtaining better agreement between measured and calculated AP spectra, the initial-state, final-state rule enables satisfactory resolution of apparently contradictory results obtained in the analysis of APS, x-ray absorption spectra (XAS), and electron energy-loss spectra (EELS). Briefly, small values of U are appropriate for the dipole excitations in XAS and in EELS at high incident electron energies, but larger values of U are appropriate for the non-dipole final states excited in APS and in EELS at near-threshold incident electron energies.

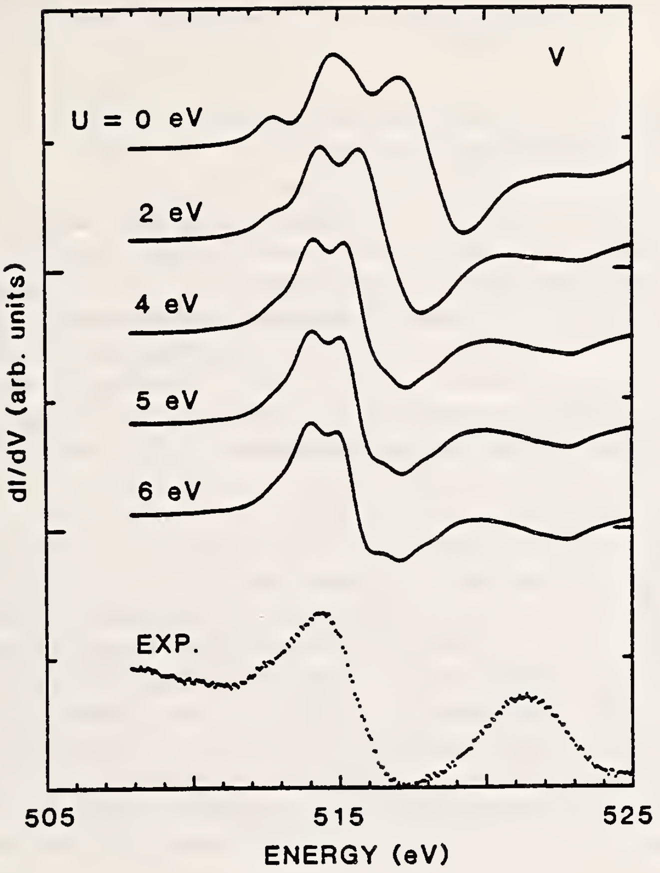


Fig. 3.4 Comparison of measured (bottom) and calculated L_3-shell appearance-potential spectra for vanadium. The top curve (U=0) was calculated with the empty density of states and the other curves with modifications to the density of states due to the core hole. The parameter U is the effective core-hole, valence-electron attractive energy. The calculated spectra were plotted using an L_3-shell binding energy measured by x-ray photoelectron spectroscopy.

We plan to test our model further by examining APS and EELS data of other types of metals.

I. Laser Diagnostics of Surface Dynamics
(D. R. Burgess, Jr. and R. R. Cavanagh)

The pathways and rates of energy transfer at surfaces remain the key unresolved issues for understanding chemical reactions at interfaces. Such information has eluded experiments which rely on conventional surface-characterization technique. A variety of laser-based techniques, however, have recently demonstrated their utility in probing such molecular dynamics in both the gaseous and liquid states. This program utilizes both the temporal and spectra characteristics available in state-of-the-art lasers. Strong collaborations with Drs. M. P. Casassa, E. J. Heilweil, D. S. King and J. C. Stephenson of the NBS Molecular Spectroscopy Division play a vital role in these efforts.

1. Laser-Excited Fluorescence as a Probe of Adsorbate Interactions During Thermal Desorption

Characterization of the mechanisms involved in energy transfer between an adsorbate and a substrate stands as the primary objective of this work. Measurements are made of the translational, rotational and vibrational energy content of desorbed molecules. These population distributions provide an indication of the interaction potentials which are involved in different desorption processes. By measuring the state-specific populations which result from elementary surface processes, it is anticipated that the fundamental steps which influence a variety of surface reactions can be examined.

We have recently completed a series of measurements of co-adsorbed NO and NH_3 thermally desorbed from Pt(111). The co-adsorption system was known to exhibit a strong NO-NH_3 interaction from earlier EELS and TPD measurements. The formation of an NO-NH_3 complex had been suggested by the previous studies. Our measurements of the rotational-state distributions by laser-excited fluorescence (LEF) of the thermally desorbed NO indicate that, despite the concerted desorption of both NH_3 and NO, strong adsorbate interactions are not manifested in the rotational-state distribution. The desorbed NO was found to exhibit a Boltzmann distribution with a rotational temperature 95% of the surface temperature.

2. Laser-Induced Desorption

The nature of the surface processes which can be induced by laser heating has been the subject of recent experiments on a polycrystalline platinum foil. In these experiments, NO was adsorbed on the substrate at 200 K and a laser (532 nm, 3 ns FWHM) was used to induce a temperature jump of 100 K. The NO liberated by this heating processes was detected by a second laser using LEF. Approximately 10^{-5} monolayers were desorbed within the illuminated region of the sample on every heating pulse. By varying the time delay between the heating pulse and the probing (LEF) pulse, a time-of-flight distribution could be measured for individual rovibronic levels. Tuning the wavelength of the LEF probe laser then provided a measure of the population in different rotational states of the desorbed NO.

These measurements have revealed several unexpected results. TOF distributions observed for two experiments, where the only variable is the rotational state probed by the LEF laser, illustrate the observed trends. The TOF data for NO with $J = 19.5$ are characterized by a prompt signal for a time delay between the heating and probe pulses of 0.5 μs. This result is in contrast to the TOF data for NO with $J = 3.5$ where the peak position is shifted to a time delay of about 8 μs. The data have been fitted to the sum of two (non-Maxwell-Boltzmann) velocity distributions. Our results indicate:

- For all rotational states, there is a slow component with a mean kinetic energy of 300 K.
- The rotational temperature for these slow species is ≈ 170 K.
- The mean kinetic energy of the fast component is a function of rotational state, ranging between 1400 K for $J = 3.5$ and 2650 K for $J = 19.5$.
- The population in $v = 1$ is dominated by fast NO molecules, and corresponds to a vibrational temperature of ≈ 900 K and a rotational temperature of approximately 155 K.

These results indicate that it may not be possible to account for the molecular processes induced by ≈ 5 nsec laser-heating pulses by simple thermal heating models. Atom-atom recombination, precursors, transient electron-hole pairs, and exit-channel effects are all consistent with our present data. Still, it should be possible to clarify the source of the two velocity components in future experiments. For instance, in the coming year we anticipate exploring the influence of the laser-heating pulse duration, the sensitivity to surface structure, the influence of co-adsorbates, the role of the heating laser wavelength, and the extent of correlation with surface cleanliness. Initial experiments on Pt(111) are currently in progress as well as work using a laser wavelength of 1.06 μm to heat the platinum foil. In addition, further work is anticipated which will permit direct measurement of the peak temperature jump induced by the heating pulse. This work is supported in part by the Department of Energy.

3. Time-Resolved Measurements of Vibrational Energy Transfer

Direct characterization of the time scales and mechanisms for relaxation and dephasing of vibrational excitation in adsorbed layers is the aim of this work. Such measurements can provide a quantitative understanding of a substrate's ability to quench the energy released upon chemisorption, reaction, or irradiation.

Two new picosecond sources have been developed for probing vibrational relaxation at surface. Both sources are capable of generating picosecond infrared pulses in the frequency range between 1700 and ≈ 4000 cm^{-1}. One system produces pulses of 30 psec duration with energies near 20 μJ. The second system produces shorter pulses (3 ps), but with reduced energy (3 μJ). The extension to longer wavelengths offered by these systems opens the opportunity to study a range of new surface-related problems.

Planned experiments will use pump-probe techniques to generate excited-state populations at surfaces and follow the subsequent time evolution of the excited species. Transmission measurements (on high-surface-area model catalyst systems) and reflection measurements (on single-crystal substrates) are anticipated. However, the reduced energy available in this spectra range (compared to the 300 μJ available at 3 μm), requires a more sensitive detection method than had been employed previously. Not only is the total energy per laser shot reduced, but the transmission (or reflection) transient induced by the laser is expected to be diminished. The first point has required the development of ratiometer techniques based on photoconductive and photovoltaic detectors. The second factor dictated that we improve our ability to measure reflectivities of individual laser shots to better than 1%. This performance must be achieved under conditions where the total energy in sequential shots can fluctuate by a factor of two. We are now able to reproducibly measure changes in transmitted light at the level of 3 parts in 10^3, and anticipate that we will shortly acquire the ability to measure such reflectivities to a few parts in 10^4.

Preliminary measurements have now been made on model compounds [$Cr(CO)_6$, $Rh(CO)H(triphenyphosphine)_3$, and $Rh(CO)Cl(triphenyphosphine)_2$] in preparation for probing the vibrational relaxation rate of CO bound to supported metal particles. The relaxation of the CO ($v = 1$) stretch mode was characterized using 5 μJ pulses with InSb detectors to monitor the relative sample transmission. These preliminary results indicate that the CO ($v = 1$) relaxation time in the hexacarbonyl is significantly longer than that found for OH/SiO_2. In the monocarbonyls, however, the relaxation times are significantly shorter. The applicability of these techniques for adsorbates on supported metal particles will be explored in the coming year. This work is supported in part by the Air Force Office of Scientific Research.

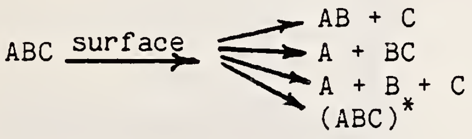
J. Theory of Dynamical Molecular Processes at Surfaces
(J. W. Gadzuk)

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 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.

Work has remained focused on the role of excited electronic states and intra-molecular vibrational degrees of freedom in reactive surface dynamics. In these situations, energy must be directed in order to break bonds or be extracted to stabilize highly vibrationally excited species formed for instance at curve crossings where electronic rearrangement takes place. There has been significant progress in several different directions in the application of an analytic model describing the dynamics of a diatomic molecular beam incident upon a surface and in which charge-transfer/curve-crossing events takes place. This has been carried out in parallel with numerical trajectory studies over realistic potential-energy surfaces (PES) in order to assess the reliability of the easily-used analytic models.

An extensive study has been carried out on the vibrational excitation/dissociative adsorption/dissociative scattering of heavy diatomic molecules such as I_2 incident upon metal surfaces. Classical trajectories for the molecule-surface collision have been calculated as a function of incident energy and for various values of the parameters characterizing the PES. A series of examples illustrating the various outcomes are shown in Fig. 3.5 for incident I_2 oriented parallel to the surface. Here z is the molecule-surface separation and ρ is the intra-molecular stretch coordinate. The low-energy events shown in Figs. 3.5(a) and (b), result in dissociative adsorption. Increasing the energy, as in Fig. 3.5(c) leads to resonance-assisted vibrational excitation. Finally, for energies $\gtrsim$ 1 eV, simple in-out scattering with substantial translational to vibrational (T→V) conversion occurs. Calculated values of the energy transfer from translation to vibration versus incident energy, treating the desorption energy parametrically, are shown in Fig. 3.6(a). Results obtained from our analytic modelling are shown in Fig. 3.6(b). It is apparent that for energies greater than ~ 1 eV where in-out trajectories occur, the analytic models provide reasonable representations of reality. This is encouraging and has provided stimulus for new modeling of more complex phenomena in surface chemical dynamics.

One such example is our recent theory on controlling chemical selectivity of reactivity in polyatomic molecule-surface collisions involving the formation of temporary negative-molecular ions due to molecule-surface charge transfer. As a final example, we have considered selectivity in the scattering of a prototypical polyatomic, say ABC, from a surface in which several outgoing channels are possible.



Selectivity is possible if an excited electronic state (negative molecular ion) is used to assist chemistry on the ground electronic state. Creation of a temporary negative ion whose geometry differs from the ground-state neutral permits molecular-ion distortion into configurations which favor one or the other of the outgoing channels when the ion is neutralized. Over the past two years, we have developed theory which shows how the lifetime of such temporary negative ions formed in surface collisions can be easily controlled. Selectivity is achieved by chosing an ion lifetime commensurate with the intermediate-state distortion which leads to the desired outgoing channel (reaction products). Thin exciting prospect has been demonstrated within the context of classical trajectory modeling.

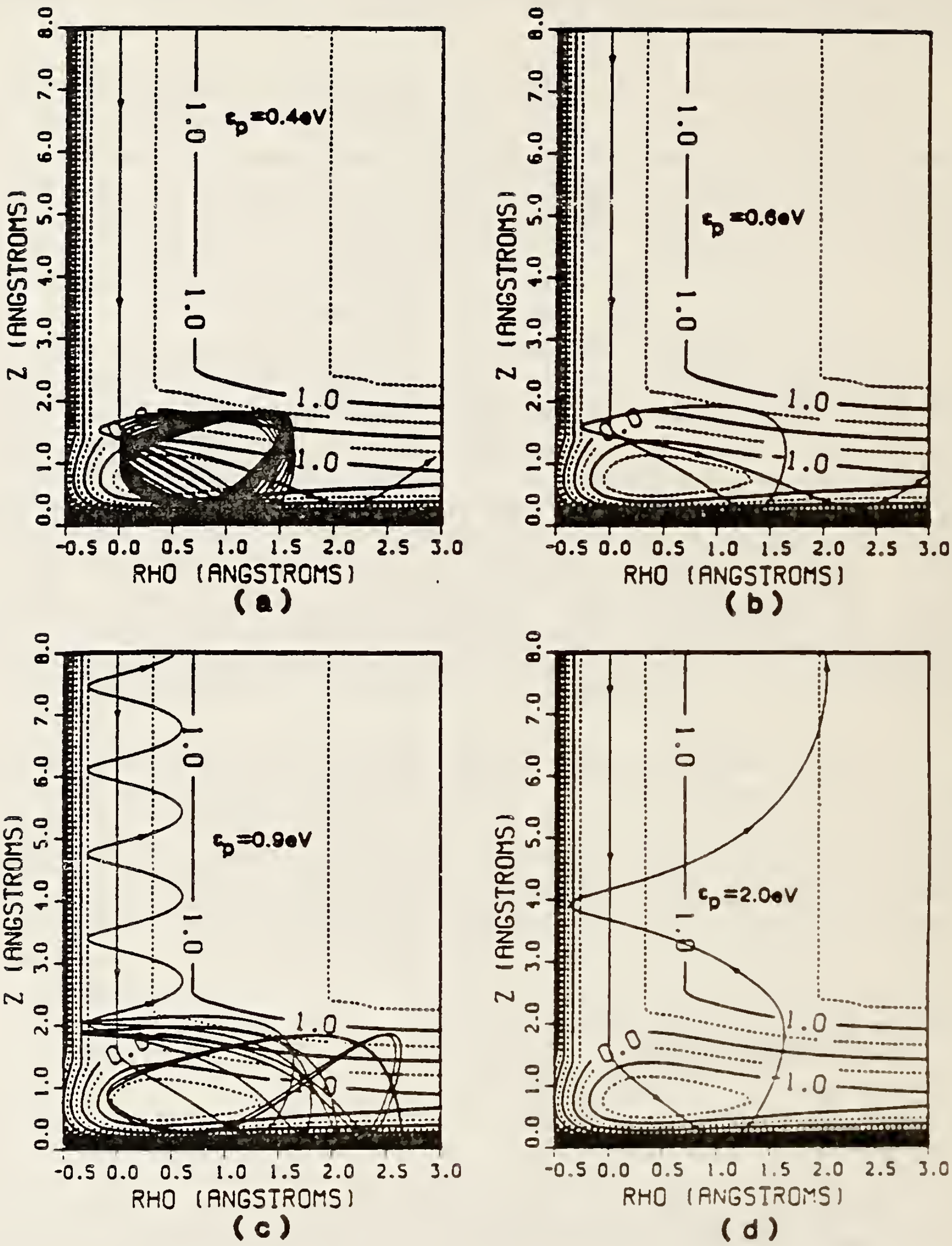


Fig. 3.5 Potential energy surface contours for an iodine molecule incident upon a physical surface in which dissociative adsorption is possible. The z axis is the molecule-surface separation and the ρ-axis is the intra-molecular stretch coordinate. A progression of trajectories for increasing incident translational energy is shown. Figures 3.5(a) and 3.5(b) show dissociative adsorption, Fig. 3.5(c) shows resonance-assisted T→V conversion, and Fig. 3.5(d) the basic in-out behavior leading to substantial T→V conversion.

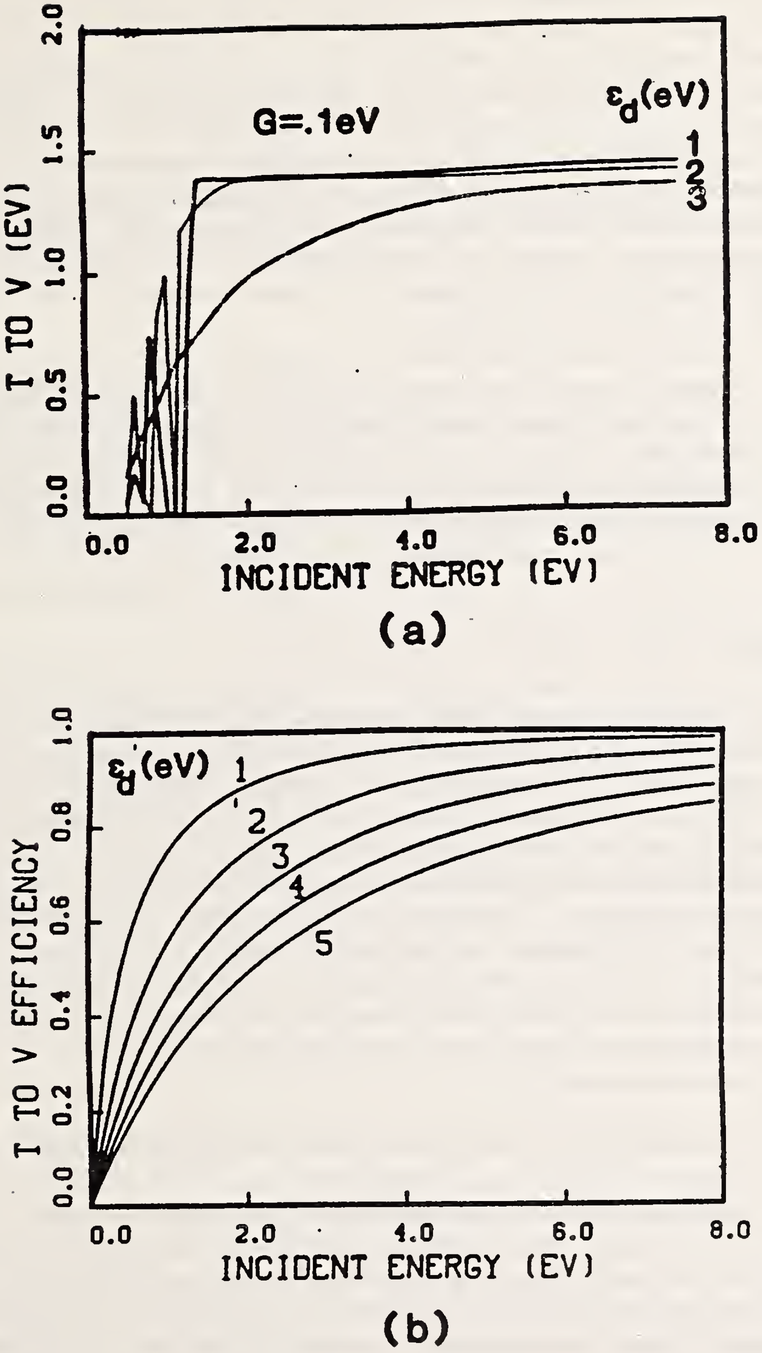


Fig. 3.6 (a) T→V conversion vs. incident I_2 translational energy, obtained from trajectory calculations, treating desorption energy parametrically, as labeled. (b) Ratio of $\Delta\varepsilon_{T\to V}$ to $\Delta\varepsilon_{T\to V}^{max}$ (T to V efficiency) versus incident I_2 energy, obtained from the analytic modeling of Fig. 3.5.

Theory has been worked out for a number of other new molecular-beam experiments, which will be carried out in laboratories, other than NBS, which have beam facilities. Amongst the proposals include scattering of oriented atoms or molecules in which the orientation is achieved by initial preparation of electronically excited states. These experiments should be very useful in providing new information on charge-transfer dynamics. Another proposal has been put forth for the design of neutral molecular beams with kinetic energies possibly up to 1 keV. This development may permit a totally new class of beam scattering experiments outside the extremely limited domain of beams prepared by the current supersonic nozzle-expansion method.

Finally, vibrational lineshapes and spectra of adsorbed molecules have been studied in terms of the quasi-periodic trajectories over a multi-dimensional PES. This is a prudent way to include the anharmonic effects which lead to dynamically interesting lineshapes because one can "see" what the oscillator is doing to acquire the lineshape. The lineshape or vibrational spectrum of an excited oscillator is

$$I(\omega) = \frac{1}{2\pi} \lim_{T\to\infty} \frac{1}{2T} \langle \left| \int_0^{2T} y(t)\, e^{i\omega t}\, dt \right|^2 \rangle$$

where y(t) is the oscillator displacement as a function of time after initial excitation. A particularly interesting situation exists when the adsorbed molecule can migrate between inequivalent adsorption sites, as in the bridge-3-fold site conversion seen for CO/Pt(111). Questions arise as to how the site conversion affects vibrational lineshapes, or turned around, how one extracts information on site conversion and/or surface diffusion from lineshapes. We have investigated this phenomenen in detail by calculating spectroscopic trajectories and from them, lineshapes. Relationships between the time scales for vibration, anharmonic "damping", and site conversion have been established which enable one to use experimental information such as line widths and shapes to gain additional insights on the surface PES.

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, and other experimental probes of non-adiabatic effects.

4. SURFACE COMPETENCE PROGRAM

W. F. Egelhoff, Jr., J. Fine, S. M. Girvin, M. J. DeWeert,
T. E. Madey, A. J. Melmed, D. A. Steigerwald, and R. Stockbauer

The Surface Competence Program is a part of the NBS "Competence Program." The NBS program was introduced to provide long-term support of the establishment and maintenance of areas of excellence in science and technology contributing to the NBS mission and the projected needs of the NBS clientele.

The Surface Competence Program was established October, 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 enhanced 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 three project areas. First, we are planning to develop the techniques needed to synthesize, by alternating monolayer deposition, a new class of materials: non-equilbrium 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 resolution. Finally, we are applying modern many-body theoretical techniques to the study of the quantum Hall effect, magnetism and other electronic properties of layered structures and thin films.

1. Surface and Interface Chemical Physics of Ultrathin Films
(W. F. Egelhoff, Jr., and D. A. Steigerwald)

Interest in ultrathin metal films (down to the two-dimensional limit of one atomic layer) on the part of the surface-science community has greatly increased in the past several years as it has become clear than an understanding of such structures will contribute to solving a wide range of problems in surface science. Among these are an understanding of the differences between surface and bulk electronic structure, the changes of surface electronic structure associated with chemisorption, the basis of surface magnetism, the modification of surface-layer properties by the substrate, the relationship between electronic structure and epitaxial growth, and the surface properties of alloys. The experimental program presently underway is using an integrated approach to study single-crystal surfaces, alloys and ultrathin films to contribute to an understanding of all of the above problems.

We have recently developed and applied a technique termed the "searchlight effect" in which enhanced electron intensities in x-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES) occur along nearest-neighbor and next-nearest-neighbor axes of single crystals. The searchlight effect is a powerful probe of the short-range order in the near-surface region and is well suited to studies of epitaxial growth, surface segregation, and interdiffusion.

During the past year, the searchlight effect has been applied to the investigation of various surface morphological phenomena as well as studied in its own right to determine how it can be applied with maximum benefit. Progress has been made in the following areas.

- Epitaxial films and sandwich structures of Au and Ag on Ni(100) were studied and found to have cubic short-range order by XPS but hexagonal long-range order by low-energy electron diffraction (LEED). This combination of results implies a very unusual surface reconstruction.

- The rate of Cu surface segregation in Ni-Cu-Ni sandwich structures was investigated as a function of depth of the copper layer. One such structure is illustrated in Fig. 2.4. It was found that different segregation mechanisms operate at different depths of the Cu monolayer.

- The effect of surface contamination on epitaxy was investigated. It was found that, for up to 0.5 monolayers (ML) of carbon or oxygen contamination on Ni(100), the epitaxy of Cu or Ni at 300 K was hardly inhibited. While the top atomic layer was quite disordered (LEED data), the searchlight effect indicated that the deeper layers were well ordered. The carbon and oxygen diffuse rapidly to remain at the growing surface. Even at substrate temperatures of 100 K, many layers of overgrowth (>>10 ML) are required to, in effect, bury the carbon and oxygen.

- A search was made for a theoretically predicted surface-melting phase transition using the searchlight effect [in this case on Hg(111)] but none was found to occur.

- The temperature dependence of the diffusion of a Ni monolayer into a Cu(100) substrate was investigated. This interdiffusion begins around 350 K and is essentially completed by 450 K.

- The effects of multiple scattering on the searchlight effect have been examined. It was found, as predicted theoretically by Tong *et al.*, that the first two or three scattering events enhance the intensity along interatomic axes but that further scattering events break up the searchlight beams. Figure 2.4(a) shows that the peak at 45° is strong for a 4 ML Ni overlayer but vanishes for a 10 ML Ni overlayer. The peak at 0° shows a lesser weakening effect at 10 ML Ni since there are fewer Ni atoms along this axis, as shown in Fig. 2.4(b).

- It was found that multiple scattering events tend to sharpen the searchlight-effect peaks. The peak at 45° in Fig. 2.4(a) is considerably narrower for a 4 ML Ni overlayer than for a 1 ML Ni overlayer.

Much of the experimental work of the past year has been conducted to develop the techniques needed for the next major effort to be undertaken. This will be the synthesis of a new class of materials, non-equilibrium ordered alloys, by epitaxial growth of alternating metal monolayers. This work has the potential for opening up a new area of materials science. The XPS searchlight effect is a near-perfect tool for diagnosing, in real time, any growth processes that interfere with the desired synthesis and should thus aid greatly in recognizing and overcoming barriers. We anticipate the capability of producing novel material properties by tailor-making the lattice structure. Later, we expect to characterize the materials with x-ray diffraction and electron microscopy and to study their chemical reactivity, catalytic activity, and magnetic properties.

During the past year, much effort has gone into upgrading the instrumentation in preparation for the synthesis of the ordered alloys. Changes have been made in the electron optics and in the computer control of the XPS system to improve its operating characteristics. Conversion of the detector system from a single channeltron to a position-sensitive detector is in progress. These changes will permit an increase in the diagnostic power of the searchlight effect.

Another major effort of the past year has been the design, construction, and testing of molecular-beam epitaxy ovens. These ovens produce the stable metal flux that will be required for synthesis of high-quality ordered alloys. The ovens are presently in the final testing stages.

The first alloys to be synthesized will be of the Cu-Fe system. No ordered alloys of Cu and Fe have been produced by conventional metallurgy. However, we believe that our approach of epitaxial growth combined with the XPS searchlight effect (to guide our understanding of how growth parameters affect morphology) will enable us to produce a variety of novel structures. Among these are alternating monolayers of Fe and Cu, monolayers of Fe separated by thicker Cu layers, and alternating bilayers, trilayers, etc. We have a collaboration planned with a group at Simon Frasier University in Canada to study the magnetic properties of these novel materials and we expect to set up other collaborative investigations of other physical properties in the near future.

2. Microcomposition and Microstructure of Thin Films

(A. J. Melmed)

This effort is directed to the measurement of microcomposition in relation to microstructure of thin layers on well-characterized solid substrates and the determination of interfacial diffusion. The methods of investigation for these purposes are field-ion microscopy (FIM), capable of qualitative atomic structural determination, and atom-probe analysis for compositional depth-probing on an atomic scale. Both in situ and ex situ specimen preparation will be used in order to vary widely the layer-formation process parameters.

Further progress was made towards understanding the atomic structure of the recently discovered icosahedral phase of rapidly solidified Al_6Mn, produced in thin ribbon form. Extensive analysis of FIM images obtained last year indicated the presence of a hierachy of cluster or grain sizes from about 1.3 to at least 8 nm in width, and two sizes of discrete pentagonal arrays, each of five atoms. These features agree qualitatively with recently proposed models which describe the structure in terms of an aggregation of small icosahedra (see Fig. 4.1). Furthermore, the unusually irregular appearance of the FIM micrographs is explainable on the basis of such cluster models. Computer simulations of selected areas of the FIM images, based on a cluster model and performed by Dr. H. A. Fowler of the NBS Center for Applied Mathematics, exhibited good qualitative agreement with the experimental images. Additional support for the cluster type of structural model comes from some new transmission-electron-microscopy (TEM) results obtained in collaboration with Dr. M. J. Kaufmann of the NBS Metallurgy Division. We have shown that selected-area electron-diffraction patterns from the icosahedral structure contain diffusely scattered intensity, as well as the well-known sharp diffraction features; we have attributed this diffuse intensity to scattering from atoms filling in the necessary small gaps between clusters. Further low-temperature FIM is underway in an attempt to provide a complete description of the atomic structure of the icosahedral phase.

The composition of the icosahedral phase (i-phase) of rapidly solidified Al_6Mn was determined by our general-purpose atom probe FIM in connection with the FIM structural investigation of this new material. The composition of the i-phase was found to be approximately Al_4Mn, in agreement with recently published analytical TEM results.

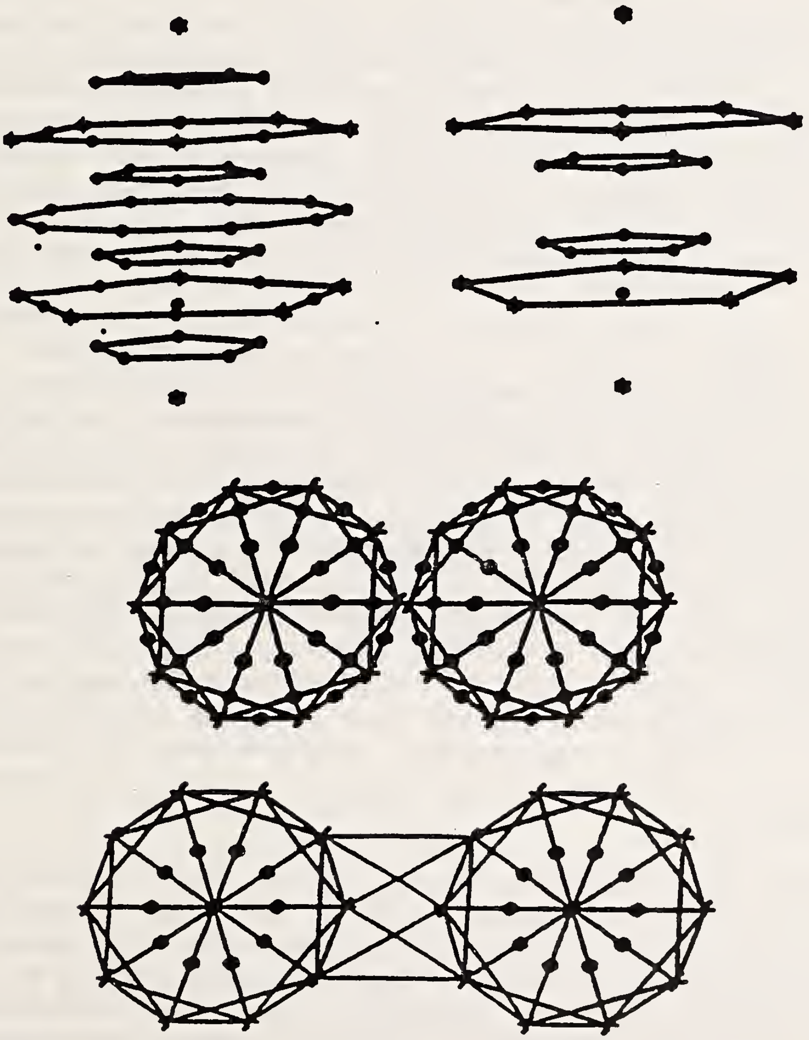


Fig. 4.1 Two proposed cluster models of the icosahedral phase of Al_6Mn. Top: exploded views of the two icosahedral clusters. Middle: top view of one coupling scheme for two icosahedra. Bottom: another coupling scheme. Asterisks indicate Mn atoms and the other symbols indicate Al atoms.

In addition to microcompositional analyses of novel alloys, future efforts will include depth-probing of various layered structures. These will consist of thin film/substrate combinations of metal/metal, metal/semiconductor and metal/glass. The aim will be to determine composition profiles in the films, the interfaces and into the substrates, using the unique analytic capabilities of the atom probe FIM. Initially, specimen preparation for such studies will be done by vapor deposition under well-characterized ambient conditions.

Epitaxial crystal growth of Cr on W and Cr on Re is being studied by field-electron emission microscopy. In both systems, the nucleation and growth, at temperatures sufficiently high to enable rapid surface diffusion of Cr, proceeds as expected, with nucleation occurring at surface steps after about a monolayer of Cr coverage (Stranski-Krastanov growth mode). However, the lateral growth of Cr crystals is inhibited by certain substrate geometries; crystal growth does not extend into (001) planes of W, for example. In addition, a lower-temperature epitaxial growth is found to occur on (001) W, where small 3-D crystals nucleate directly on the clean surface (Volmer-Weber growth mode).

Metal layer deposition on Si is being studied in collaboration with Dr. W. A. Schmidt and Prof. J. H. Block at the Fritz Haber Institut, W. Berlin. Thusfar, we have demonstrated that for thin layers ((3-4 nm) of Au, the method of field-ion appearance spectroscopy can be used to determine the Schottky barrier height for Au/Si. We studied the field ion energy distributions of inert gases (Kr and Ar) for Au-covered n- and p-type Si(111) specimens. Thin layers of Au were vapor-deposited, with the substrate at 78 K, such that diodes were formed and subsequent electrical charging occurred through the bulk Si. The measured field dependence of the ion distribution onset potential was used to calculate a barrier height of about 0.3 eV for the p-type Si, in good agreement with the literature value of 0.34 eV. Similar measurements for n-type Si are presently being completed and the work is being extended to other metals. The method is being considered as a possible route to further understanding of the controversial nature of metal/semiconductor Fermi-level pinning.

The NBS Electrodeposition Group has been producing layered material by controlled alternate deposition of Ni and Cu in layers intended to be uniformly some 10-20 nm thick. There are several questions concerning the resulting material which we have begun to address using FIM and atom-probe methods. These are: (1) uniformity of the layer thickness, (2) composition of the two types of layers, (3) defect densities in the layers, and (4) coherence of layer interfaces. Thusfar, we have developed specimen preparation techniques, done initial FIM studies to address qualitatively points (1) and (4) above, and established feasibility of doing atom probe analysis.

3. Theory of Novel Two-Dimensional Materials
(S. M. Girvin and M. J. DeWeert)

Recent progress in the fabrication of novel two-dimensional materials has generated intense theoretical and experimental activity in several areas of condensed matter physics. The present project is addressing theoretical issues in three of these areas: artificial semiconductor superlattices, thin metallic films, and a new field now being referred to as 'meso-scale' physics. Each of these will be discussed in turn below.

The quantum Hall effect is one of the most remarkable phenomena discovered in recent years. It occurs in the two-dimensional electron gas (inversion layer) which can be formed in artificially layered semiconductor systems. One finds at high magnetic fields and low temperatures that electron transport in the inversion layer becomes nearly dissipationless and that the Hall conductance takes on universal quantized values e^2i/h where e is the fundamental charge, h is the Planck constant and i is an integral or rational fractional quantum number. This discovery has had profound implications for both fundamental physics and electrical resistance metrology.

The theory project has in the recent past focused strongly on the quantum Hall effect. In addition to providing support for the experimental effort in the NBS Electricity Division, recent accomplishments include development of a rather complete and quantitative theory of the collective excitations in the fractional regime (done in collaboration with Dr. A. H. MacDonald, National Research Council, Ottawa and Dr. P. M. Platzman of AT&T Bell Laboratories, Murray Hill) and the editing of a book giving the first major review of the field (done in collaboration with Prof. R. E. Prange of the University of Maryland). The latter is based on a ten-part lecture series which enjoyed a large attendance from academic, governmental and industrial organizations in the greater Washington area (see section 2.c.3(a)).

Theoretical developments in the area of the fractional Hall effect have proceeded rapidly and a general picture of how the effect arises from Coulomb correlations is now in hand. The one remaining area which has been poorly explored is that of the statistical mechanics at finite temperatures and the question of whether the fractional state is reached via a phase transition (and hence whether or not there is an order parameter in the problem). Our work on the collective-excitation spectrum showed that there exists a deep analogy between the fractional Hall effect and superfluidity in helium films. This analogy has been pursued further to develop a phenomenological Landau-Ginsburg theory describing the statistical mechanics and which exhibits, in a natural way, fractionally-charged quantized vortices. In collaboration with Dr. R. B. Laughlin of Stanford University, this phenomenological theory is now being given a microscopic justification.

Until the next generation of experiments arrives to bring new challenges to theorists, it is probably safe to say that theoretical developments in the fractional Hall effect have reached at least a preliminary stage of maturity and it will prove useful to begin exploring other aspects of novel two-dimensional materials. Some new directions which are now getting under way are discussed below.

There has been considerable interest in recent years in the electronic-transport properties of thin metallic films, particularly in connection with weak Anderson localization and the interplay between superconductivity and localization. A related problem is superfluidity in layers of helium adsorbed on a disordered substrate. A fascinating experimental result which has not yet been fully understood has been obtained recently by Goldman et al. at the University of Minnesota. They find in partially-oxidized tin films that if the high-temperature sheet resistance of the film exceeds a critical value R_c of order $h/(2e)^2$, the system becomes insulating at low temperatures. However, if the high-temperature sheet resistance is less than R_c, the system becomes superconducting at low temperatures. This remarkable result is believed to be due to macroscopic quantum tunneling effects in the superconducting grains in the presence of dissipation. These questions are being further explored. A useful spin-off of studies of tunneling in the presence of dissipation will be a greater understanding of how to treat problems such as hydrogen and muon diffusion in metals and at the surface of metals.

A newly developed field known as 'meso-scale physics' is generating intense experimental and theoretical activity. Modern lithographic techniques allow one to produce small one- and two-dimensional structures which are smaller than the inelastic mean free path at low temperatures. This leads to a variety of interesting coherence effects even though the elastic mean free path may be small on the scale of the system size. This is because phase information is scrambled but not destroyed by elastic scattering. One of the most interesting effects is the existence of universal conductance fluctuations in which any small perturbation (displacing a single impurity, adding one quantum of magnetic flux to the sample, etc.) causes a change of order e^2/h in the conductance, independent of the sample size and dimensionality. As an alternative to the usual diagrammatic techniques, this problem will be investigated using replica field theory methods. Another problem of particular interest in one-dimensional structures (quantum well wires) is the nature of Coulomb correlations at low temperatures. This is being investigated in collaboration with Dr. A. H. MacDonald using variational wave functions analogous to those developed for the quantum Hall effect.

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 all 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 combining ultrahigh-vacuum surface-science techniques with state-of-the-art spectroscopy in several experiments involving electron-stimulated desorption (ESD), photon-stimulated desorption (PSD), and ion sputtering. Specifically, we propose to use multiphoton ionization and other laser-spectroscopic techniques to detect and analyze neutral species released from crystalline surfaces by electron, photon, and ion bombardment. These measurements will provide unique insights into the mechanisms of desorption induced by both electronic transitions and by direct momentum transfer. Measurements of neutral angular distributions will be compared directly with ion angular distributions using a new two-dimensional display analyzer, thus providing a detailed description of competing desorption pathways.

We are performing work in three project areas. First, we are designing 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 collaborating with scientists at Vanderbilt University on a similar experiment in which neutral species desorbed from surfaces by electron or photon excitation will be detected and characterized. This experiment may lead later to similar work at NBS. Finally, 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.B, 3.D, 3.I and 3.J.

1. Energy States of Neutral Species Sputtered from Surfaces (J. Fine)

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; (3) analyzing the emitted secondary-electron energy distributions. Progress made during the first year of this project in each of these areas is described below.

(a) Laser Spectroscopy of Sputtered Atoms and Ions

In collaboration with Drs. J. D. Fassett (NBS Inorganic Analytical Research Division) and Dr. J. Boulmer (NBS Inorganic Analytical Research Division and Université Paris, France), a new series of experiments has been designed to determine the kinetic energy distributions of specific sputtered atoms (ions) and their states of excitation. 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 sates. Resonance multiphoton laser-ionization schemes have been developed to detect sputtered atoms in specific excited states.

Construction began on a new instrument this past year. A stainless steel ultrahigh vacuum (uhv) chamber was constructed at NBS to contain a sample manipulator, pulsed ion gun, pulsed time-of-flight (TOF) extraction optics and detector, Auger-electron spectrometer, and windows for the two ultraviolet laser beams. Some of this instrumentation is described below.

The UHV sample manipulator incorporates the usual XYZ translations and rotation about the Z axis, as well as a special sample holder which permits rotating the sample about an axis in the plane of the surface (the laser beams are parallel to this axis). This sample rotation, in conjunction with the two ion gun ports directed at different angles with respect to the target surface, will allow us to vary the ion beam angle from near-grazing to near-normal incidence.

The ion gun used can produce a 1 mm wide beam with about 0.5 µA current in the 1-5 keV energy range. We have designed and built an additional high-speed beam switcher that can turn the bean on and off in about 50 ns (rise time). The complete pulsed ion gun can be mechanically aligned with the target.

The TOF analyzer, which we designed and built, was optimized for maximum collection efficiency; it is short (about 5 inches long) and has apertures 1.2 inches in diameter. The extraction and collection grids are spherical and operate as a modified Pierce lens in order to increase the collection of sputtered ions which are ejected with a cosine-type distribution from the surface. Pulsed fields are applied to these spherical grids to accelerate those sputtered ions produced by the incident pulse of ions from the gun. Electrons also can be measured with this TOF analyzer using reversed fields. Both ions and electrons, as well as x-rays, are detected by a microchannel plate TOF detector.

Data acquisition of TOF spectra is accomplished with a transient digitizer oscilloscope with internal signal averaging that permits spectra with high time resolution (10 ns) to be acquired over periods of many microseconds.

The completed system as described above was put into operation in early July, 1986. Using a polycrystalline magnesium target with pulsed ion beam and TOF extraction, we have observed the three Mg ion isotopes, MgO^+, virtually no Mg^{++}, and ejected electrons. The system seems to work very well with high sensitivity and good time resolution; calculated flight times are in good agreement with those measured. Work is in progress to characterize and understand the details of the spectra observed.

(b) Auger-Electron De-Excitation of Sputtered Atoms

In collaboration with Drs. C. Le Gressus and J. P. Duraud (Centre d'Etudes Nucleaires de Saclay, France), a series of measurements were begun 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. Preliminary results indicate a very marked change in the total Auger-electron 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 of underlying atoms by the outermost surface atom of a given string).

An example of our results is shown in Fig. 4.2 where we show the total Auger yield and the ratio of the atomic-like and band-like Auger-electron emission as a function of azimuthal angle. Both the total signal and the ratio show minima at the same angles. This result strongly suggests that most of the collisional inner-shell excitation, for an ion beam aligned with an atom string, occurs deep below the surface so that the probability of an atom being sputtered before it can deexcite is low.

Measurements of this phenomena are still in progress in Saclay; we anticipate extending this investigation of collisional excitation processes in single-crystal solids at NBS.

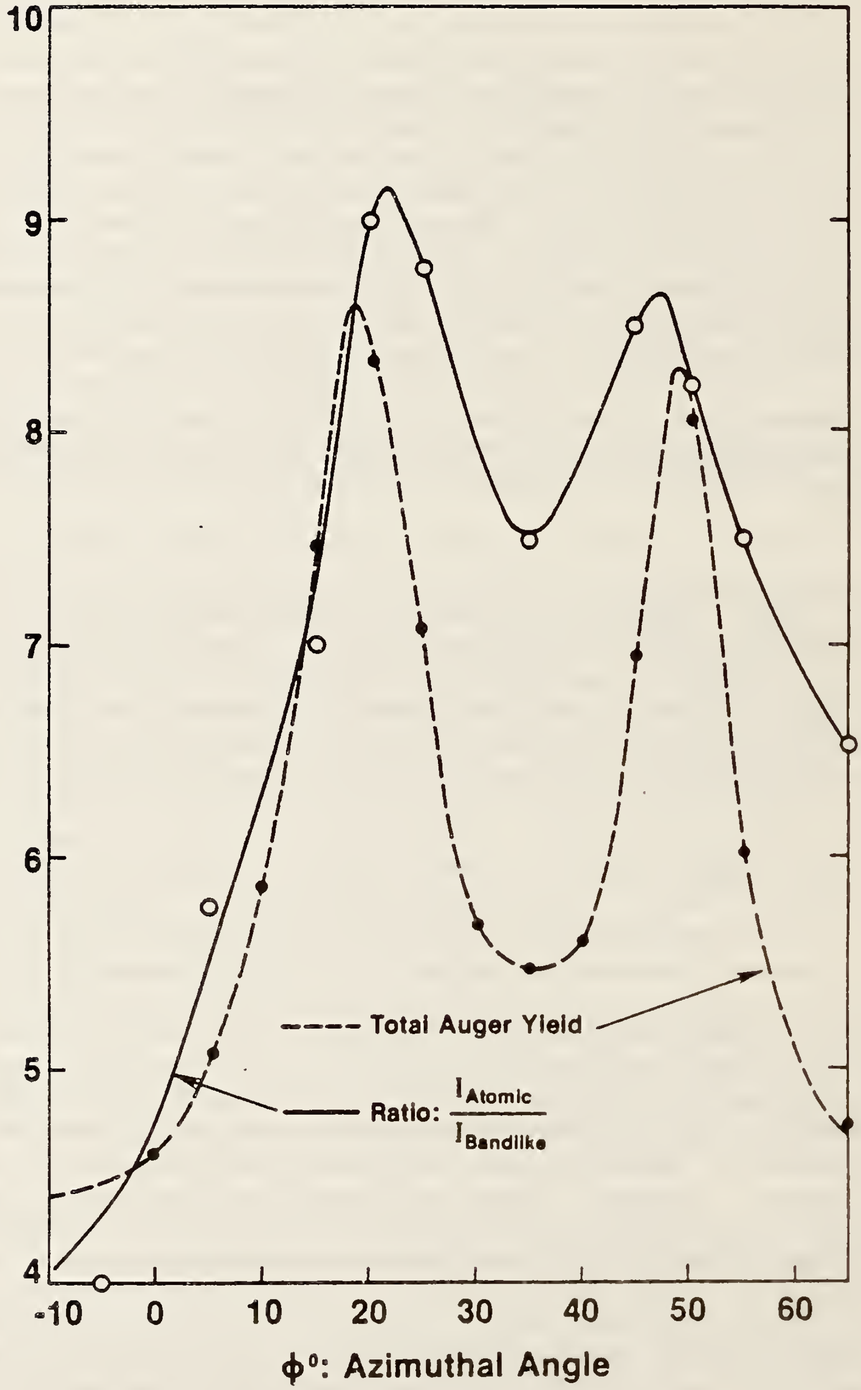


Fig. 4.2 Plot of the total Auger yield and the ratio of atomic-like and band-like Auger-electron emission from an Al(100) surface bombarded by 4 keV argon ions as a function of the angle of rotation of the sample about its normal.

(c) Secondary-Electron Energy Distributions Due to Ion Bombardment

In collaboration with Dr. I. Terzic (Boris Kidric Institute, Belgrade, Yugoslavia), an experiment has been designed to study the secondary-electron energy distributions that result from Ga^+-Ga collision at ion energies from 20 to 60 keV. Previous measurements at NBS indicate that collisional excitation may account for the high energy (> 100 eV) emitted electrons observed. An apparatus is presently under construction in Belgrade which will enable us to examine inner-shell excitation thresholds in this system.

2. Electron- and Photon-Stimulated Desorption of Neutral Species Using Laser Detection Techniques

(T. E. Madey)

In a collaborative effort with Prof. N. Tolk at Vanderbilt University, we have initiated measurements to characterize the mechanisms by which neutral species are excited and desorbed from surfaces using electron- and photon-stimulated desorption (ESD/PSD).

The majority of species removed from surfaces via ESD and PSD are neutral atoms and molecules. However, virtually all measurements of the energy and angular distributions of desorbing species have been of the more-easily-detected minority ionic species; only recently have laser techniques been applied to the detection of neutral species. Most measurements made to data have concentrated on radiation-induced decomposition of bulk solids (e.g., alkali halides).

Our experiments are designed to search for and characterize the ESD of both ground-state and excited Li and Na atoms desorbed from fractional-monolayer films of Li and Na adsorbed on both clean and oxygen-covered W(100) surfaces. We will employ laser-induced fluorescence to detect the ground-state neutrals, and light emission following metastable deexcitation to detect excited neutral species. Depending on signal levels, a later stage of the measurements involve the use of synchrotron radiation to determine the threshold energies for desorption via photon-stimulated desorption. The choice of experimental systems for these first studies (Na, Li on O/W(100)) is based on previous related experiments involving ion desorption and the theoretical interest in these conditions.

3. Angular and Energy Distributions of Desorbed Ionic Species

(R. Stockbauer and T. E. Madey)

We have designed a special analyzer to measure simultaneously the angular, energy, and mass distributions of ions desorbed from surfaces. The analyzer will in addition be used for angle-resolved photoemission.

The construction and assembly of a new angle-resolving, display-type ion and electron energy analyzer is completed. This instrument is based on the IBM design of Dr. D. Eastman. The analyzer is undergoing initial testing in the laboratory using an electron impact source. The video processing software which will display the two-dimensional data in an appropriate form is also being developed during this initial testing. Similar software is being used to process two-dimensional data from a video display system installed for our ESDIAD project (section 3.B).

The initial test experiments using the new analyzer will be a series of quantitative ESDIAD (Electron Stimulated Desorption Ion Angular Distributions) studies of small molecules adsorbed on metal surfaces. The test systems will include NH_3 and H_2O on Ni(111), as well as the coadsorption of each of these molecules with electronegative (O, S, Br) and electropositive (K, Na) additives. Some of these systems have been studied previously but a number of longstanding and important fundamental questions remain for which the new analyzer can provide quantitative answers. Experiments are planned to address the following questions.

- What are the angular profiles of the ion beams?
- Is there quantitative structural information in individual ESDIAD beam shapes?
- How do the angular profiles of individual ion beams vary with adsorption coverage and the presence of coadsorbates?
- How do the ESDIAD patterns vary as a function of electron excitation energy?
- Are the ion energy distributions a function of desorption angle?
- How do measured ion trajectories compare with theory?

In later experiments at the NBS synchrotron radiation source SURF-II, the analyzer will be used in angle-resolved photon-stimulated desorption studies of clean and adsorbate-covered oxide surface. Desorption thresholds and energy dependences will be correlated with angle-resolved electron spectroscopic measurements (ultrviolet photoelectron spectroscopy, constant-initial-state, constant-final-state measurements). These measurements will be the first detailed, angle-resolved mechanistic studies of photon-induced bond-streaking processes at surfaces.

5. PUBLICATIONS

(a) Publications of Past Year

Anton, A. B., Avery, N. R., Madey, T. E. and Weinberg, W. H., "The Coadsorption of Nitrogen with Carbon Monoxide and Oxygen on the Ru(001) Surface: Local Chemical Interactions in Mixed Layers," J. Chem. Phys. 85, 507 (1986).

Bange, K., Madey, T. E. and Sass, J. K., "The Structure of the Surface Hydration Shell of Bromide on Ag(110)," Surf. Sci. 162, 252 (1985).

Brennan, S., Cowan, P. L., Jach, T., LaVilla, R., Perera, R. C. C. and Winick, H., "Optical and Spectral Characteristics of an Insertion Device Used Both as a Wiggler and an Undulator," Nucl. Inst. & Meth. A 246, 37 (1986).

Burgess, Jr., D. R., Mantell, D. A., Cavanagh, R. R. and King, D. S., "Dynamics of the Laser-Induced Thermal Desorption of Nitric Oxide from a Platinum Foil," J. Chem. Phys. 85, 3123 (1986).

Casassa, M. P., Heilweil, E. J., Stephenson, J. C. and Cavanagh, R. R., "Time Resolved Measurements of Vibrational Relaxation at Surfaces," J. Elect. Spec. 38, 257 (1986).

Cowan, P. L., Brennan, S., Deslattes, R. D., Henins, A., Jach, T. and Kessler, E. G., "A High Energy Resolution X-Ray Spectroscopy Synchrotron Radiation Beamline for the Energy Range 800-5000 eV," Nucl. Inst. & Meth. A 246, 154 (1986).

Cox, D. F., Semancik, S. and Szuromi, P. D., "Summary Abstract: Structural and Electron Properties of Clean and Water-Dosed SnO_2 (110)," J. Vac. Sci. Tech. A 4, 627 (1986).

Egelhoff, Jr., W. F., "The XPS Searchlight Effect: A New Analytical Tool for Layered Structures, Epitaxy, and Interfaces," Mat. Res. Soc. Symp. Proc. 37, 443 (1985).

Egelhoff, Jr., W. F., "Summary Abstract: X-Ray Photoelectron and Auger Electron Forward Scattering: A Structural Probe for Studying Ultra-Thin Epitaxial Films and Interfaces," J. Vac. Sci. Tech. A 4, 758 (1986)

Erickson, N. E. and Powell, C. J., "Imaging Properties and Energy Aberrations of a Double-Pass Cylindrical-Mirror Electron Energy Analyzer," J. Vac. Sci. Tech. A 4, 1551 (1986).

Erickson, N. E. and Powell, C. J., "Characterization of the Imaging Properties of a Double-Pass Cylindrical-Mirror Analyzer," Surf. & Inter. Anal. 9, 111 (1986).

Gadzuk, J. W. and Holloway, S., "Charge Transfer and Vibrational Excitation in Molecule-Surface Collisions: Trajectorized Quantum Theory," Physica Scripta 32, 413 (1985).

Gadzuk, J. W., "Dynamics of Molecular Processes at Surfaces: Vibrational Lineshapes and Spectra," J. Elec. Spect. 38, 233 (1986).

Gadzuk, J. W. and Holloway, S., "Collision Induced Dissociation of Diatomic Molecules on Surfaces: A Charge Transfer Mechanism," J. Chem. Phys. 84, 3502 (1986).

Gadzuk, J. W. and Holloway, S., "Comments on the Observation of Vibrational Excitation in Gas-Surface Collisions," Phys. Rev. B. 33, 4298 (1986).

Girvin, S. M., MacDonald, A. H. and Platzman, P. M., "Magneto-Roton Theory of Collective Excitations in the Fractional Quantum Hall Effect," Phys. Rev. B. 33, 2481 (1986).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R. and Stephenson, J. C., "Time-Resolved Vibrational Energy Relaxation of Surface Adsorbates," J. Vac. Sci. Tech. B 3, 1471 (1985).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R. and Stephenson, J. C., "Vibrational Energy Relaxation of Adsorbates on Surfaces," in Ultrashort Pulse Spectroscopy and Applications, M. J. Soileau, ed., International Society for Optical Engineering 533, 15 (1985).

Karikorpi, M., Holloway, S. and Gadzuk, J. W., "A Classical Trajectory Surface Hopping Approach to Non-Adiabatic Processes Occurring During Diatom-Surface Scattering," J. Elect. Spect. 39, 223 (1986).

Kirchhoff, W. H., Chambers, G. P. and Fine, J., "An Analytical Expression for Describing Auger Sputter Depth Profile Shapes of Interfaces," J. Vac. Sci. & Tech. A 3, 1666 (1986).

Kurtz, R. L., "The Influence of Surface Structure on Ion Emission From TiO_2," J. Vac. Sci. Tech. A 4, 1248 (1986).

Kurtz, R. L., Stockbauer, R. and Madey, T. E., "Angular Distributions of Ions Desorbing from TiO_2," Nucl. Instr. & Meth. B 13, 518 (1986).

Kurtz, R. L., Usuki, N., Stockbauer, R. and Madey, T. E., "Measurements of Electron Attenuation Lengths in Condensed Molecular Solids," J. Elect. Spect. & Rel. Phenom. 40, 35 (1986).

MacDonald, A. H. and Girvin, S. M., "Collective Excitations of Fractional Hall States in Higher Landau Levels," Phys. Rev. B. 33, 4009 (1986).

MacDonald, A. H. and Girvin, S. M., "Quasi-Particle States and the Fractional Quantum Hall Effect," Phys. Rev. B (Rapid Commun) 33, 4414 (1986).

MacDonald, A. H., Liu, K. L. and Girvin, S. M., "Disorder and the Fractional Quantum Hall Effect: Activation Energies and the Collapse of the Gap," Phys. Rev. B. 33, 4014 (1986).

MacDonald, A. H., Oji, H. C. A. and Girvin, S. M., "Magnetoplasmon Excitations from Partially Filled Landau Levels in Two Dimensions," Phys. Rev. Lett. 55, 2208 (1985).

Madey, T. E., "Electron Stimulated Desorption and its Relation to Molecular Structure at Surfaces," J. Vac. Sci. Tech. A 4, 257 (1986).

Madey, T. E. and Benndorf, C., "Evidence for Molecular Orientations in Coadsorption of CO and K on Ru(001)," Surf. Sci. 164, 602 (1985).

Madey, T. E. and Benndorf, C., "Interactions of CO+K on Ru(001): Structure and Bonding," Surf. Sci. 164, 602 (1985).

Mantell, D. A., Cavanagh, R. R. and King, D. S., "Internal State Distributions of NO Thermally Desorbed from Pt(111): Dependence on Coverage and Co-adsorbed CO," J. Chem. Phys. 84, 5131 (1986).

Melmed, A. J. and Klein, R., "Icosahedral Symmetry in a Metallic Phase Observed by Field Ion Microscopy," Phys. Rev. Lett. 56, 1478 (1986).

Melmed, A. J. and Klein, R., "Long-Range Icosahedral Symmetry in a Metallic Phase Observed by Field Ion Microscopy," Journal de Physique C 2, 287 (1986).

Miškovic, J., Vukanić, and Madey, T. E., "Calculations of Reneutralization Effects in ESDIAD," Surf. Sci. 169, 405 (1986).

Penn, D. R., Apell, S. P. and Girvin, S. M., "Theory of Spin Polarized Secondary Electrons in Transition Metals," Phys. Rev. Lett. 55, 518 (1985).

Platzman, P. M., Girvin, S. M. and MacDonald, A. H., "Conductivity in the Fractionally Quantized Hall Effect," Phys. Rev. B (Rapid Commun) 32, 8458 (1985).

Powell, C. J., editor, "Technical Activities 1985 - Surface Science Division," NBSIR 86-3304 (1985).

Powell, C. J., "The Energy Dependence of Electron Attenuation Lengths," Surf. Inter. Anal. 7, 256 (1985).

Powell, C. J., "Calculations of Electron Inelastic Mean Free Paths from Experimental Optical Data," Surf. Inter. Anal. 7, 263 (1985).

Powell, C. J., "Recent Developments in Quantitative Surface Analysis by Electron Spectroscopy," J. Vac. Sci. Tech. A 4, 1532 (1986).

Powell, C. J. and Seah, M. P., "Surface Chemical Analysis: Report on the VAMAS Project," Surf. Inter. Anal. 9, 79 (1986).

Rush, J. J., Cavanagh, R. R., Kelley, R. D. and Rowe, J. M., "Interaction of Vibrating H Atoms on the Surface of Platinum Particles by Isotope Dilution Neutron Spectroscopy," J. Chem. Phys. 83, 5339 (1985).

Schmidt-May, J., Senf, F., Voss, J., Kunz, C., Flodström, A., Nyholm, R. and Stockbauer, R., "Resonant Electron and Ion Emission and Desorption Mechanisms in Rare Earth Oxides," Surf. Sci. 163, 303 (1985).

Shinn, N. D., "Synchrotron Photoemission Evidence for 'Lying-Down' CO on Cr(110)," J. Vac. Sci. Tech. A 4, 1351 (1986).

Shinn, N. D. and Madey, T. E., "CO Chemisorption on Cr(110): Evidence for a Precursor to Dissociation," J. Chem. Phys. 83, 5928 (1985).

Shinn, N. D. and Madey, T. E., "Chemisorption and Dissociation of O_2 on Cr(110): An EELS/ESDIAD Study," Nucl. Instr. & Meth. B 13, 537 (1986).

Shinn, N. D. and Madey, T. E., "Electronic Structure Changes for 'π-bonded' CO Chemisorbed on Cr(110)," Phys. Rev. B 33, 1464 (1986).

Stockbauer, R., Kurtz, R. L., Usuki, N. and Madey, T. E., "The Use of Synchrotron Radiation to Measure Electron Attenuation Lengths in Condensed Molecular Solids," Nucl. Instr. & Meth. A 246, 820 (1986).

Wang, F. W., Lowry, R. E. and Cavanagh, R. R., "Picosecond Excimer Fluorescence Spectroscopy: Applications to Local Motions of Polymers and Polymerization Monitoring," Polymer 26, 1657 (1985).

Wax, M. J., Cavanagh, R. R. and Rush, J. R., "A Neutron Scattering Study of Zeolite Rho," J. Phys. Chem. 90, 532 (1986).

Wax, M. J., Kelley, R. D. and Madey, T. E., "Ethane Hydrogenolysis Catalyzed by W(100)," J. Catalysis 98, 487 (1986).

(b) Publications in Progress

Bange, K., Madey, T. E. and Stuve, E. M., "Summary Abstract: Coadsorption of Water and Oxygen on Ag(110): A Study of the Interactions Among H_2O, OH, and O," J. Vac. Sci. Techn. (submitted).

Bange, K., Stuve, E. M., Madey, T. E. and Sass, J. K., "The Adsorption of Water and Oxygen on Ag(110): A Study of the Interactions Among Water Molecules, Hydroxyl Groups, and Oxygen Atoms," Surf. Sci. (in press).

Burgess, Jr., D. R., Cavanagh, R. R. and King, D. S., "Accommodation of Rotational Energy in the Coadsorbed System Ammonia/Nitric Oxide on Pt(111)," J. Vac. Sci. Tech. A (submitted).

Burgess, Jr., D. R., Cavanagh, R. R. and King, D. S., "Kinetics and Dynamics of the Ammonia/Nitric Oxide Coadsorbate System on Pt(111)," Surf. Sci. (submitted).

Cavanagh, R. R., Casassa, M. P., Heilweil, E. J. and Stephenson, J. C., "Vibrational Relaxation of Adsorbed Molecules: Comparison with Model Compounds," J. Vac. Sci. Tech. A (submitted).

Cavanagh, R. R., Rush, J. J. and Kelley, R. D., "Neutron Inelastic Scattering: Vibrational Spectroscopy of Adsorbed Molecules on Surfaces," in *Vibrational Spectroscopy of Molecules on Surfaces* edited by J. T. Yates, Jr. and T. E. Madey, Vol. 1 of *Methods of Surface Characterization*, Plenum Press Publishing Co., New York, (in press).

Cowan, P. L., Brennan, S., Jach, Terrence, Bedzyk, M. J. and Materlik, G., "Observations of the Diffraction of Evanescent X-Rays at a Crystal Surface," Phys. Rev. Lett. (submitted).

Egelhoff, Jr., W. F., "Core-Level Binding-Energy Shifts in Solids and at Surfaces," Surf. Sci. Repts. (submitted).

Egelhoff, Jr., W. F., "XPS and Auger Forward Scattering in Epitaxial Films," Physics News Section of Physics Today (in press).

Egelhoff, Jr., W. F., "A Born-Haber Cycle Analysis of Core-Level Shifts for Atomic C, N, and O on Ni(100)," J. Vac. Sci. Tech. A (submitted).

Egelhoff, Jr., W. F., "The Relative Importance of the Major Factors Contributing to the Angular Variation of Intensities in XPS and AES of Crystals," J. Vac. Sci. Tech A (submitted).

Erickson, N. E., "Modified Structural Proposal for the Si(111)-(7x7) Reconstruction Based on an Analysis of Chemisorption Data," Phys. Rev. B. (submitted).

Erickson, N. E., Powell, C. J. and Ramaker, D. E., "New Correlation Effects Observed for Inner-Shell Excitations in Titanium and Vanadium," Phys. Rev. Letters (submitted).

Gadzuk, J. W., "Excitation Mechanisms in Vibrational Spectroscopy of Molecules on Surfaces," in Vibrational Spectroscopy of Molecules on Surfaces" edited by J. T. Yates, Jr. and T. E. Madey, Vol. 1 of Methods of Surface Characterization, Plenum Press Publishing Co., New York (in press).

Gadzuk, J. W., "Anisotopic Charge Transfer Rates in the Scattering of Oriented Atoms or Molecules from Surfaces," Surf. Sci. (in press).

Gadzuk, J. W., "Vibrational Excitation in Molecule-Surface Collisions: Analytical Modeling vs. Classical Trajectories," J. Chem. Phys. (submitted).

Gadzuk, J. W., "Core Level Spectroscopy: A Dynamics Perspective," Physica Scripta (in press).

Gadzuk, J. W., "Role of Site Conversion in Vibrational Spectroscopy of Adsorbed Molecules," J. Opt. Soc. Am. (in press).

Gadzuk, J. W. and S. Holloway, "Dynamics of Molecular Collisions with Surfaces: Excitation, Dissociation, and Diffraction," Nucl. Instr. & Meth. B. (submitted).

Gadzuk, J. W., "Dynamics of Dissociative Adsorption and Vibrational Excitation in Molecule-Surface Collisions," J. Vac. Sci. Tech. A (submitted).

Gadzuk, J. W., "Selectivity of Elementary Molecular Processes in Molecule-Surface Collisions," Phys. Rev. Letters (submitted).

Gadzuk, J. W., "Intramolecular Dynamics in Molecule-Surface Collisions: Excitation, Dissociation, and Selectivity of Reactivity," Surf. Sci. (submitted).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R. and Stephenson, J. C., "Population Lifetimes of OH(v=1) and OD(v=1) Stretching Vibrations of Alcohols and Silanols in Dilute Solution," J. Chem. Phys. (in press).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R. and Stephenon, J. C., "Vibrational Energy Decay of Surface Adsorbates," Proceedings of the 1985 Conference on Time-Resolved Vibrational Spectroscopy, Springer-Verlag (in press).

Holloway, S., Karikorpi, M. and Gadzuk, J. W., "Dynamics of Molecular Collisions with Surfaces: Excitation, Dissociation, and Diffraction," Nucl. Instr. & Meth. (submitted).

Jach, T., Kirkland, J. P., Wolf, P. and Neiser, R., "A Harmonic Rejection Scheme for X-Ray Monochromators," Nucl. Instr. & Meth. (submitted).

Jones, T. S., Holloway, S. and Gadzuk, J. W., "Theoretical Study of the Vibrational Lineshape for CO/Pt(111)," Surf. Sci. (submitted).

Kaufman, M. J. and Melmed, A. J., "Evidence for Structural Disorder in the Icosahedral Phase," The Philosophical Magazine (submitted).

King, D. S. and Cavanagh, R. R., "Final-State Resolved Studies of Molecule-Surface Interactions, Chemistry and Structure at Interfaces," New Laser and Optical Techniques, Verlag Chemie, Deerfield Beach, FL, 1986 (in press).

Kurtz, R. L., "Stimulated Desorption Studies of Defect Structure on TiO_2," Surf. Sci. (in press).

Kurtz, R. L. and Henrich, V. E., "Surface Electronic Structure and Chemisorption on Corundum Transition Metal Oxides: αFe_2O_3," Phys. Rev. B. (submitted).

Kurtz, R. L., Stockbauer, R., Nyholm, R., Flodström, A. and Senf, F., "Photon Stimulated Desorption Induced by Core Exciton States in MgO," J. Vac. Sci. & Tech. A (submitted).

Kurtz, R. L., Stockbauer, R., Nyholm, R., Flodström, A. and Senf, F., "Core Exciton Induced Desorption from MgO," Physical Review Letters (submitted).

Kurtz, R. L., Stockbauer, R. and Madey, T. E., "Site Specificity in Stimulated Desorption from TiO_2," J. Vac. Sci. Tech. (in press).

Larsson, C. U. S., Johnson, A. L., Flodström, A. and Madey, T. E., "Structure of H_2O Adsorption on Planar and Stepped Si(100)2x1," J. Vac. Sci. Tech. (submitted).

Madey, T. E., "Mechanisms and Applications of Electron Stimulated Desorption in Surface Science," Vacuum TAIP (in press).

Madey, T. E., "Electron and Photon Stimulated Desorption: Probes of Structure and Bonding at Surfaces," Science (in press).

Melmed, A. J., "Field Emission Microscopy - Trends and Perspectives," Chemistry and Physics of Solid Surfaces, Springer-Verlag (in press).

Melmed, A. J., "Progress in Understanding Atomic Structure of the Icosahedral Phase," Journal de Physique (in press).

Melmed, A. J., Schmidt, W. A., Block, J. H., Naschitzki, M. and Lovisa, M., "Effects of a Gold Shank-Overlayer on the Field Ion Imaging of Silicon," Journal de Physique (in press).

Oji, H. C. A., MacDonald, A. H. and Girvin, S. M., "Superlattice Magnetoroton Bands," Phys. Rev. B (submitted).

Powell, C. J., "The Energy Dependence of Electron Inelastic Mean Free Paths," Surf. Interface Anal. (submitted).

Powell, C. J. and Erickson, N. E., "Comparison of L_3-Shell Binding Energies in Six 3d Metals Measured by X-Ray Photoelectron Spectroscopy, Appearance-Potential Spectroscopy, and Electron Energy-Loss Spectroscopy, Phys. Rev. B (submitted).

Schmidt, W. A., Melmed, A. J., Naschitzki, M. and Lovisa, M. F., "Field Ion Appearance Spectroscopy of Gold Overlayers on Silicon," Journal de Physique (in press).

Semancik, S., Doering, D. L. and Madey, T. E., "Coadsorption of Water and Lithium on the Ru(001) Surface," Surf. Sci. (in press).

Shinn, N. D. and Madey, T. E., "Stimulated Desorption from CO Chemisorbed on Cr(110)," Surf. Sci. (submitted).

Shinn, N. D. and Madey, T. E., "Oxygen Chemisorption on Cr(110): I. Dissociative Adsorption," Surf. Sci. (in press).

Shinn, N. D. and Madey, T. E., "Oxygen Chemisorption on Cr(110): II. Evidence for Molecular O_2(ads)," Surf. Sci. (in press).

Shinn, N. D. and Szuromi, P. D., "Alkali Interactions over Cu(311)," J. Vac. Sci. Tech. A (submitted).

Szuromi, P. D., Kelley, R. D. and Madey, T. E., "The Influence of Sulfur on Methanation on W(110)," J. Phys. Chem. (submitted).

Szuromi, P. D., Kelley, R. D. and Madey, T. E., "The Effect of Sulfur on the Methanation of CO over W(110)," J. Phys. Chem. (in press).

Udovic, T. J., Cavanagh, R. R., Rush, J. J., Stucky, G. D., Jones, D., Corbin, D. R. and Wax, M. J., "Neutron Scattering as a Probe of Adsorbate Dynamics: Ammmonia in Zeolite Rho," J. Phys. Chem. (submitted).

Udovic, T. J. and Kelley, R. D., "Neutron Scattering Studies of Hydrogen in Catalysts," to appear in Hydrogen in Catalysis: Theoretical and Practical Aspects, Z. Paal and P. G. Menon, eds., Marcel Dekker, Inc., New York, New York, 1986, (submitted).

Yates, Jr., J. T., Madey, T. E. and Campuszano, J. C., "The Chemisorption of Carbon Monoxide by the Transition Metals," The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, D. A. King and D. P. Woodruff, eds., Elsevier (in press).

c) Recent Publications of New Staff Members Resulting From Previous Positions (Burgess, DeWeert, Johnson and Steigerwald)

Burgess, Jr., D. R., Stair, P. C. and Weitz, E., "Calculations of the Surface Temperature Rise and Desorption Temperature in Laser-Induced Thermal Desorption," J. Vac. Sci. Technol. A 4, 1362 (1986).

DeWeert, M. J. and Arnold, G. B., "Superconducting-Quasi Particle Interface States," Phys. Rev. Lett. 55, 1522 (1985).

Hitchcock, A. P., Newbury, D. C., Ishii, I., Stöhr, J., Horsely, J. A., Redwing, R. D., Johnson, A. L., and Sette, F., "Carbon K-Shell Excitation of Gaseous and Condensed Cyclic Hydrocarbons: C_3H_6, C_4H_8, C_5H_8, C_6H_{10}, C_5H_{10}, C_6H_{12}, and C_8H_8," J. Chem. Phys. (in press).

Horsley, J. A., Stöhr, J., Hitchcock, A. P., Johnson, A. L. and Sette, F., "Resonances in the K Shell Excitation Spectra of Benzene and Pyridine: Gas Phase, Solid and Chemisorbed States," J. Chem. Phys. 83, 6099 (1985).

Johnson, A. L., Muetterties, E. L., Sette, F. and Stöhr, J., "Chemisorption Geometry of Pyridine on Pt(111) by NEXAFS," J. Phys. Chem. 89, 4071 (1985).

Sette, F., Stöhr, J., Kollin, E. B., Dwyer, D. J., Gland, J. L., Robbins, J. L. and Johnson, A. L., "Na Induced Bonding and Bond Length Changes for CO on Pt(111): A Near Edge X-Ray Absorption Fine Structure Study," Phys. Rev. Lett. 54, 935 (1985).

Steigerwald, D. A., Miller, S. J. and Wynblatt, P., "Anisotropy of Surface Composition in a Ni-Au Alloy," Surf. Sci. 155, 79 (1985).

Wynblatt, P. and Steigerwald, D. A., "Equilibrium Segregation to Terraces and Steps," Surf. Sci. 150, 289 (1985).

6. TALKS

Burgess, Jr., D. R. F., "Calculations of the Surface Temperature Rise and Desorption Temperature in Laser-Induced Thermal Desorption," American Vacuum Society Meeting, Houston, TX, November 20, 1985.

Burgess, Jr., D. R. F., "Laser-Excited Fluorescence Measurements of Rotational and Translational Energy Distributions of NO Desorbed from Platinum by Laser-Induced Thermal Desorption," American Vacuum Society Meeting, Houston, TX, November 21, 1985.

Burgess, Jr., D. R. F., "Laser-Excited Fluorescence Measurements of Rotational and Translational Energy Distributions of NO Desorbed from Platinum by Laser-Induced Thermal Desorption," American Physical Society Meeting, Las Vegas, NV, April 2, 1986.

Burgess, Jr., D. R. F., "Dynamical Interactions of Molecules with Surfaces," Applied Physics Division Seminar, U.S. Army Harry Diamond Laboratories, April 22, 1986.

Burgess, Jr., D. R. F., "Dynamical Interactions of Molecules with Surfaces," Materials Science Group Seminar, Johns Hopkins University Applied Physics Laboratory, May 1, 1986.

Burgess, Jr., D. R. F., "Dynamical Interactions of Molecules with Surfaces," Laser Group Seminar, National Bureau of Standards, Gaithersburg, MD, May 12, 1986.

Burgess, Jr., D. R. F., "Dynamics of the Laser-Induced Thermal Desorption of Nitric Oxide from Platinum," 46th Annual Conference on Physical Electronics, University of Texas, Austin, TX, June 16, 1986.

Burgess, Jr., D. R. F., "Dynamical Interactions of Molecules with Surfaces," Chemistry Division Seminar, Naval Research Laboratory, July 31, 1986.

Burgess, D. R. F., "Laser-Induced Thermal Desorption: Characterization of Rotational, Virbrational, and Translational Energy," 192nd American Chemical Society, Anaheim Convention Center, Anaheim, CA, September 10, 1986.

Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Energy Transfer on Surfaces," Davison Division, W.R. Grace & Co., Columbia, MD, November 20, 1985.

Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," University of Chicago, Chicago, IL, February 11, 1986.

Cavanagh, R. R., "Neutron Scattering as a Probe of Surfaces: Adsorbate Bonding and Dynamics," National Measurement Laboratory Review Panel, Gaithersburg, MD, March 6, 1986.

Cavanagh, R. R., "Energy Transfer to Chemical Bonds on Surfaces," Gordon Research Conference on Chemistry of Electronic Materials, Concord, NH, August 20, 1986.

Chambers, G. P., "An Analytical Expression for Auger Sputter Depth Profiles," American Vacuum Society Meeting, Houston, TX, November 21, 1985.

DeWeert, M., "Magnetic Field Dependence of Superconducting Quasi Particle Interface States," American Physical Society Meeting, Las Vegas, NV, April 1, 1986.

DeWeert, M., "Theory of Magnetically-Induced Quasiparticle Bound States at Super Conductor-Ferromagnet Interfaces," Washington Area Statistical Physics Symposium, Gaithersburg, MD May 6, 1986.

Egelhoff, Jr., W. F., "Photoelectron Forward Scattering," American Vacuum Society Meeting, Houston, TX, November 21, 1985.

Egelhoff, Jr., W. F., "Auger and XPS Forward Scattering," American Physical Society Meeting, Las Vegas, NV, March 31, 1986.

Egelhoff, Jr., W. F., "Forward Scattering in XPS as a Tool for Studying Surface Segregation and Interdiffusion in Thin Films," Eastern Electron Spectroscopy Society, W.R. Grace & Company, Columbia, MD, May 8, 1986.

Erickson, N. E., "Study of the Performance Characteristics of Programmable Power Supplies & DVMs: Possible Relevance to Electron Energy Measurements," Eastern Electron Spectroscopy Society, W. R. Grace & Co., Columbia, MD, May 8, 1986.

Erickson, N. E., "Effects of Operational Faults of Programmable Power Supplies and DVMs on Measured Line Positions," Physical Electronics Users' Meeting, Hagerstown, MD, September 23, 1986.

Fine, J., "Characteristics of NBS Standard Reference Material 2135 for Sputter Depth Profile Analysis," European Conference on Applications of Surface and Interface Analysis, Veldhoven, The Netherlands, October 15, 1985.

Fine, J., "Collisionally Excited Auger Electron Emission from Al(100): Dependence on Azimuthal Orientation," Thirteenth Symposium on the Physics of Ionized Gases," Sibenik, Yugoslavia, September 1, 1986.

Gadzuk, J. W., "Common Ground in Surface Science and Electrochemistry," Summary talk at "Fourth Electrochemical Study Group, Fritz-Haber-Institute, Berlin, W. Germany, September 27, 1985.

Gadzuk, J. W., "Dynamics of Molecular Processes at Surfaces: Vibrational Excitation and Dissociation," Solid State Physics Seminar, Institut für Festkörperforschung der KFA Julich, Julich, West Germany, January 22, 1986.

Gadzuk, J. W., "Molecular Dynamics at Surfaces: Harpooning, Vibrational Excitation, and Dissociative Adsorption," Chemistry Department, University of Toronto, Toronto, Canada, February 13, 1986.

Gadzuk, J. W., "Molecular Dynamics at Surfaces: Harpooning, Vibrational Excitation, and Dissociative Adsorption," Physics Department Colloquium, University of Waterloo, Waterloo, Canada, February 14, 1986.

Gadzuk, J. W., "Exciting Vibrations: Scattering and Spectroscopy at Surfaces," Rutgers University, Piscataway, NJ, February 26, 1986.

Gadzuk, J. W., "Dynamics of Molecular Processes at Surfaces: Vibrational Lineshapes and Spectra," American Physical Society Meeting, Las Vegas, NV, March 31, 1986.

Gadzuk, J.W., "Site Conversion, Chaos, and Vibrational Lineshapes of Adsorbed Molecules," Institute of Theoretical Physics Seminar, Chalmers University, Goteborg, Sweden, April 22, 1986.

Gadzuk, J.W., "Exciting Vibrations: Scattering, Spectroscopy, and Wavepackets at Surfaces," Physics Department Colloquium, Rice University, Houston, TX, May 19, 1986.

Gadzuk, J.W., "Exciting Vibrations: Spectroscopy and Scattering at Surfaces," Solid State Seminar, Georgia Institute of Technology, Atlanta, GA, May 21, 1986.

Gadzuk, J. W., "Core Level Spectroscopy: A Dynamics Perspective," Adriatico Research Conference, "Dynamical Screening and Spectroscopy of Surfaces," International Centre for Theoretical Physics, Trieste, Italy, June 25, 1986.

Gadzuk, J. W., "Theoretical Aspects of Electronic, Vibrational, and Rotational Energy Flows in Molecular-Surface Interactions," Sixth International Workshop on Inelastic Ion-Surface Collisions, Argonne National Laboratories, Chicago, IL, August 27, 1986.

Girvin, S. M., "Introduction to the Quantum Hall Effect," University of British Columbia, Vancouver, B.C., Canada, October 17, 1985.

Girvin, S. M., "Wave Functions for the Fractional Quantum Hall Effect," Department of Physics, University of Maryland, College Park, MD, October 28, 1985.

Girvin, S. M., "The Quantum Hall Effect," Physics Department, University of Maryland, College Park, MD, October 29, 1985.

Girvin, S. M., "Collective Excitations in the Fractional Quantum Hall Effect," Physics Department, University of Maryland, College Park, MD, November 11, 1985.

Girvin, S. M., "Unsolved Problems in the Quantum Hall Effect," Physics Department, University of Maryland, College Park, MD, November 18, 1985.

Girvin, S. M., "Collective Excitations in the Fractional Quantum Hall Effect," Institute of Theoretical Physics, Chalmers University, Gothenburg, Sweden, December 4, 1985.

Girvin, S. M., "The Fractional Quantum Hall Effect: Superfluidity, Rotons and Fractionally Charged Vortices", Physics Department, University of Virginia, Charlottesville, VA, February 28, 1986.

Girvin, S. M., "Collective Excitations in the Fractional Quantum Hall Effect: Superfluidity, Phonons, Rotons, and Fractionally Charged Vortices," American Physical Society Meeting, Las Vegas, NV, March 31, 1986.

Girvin, S. M., "The Fractional Quantum Hall Effect: Superfluidity, Phonons, Rotons and Fractionally Charged Vortices," Department of Physics, Massachusetts Institute of Technology, Cambridge, MA, June 3, 1986.

Girvin, S.M., "Collective Excitations in the Fractional Quantum Hall Effect," Fourth Summer Institute of Theoretical Physics, Queen's University, Kingston, Ontario, Canada, July 15, 1986.

Girvin, S.M., "Collective Excitations in the Fractional Quantum Hall Effect," NORDITA Conference on Fundamental Effects in Semiconductors, Copenhagen, Denmark, August 7, 1986.

Girvin, S. M., "Collective Excitations in the Fractional Quantum Hall Effect," Physics Department, University of Notre Dame, IA, September 17, 1986.

Jach, T., "Dynamical Diffraction of X-rays from Crystal Surfaces at Grazing Incidence", Eidigenossiche Technische Hochschule, Zürich, Switzerland, October 15, 1985.

Jach, T., "Dynamical Diffraction of X-rays from Crystal Surfaces," Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Universite Paris-Sud, Orsay, France, November 4, 1985.

Jach, T., "Dynamical Diffraction of X-rays from Crystal Surfaces and Its Use in Surface Science", University of California at Berkeley, Physics Department, Berkeley, CA, November 13, 1985.

Jach, T., "Dynamical Diffraction of X-rays form Crystal Surfaces and Its Use in Surface Science", Applied Physics Department, Stanford University, Stanford, CA, November 14, 1985.

Jach, T., "Dynamical Surface X-ray Diffraction and its Requirements of a High Brightness Source", Advance Light Source Workshop, Lawrence Berkeley Laboratory, Berkeley, CA, November 15, 1985

Jach, T., "Determination of Dispersion Surfaces by Surface Dynamical Diffraction at Grazing Incidence," American Physical Society Meeting, Las Vegas, NV, April 1, 1986.

Jach, T., "Energy-Dependent Intensities of the Kβ Fluorescent Line and its Satellites in Ar Gas," American Physical Society Meeting, Washington, DC, April 30, 1986.

Jach, T., "PIN Diodes as Detectors of X-Ray Reflectivity from Optical Surfaces," Brookhaven Workshop on X-Ray Optics, Brookhaven National Laboratory, Upton, NY, June 2, 1986

Jach, T., "PIN Diodes as X-Ray Detectors for Synchrotron Experiments," National Synchrotron Light Source Annual User's Meeting, Brookhaven National Laboratory, Upton, NY, June 5, 1986.

Jach, T., "Dynamical Diffraction of X-Rays from Crystal Surfaces at Glancing Incidence--A New Surface Science Technique," AT&T Bell Laboratories, Murray Hill, NJ, July 21, 1986.

Johnson, A. J., "Small Particles Chemisorbed on Si(100) Studied by ESDIAD: Water," Gordon Research Conference on Chemistry of Electronic Materials," Concord, NH, August 18, 1986.

Johnson, A. J., "Small Molecules Chemisorbed on Si(100) Studied by ESDIAD: Water," Chemistry Department, Harvard University, Cambridge, MA, August 22, 1986.

Kelley, R. D., "Surface Science and Catalysis," Chemical Engineering Department, Auburn University, Auburn, AL, May 22, 1986.

Kelley, R. D., "Oxygen Atom-Olefin Reactions in Low Temperature Films: Relation to Catalytic Epoxidation of Ethylene," Gordon Research Conference on Catalysis, New London, NH, June 26, 1986.

Kurtz, R. L., "The Influence of Surface Structure on Ion Emission from TiO_2," American Vacuum Society Meeting, Houston, TX, November 20, 1985.

Kurtz, R.L., "Structural Dependence in Stimulated Desorption from TiO_2," American Chemical Society Meeting, New York, NY, April 17, 1986.

Kurtz, R. L., "Measurements of Electron Attenuation Lengths on Condensed Molecular Solids," Georgia Institute of Technology, Atlanta, GA, May 9, 1986.

Madey, T. E., "Mechanism of Applications of Electron Stimulated Desorption in Surface Science," Joint Vacuum Congress of Hungarian, Yugoslavian and Austrian Vacuum Societies, House of Debrecen Committee of the Hungarian Academy of Science, Debrecen, Hungary, October 7, 1985.

Madey, T. E., "The Influence of Surface Additives on the Structure and Chemistry of NH_3 and H_2O on Metal Surfaces," Josef Atilla University, Dept. of Chemistry, Szeged, Hungary, October 10, 1985.

Madey, T. E., "Recent Advances in Electron and Photon Stimulated Desorption," American Vacuum Society Meeting, Houston, TX., November 21, 1985.

Madey, T. E., "Recent Applications of Electron Stimulated Desorption in Surface Structure Determination," Physics Department Colloquium, Cornell University, Ithaca, NY, December 4, 1985.

Madey, T. E., "The Surface Chemistry of Water," Gordon Research Conference on Electrochemistry, Santa Barbara, CA, January 20, 1986.

Madey, T. E., "Uses of Electron Stimulated Desorption in Surface Science," Materials Research Division, University of California at Berkeley, Berkeley, CA, January 23, 1986.

Madey, T. E., "Mechanisms and Applications of Electron and Photon Stimulated Desorption," Joint Institute for Laboratory Astrophysic, NBS, Boulder, CO, January 28, 1986.

Madey, T. E., "Mechanisms and Applications of Electron and Photon Stimulated Desorption," Physics Department, University of Pennsylvania, Philadelphia, PA, February 5, 1986.

Madey, T. E., "Early Applications of Vacuum Science and Technology," American Vacuum Society Symposium on Ion Beam Technology and Applications, Anaheim, CA, March 18, 1986.

Madey, T. E., "The Structure and Chemistry of H_2O on Surfaces," Beijing Laboratory of Vacuum Physics, Beijing, China, April 9, 1986.

Madey, T. E., "Advances in Electron and Photon Stimulated Desorption," Beijing Laboratory of Vacuum Physics, Beijing, China, April 9, 1986.

Madey, T. E., "History of Vacuum Science and Technology," Beijing Laboratory of Vacuum Physics, Beijing, China, April 10, 1986.

Madey, T. E., "The Use of Electron Stimulated Desorption to Determine the Structures of Surface Molecules," Fudan University, Shanghai, China, April 17, 1986.

Madey, T. E., "Secondary Electron Effects in Photon Stimulated Desorption," Sixth International Workshop on Inelastic Ion-Surface Collisions, Argonne, IL, August 16, 1986.

Madey, T. E., "Influence of Electronic and Geometrical Structure on Desorption Kinetics of Isoelectronic Polar Molecules: NH_3 and H_2O," Joint Workshop on Interface Phenomena, 'Kinetics of Interface Reactions,' Campobello International Park, ME, September 26, 1986.

Melmed, A. J., "Field Ion Appearance Spectroscopy of Gold Overlayers on Silicon," 33rd International Field Emission Symposium, W. Berlin, Germany, July 10, 1986.

Melmed, A. J., "Effects of a Gold Shank-Overlayer on the Field Ion Imaging of Silicon," 33rd International Field Emission Symposium, W. Berlin, Germany, July 10, 1986.

Melmed, A. J., "Progress in Understanding Atomic Structure of the Icosahedral Phase," 33rd International Field Emission Symposium, W. Berlin, Germany, July 11, 1985.

Melmed, A. J., "Atomic Structure of the Icosahedral Phase in AlMn," University of Erlangen-Nurnberg, Erlangen, W. Germany, July 14, 1986.

Powell, C. J. "Overview of Surface Analysis Techniques," New England Section of the Society for Applied Spectroscopy, Newton, MA, October 9, 1985.

Powell, C. J. "Surface Chemical Analysis - Report on the VAMAS Project," European Conference on Applications of Surface and Interface Analysis, Veldhoven, The Netherlands, October 17, 1985.

Powell, C. J. "Characterization of the Imaging Properties of a Double-Pass Cylindrical-Mirror Analyzer," European Conference on Applications of Surface and Interface Analysis, Veldhoven, The Netherlands, October 17, 1985.

Powell, C. J. "L_3-Level Binding Energies and Excitation Spectra of 3d Transition Metals by Different Techniques," Physical Chemistry Department, University of Nijmegen, Nijmegen, The Netherlands, October 18, 1985.

Powell, C. J., "Recent Developments in Quantitative Surface Analysis by Electron Spectroscopy," American Vacuum Society Meeting, Houston, TX, November 19, 1985.

Powell, C. J., "Imaging Properties and Energy Aberrations of a Double-Pass Cylindrical-Mirror Electron Energy Analyzer," American Vacuum Society National Symposium, November 19, 1986.

Powell, C. J., "Lectures on Surface Science and Surface Analysis," Short Course of the Mexican Vacuum Society, Mexico City, Mexico, March 17-18, 1986.

Powell, C. J., "Auger Electron Spectroscopy," Short Course on Microanalytical techniques in Materials Science, Washington Chapter of the American Society for Metals, NBS, Gaithersburg, MD, April 22, 1986.

Powell, C.J., "Comparison of L_3-Shell Binding Energies in 3d Metals by XPS, APS, and EELS," IBM Almaden Research Center, San Jose, CA, May 20, 1986.

Powell, C.J., "Comparison of Measured and Calculated Appearance-Potential Spectra of 3d Metals," Physical Electronics Conference, University of Texas at Austin, Austin, Texas, June 16, 1986.

Powell, C.J., "Comparison of Measured and Calculated Appearance-Potential Spectra of 3d Metals," Gordon Research Conference on Electron Spectroscopy, Wolfeboro, NH, July 14, 1986.

Powell, C.J., "Energy Dependence of Electron Inelastic Mean Free Paths," Physical Electronics Users' Meeting, Hagerstown, MD, September 23, 1986.

Shinn, N. D., "Dossier of a Molecular Precursor to Dissociation: The Cr(110/CO) Case," Department of Chemistry, University of Texas, Austin, TX, November 19, 1985.

Shinn, N. D., "Synchrotron Photoemission Evidence for Lying-Down CO on Cr(110)," American Vacuum Society Meeting, Houston, TX, November 19, 1985.

Shinn, N. D., "Synchrotron Photoemission Study of π-Bonded CO on Cr(110)," American Chemical Society Meeting, New York, NY, April 16, 1986.

Shinn, N. D., "Alkali Overlayer Ordering on the Atomically Corrugated Cu(311) Surface," American Chemical Society Meeting, New York, NY, April 17, 1986.

Stockbauer, R. L., "Photon and Electron Stimulated Desorption of Ions from Surfaces," Department of Physics, Lehigh University, Bethlehem, PA, October 17, 1985.

Stockbauer, R.L., "Use of Synchrotron Radiation in Studies of Adsorbed H_2O: Surface Chemistry and Radiation Damage," American Chemical Society Meeting, New York, NY, April 16, 1986.

Szuromi, P. D., "Sulfur Poisoning of CO Hydrogenation over a Tungsten Catalyst," Chemistry Department, George Washington University, Washington, DC, February 7, 1986.

Szuromi, P. D., "Inhibition by Sulphur of Catalytic CO Hydrogenation over Tungsten," Inorganic Materials Division Seminar, National Bureau of Standards, Gaithersburg, MD, March 25, 1986.

Szuromi, P. D., "Inhibition by Sulfur of Catalytic CO Hydrogenation over Tungsten," Surface Chemistry Branch, Naval Research Laboratory, Washington, DC, April 7, 1986.

Szuromi, P. D., "Effect of Sulfur and Oxygen on the Hydrogenation of CO over W(110)," American Chemical Society Meeting, New York, NY, April 17, 1986.

Szuromi, P.D. "Effects of Metallic Surface Structure on Molecular Dissociation," Physics Department, Stevens Institute of Technology, Hoboken, NJ, April 28, 1986.

Szuromi, P. D., "Sulfur Inhibition of Methanation over W(110)," Gordon Research Conference on Catalysis, New London, NH, June 24, 1986.

7. SURFACE SCIENCE DIVISION SEMINARS

Adelman, S. A., Purdue University, West Lafayette, IN, "Some Concepts in Condensed Phase Chemical Kinetics," October 30, 1985.

Behm, R. J., University of Munich, Munich, W. Germany, "Local Surface Processes Detected by Scanning Tunneling Microscopy," Joint Seminar with Electron Physics Group, December 2, 1985.

Bono, J., Pennsylvania State University, University Park, PA, "Free-Electron Theory of Scanning Tunneling Microscopy," November 13, 1985.

Bonzel, H. P., KFA, Jülich, Germany, "Morphological Changes of Periodic Surface Profiles on Pt(110): Surface Self Diffusion, Anisotropy of Surface Energy, and Surface Reconstruction," June 26, 1986.

Burgess, Jr., D. R. F., "Laser-Induced Thermal Desorption as a Probe of Surface Processes," Surface Science Division Seminar, Gaithersburg, MD, October 23, 1985.

Ceyer, S. T., Massachusetts Institute of Technology, Cambridge, MA, "Dynamics of Molecular Chemisorption, Site Conversion and Activated Dissociative Adsorption on Ni(111)," May 29, 1986.

Chabal, Y., AT&T Bell Laboratories, Murray Hill, NJ, "Structure and Dynamics of Hydrogen on Si(100) and W(100) - An Infrared Study," January 6, 1986.

Chambers, G. P., Nuclear Engineering Dept., Univ. of Maryland, and Guest Worker, Surface Science Division "Design of an Interactive Sputtering Yields Database Using Commerical and In-House Software", October 25, 1985.

Davenport, J., Brookhaven National Laboratory, Upton, NY, "Surface Relaxation in Gold (110)," September 11, 1986.

Demmin, R. A., University of Pennsylvania, Philadelphia, PA, "Methanation Reaction Kinetics over Model Pt Catalysts," September 5, 1986.

Eesley, G., General Motors Research Laboratories, Warren, MI., "Energy Relaxation in Metals on the Picosecond Timescale", October 18, 1985.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: I. General Introduction to Concepts in Critical Phenomena," April 8, 1986.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: II. Application to Surfaces," April 9, 1986.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: III. Chemisorbed Systems and Universality Classes," April 10, 1986.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: IV. Transfer Matrix and Monte Carlo Methods," May 28, 1986.

Einstein, T. L., University of Maryland, College Park, MD, "Informal Lecture Series on Phase Transitions at Surfaces: V. Aspects of Roughening on Surfaces, How to Measure It, and How It Relates to Other Models", June 5, 1986.

Gallagher, A., Joint Institute for Laboratory Astrophysics, NBS, Boulder, CO, "Issues Concerning Hydrogenated Amorphous Silicon Surfaces", June 6, 1986.

Glaus, U. W., University of Maryland, College Park, MD, "Adsorbed Phases with Impurities and the Random Field Ising Model," June 11, 1986.

Heller, E., University of Washington, Seattle, WA, "Chaos, Quantum Mechanics, and the Mexico City Earthquake," February 18, 1986.

Holloway, S., Liverpool University, Liverpool, England, "Surface Dynamics: The Liverpool Perspective," January 15, 1986.

Hall, R., EXXON Research & Engineering Co., Annandale, NJ, "Surface Chemistry Induced by Pulsed Lasers--Competition Between Desorption and Reaction", May 16, 1986.

MacDonald, A. H., National Research Council of Canada, Ottawa, Canada, "In Defense of Normalcy: Why Potassium Ought Not to Have a Charge-Density-Wave Ground State," April 14, 1986.

Marton, D., Technical University of Budapest, Budapest, Hungary and Guest Scientist, Surface Science Division, "Depth Resolution in Sputter Depth Profiling," January 15, 1986.

Mitchell, G. E., University of Texas, Austin, TX, "The Surface Chemistry of Ketene on Pt(111)," September 9, 1986.

Netzer, F., University of Innsbruck, Innsbruck, Austria, "Angle Resolved Photoemission of Aromatic Molecules Adsorbed on Transition Metals," Joint Seminar with Photon Physics Group, July 11, 1986.

Nicol, J. M., "Infrared Studies of Zeolite--Adsorption Complexes," Surface Science Division Seminar, Gaithersburg, MD, January 30, 1986.

Nordlander, P., Chalmers University, Goteborg, Sweden, "Potential Energy Surfaces for Atoms and Molecules Near Metal Surfaces," March 21, 1986.

Pfluger, P., BBC Brown, Boveri & Company, Ltd., Baden, Switzerland, "Electronic Processes in Organic Dielectrics Under High Electrical Fields", October 18, 1985.

Sanche, L., Universite de Sherbrooke, Sherbrooke (Quebec), Canada, "Electron Spectroscopy of Molecular Solids Condensed on Metal Surfaces", February 14, 1986.

Sarma, S. D., Physics Department, University of Maryland, College Park, MD, "Molecular Statics and Dynamics Studies of Epitaxy", June 10, 1986.

Sass, J. K., Fritz-Haber-Institute, Berlin, Germany, "Tuneable Laser Radiation and Surface Plasmon-Polariton Excitation in Infrared Spectroscopy at the Metal-Electrolyte Interface", October 21, 1985.

Schuetzle, D., Ford Motor Company Research Laboratories, Dearborn, MI, "Recent Advances in ESCA and SIMS: Applications to Materials Science," Joint Seminar with Center for Analytical Chemistry, May 15, 1986.

Snowdon, K., Vanderbilt University, Nashville, TN and University of Osnabruck. Osnabruck, Germany, "Surface Neutralization of Low Energy Atomic and Molecular Ions", June 9, 1986

Stiles, M., Cornell University, Ithaca, NY, "Inelastic Molecular Hydrogen Surface Scattering," February 21, 1986.

Tobin, R., University of California, Berkeley, CA, "Infrared Spectroscopy of Molecules Adsorbed on Metal Surfaces," March 17, 1986.

Umbach, E., Technical University of Munich, Munich, W. Germany, "Photoemission and Auger Spectroscopy as Probes for the Investigation of Adsorbate Systems," April 24, 1986.

8. TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Cavanagh, R. R.
Surface Science Division Safety Officer (through 1/86)

Treasurer, General Committee of the Physical Electronics Conference

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-Partenkirchen, FRG, September, 1987

Girvin, S. M.
Member, Program Committee, 7th International Conference on the Electronic Properties of Two-Dimensional Materials (Sante Fe, July 1987)

Jach, T.
Invited participant, Workshop on an Advanced Soft X-Ray and Ultra-violet Synchrotron Source, Berkeley, CA, Nov. 13-15, 1985

Participant, Workshop on X-Ray Optics, Brookhaven National Laboratory, June 2-4, 1986

Kelley, R. D.
Chairman, Subcommittee D-32.03 on Chemical Analysis of ASTM Committee D-32 on Catalysts

Kurtz, R. L.
Member, Local Arrangements Committee, 10th International Vacuum Congress, 6th International Conference on Solid Surfaces, 33rd National Symposium of the American Vacuum Society, Baltimore, MD, October, 1986

Madey, T. E.
Member, American Institute of Physics Subcommittee on Electronic Publishing

Program Chairman, 10th International Vacuum Congress/6th International Congress on Solids Surfaces/33rd National Symposium of the American Vacuum Society, Baltimore, MD, October, 1986

U.S. Representative to Surface Science Division of the International Union of Vacuum Science, Technique and Applications (IUVSTA) and Secretary of Committee

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

Chairman, Committee for Foreign Interactions, American Vacuum Society

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

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 (from 7/86) and Secretary, International Field Emission Society

Division Safety Officer (from 2/86)

Powell, C. J.
Chairman, ASTM Committee E-42 on Surface Analysis (through 12/85) and International Liaison (from 1/86)

Chairman, Surface Chemical Analysis Working Party, Versailles Project on Advanced Materials and Standards

Chairman, Board of Trustees, Gordon Research Conferences

Chairman, American Vacuum Society Applied Surface Science Division

Chairman, American Vacuum Society Scholarships and Awards Committee

Member, Ad Hoc Committee on Topical Conferences, American Vacuum Society

Chairman, Applied Surface Science Division Steering Committee, International Union of Vacuum Science, Technique, and Applications

Member, Board of Visitors, Research Advisory Board, Physics Program, Office of Naval Research

National Representative, Commission I.6 on Colloid and Surface Chemistry including Catalysis, International Union of Pure and Applied Chemistry

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

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

9. PROFESSIONAL INTERACTIONS, CONSULTING AND ADVISORY SERVICES

Cavanagh, R. R.

Collaborating with Dr. D. S. King of the NBS Molecular Spectroscopy Division on state-specific diagnostics of molecular desorption processes

Collaborating with Drs. M. P. Casassa, E. J. Heiweil and J. C. Stephenson of the NBS Molecular Spectroscopy Division on real time measurements of vibrational relaxation processes at surfaces

Collaborating with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Radiation Division on neutron inelastic scattering studies of adsorbates on high-surface-area transition metals

Collaborating with Dr. J. J. Rush of the NBS Reactor Radiation Division, Dr. G. D. Stucky of the University of California at Santa Barbara, and Dr. M. J. Wax of W. R. Grace Co. on vibration and diffusion properties of hydrogen and ammonia in zeolite H-rho

Collaborating with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Radiation Division and Dr. B. J. Tatarchuck of Auburn University on neutron inelastic scattering measurements from adsorbates on dispersed ruthenium catalysts

Egelhoff, Jr., W. F.

Collaborating with Dr. J. E. Rowe of AT&T Bell Laboratories in studies of semiconductor surface reconstructions by the technique of X-ray photoelectron forward scattering

Collaborating with Dr. B. Henrich of Simon Frasier University (Canada) on the synthesis and characterization of metallic superlattices

Erickson, N. E.

Collaborated with Mr. T. E. Kiess of the NBS Electricity Division on the calibration of a high-precision digital voltmeter and a high-precision programmable power supply.

Fine, J.

Collaborated with Prof. B. Navinsek of the J. Stefan Institute, Ljubljana, Yugoslavia on the effect of surface topography on measurements of sputtering yields, on depth resolution at interfaces, and on the fabrication and characterization of standard reference materials for surface analysis. This collaboration is conducted under the auspices of the U.S.-Yugoslavia Agreement for Cooperation in Science and Technology

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 Technolgoy.

Colloborating 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 NBS Inorganic Analytical Research Division and Dr. J. Boulmer of the Universite Paris, France and guest scientist in the NBS 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 NBS Chemical Thermodynamics Division on a data analysis procedure for sputter-depth-profile interface characterization.

Collaborating with Dr. R. F. Fleming of the NBS Inorganic Analytical Research Division on thin-film thickness measurements of standard reference materials for surface analysis.

Collaborating with Drs. C. Le Gressus and J. P. Duraud of the Centre d'Etudes Nucleaires de Saclay, France on the colloisional excitation and electron decay of atoms at single-crystal surfaces.

Gadzuk, J. W.

Collaborating with Prof. M. Sunjic of the Rudnor 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 classical trajectory theories of molecular processes at surfaces. This collaboration is assisted by a grant from the NATO Scientific Affairs Division.

Collaborating with Dr. E. Hood, Montana State University on a theory of high-energy neutral-molecular beams.

Collaborating with Dr. N. Satyamurthy, 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.

Consulted with Dr. J. K. Sass, Fritz Haber Institute, W. Berlin on problems of spectroscopy at electro-chemical interfaces (Nov. 25-30, 1985).

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.

Consulted with Professors S. Andersson and B. Lundqvist of the Chalmers University of Technology, Gothenburg, Sweden on molecular dynamics at surfaces.

Invited lecturer and participant at Adriatico Research Conference, "Dynamical Screening and Spectroscopy of Surfaces", International Centre for Theoretical Physics, Trieste, Italy (June 23-27, 1986).

Invited lecturer and participant at Sixth International Workshop on Inelastic Ion-Surface Collisions, Argonne National Laboratory (August 25-29, 1986).

Invited discussion leader at Gordon Research Conference on Electron Spectroscopy, Wolfeboro, NH (July 14-18, 1986).

Girvin, S. M.

Collaborated with Drs. A. H. MacDonald, (National Research Council, Ottawa) and P. M. Platzman (AT&T Bell Laboratories, Murray Hill) on the study of collective excitations in the fractional quantum Hall effect.

Completed a collaboration with Drs. D. R. Penn and S. P. Apell of the NBS Electron Physics Group on a theory of spin-polarized secondary electron cascades in ferromagnets.

Collaborated with Prof. R. E. Prange (University of Maryland) in organizing a ten-part lecture series on the quantum Hall effect and in editing the lecture notes for publication.

Jach, T. J.

Collaborating with Drs. P. Cowan, S. Brennan, and R. Lavilla of the NBS Quantum Metrology Group on gas-phase x-ray fluorescence experiments at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. R. Perera, Lawrence Berekely Laboratory on gas-phase x-ray fluorescence experiments at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. S. Banna, Vanderbilt University on gas-phase x-ray photoemission experiments at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. J. Kirkland, Sachs Freeman Associates on measurements of silicon photodiode yields at x-ray energies at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. J. Kirkland and P. Wolf, Virginia Polytechnical Institute and State University on harmonic detection and elimination in double-crystal monochromators at the Brookhaven National Synchrotron Light Source.

Collaborating with Dr. L. Holdeman, Comsat Corp., and Dr. G. Hembree, NBS Precision Engineering Division on measurement at the surface morphology of thin films.

Advised Mr. C. E. Bouldin of the NBS Semiconductor Electronics Division on the use of silicon photodioides for the measurement of extended x-ray absórption fine structure in a beamline to be set up at the Brookhaven National Light Source.

Kelley, R. D.

Collaborating (with J. M. Nicol) with Drs. T. J. Udovic and J. J. Rush of the NBS Reactor Division on neutron inelastic scattering measurements of adsorbates on high-surface-area transition metals.

Working on detail as a Program Manager with the Department of Energy, Office of Energy Research, Division of Chemical Sciences. This detail is on a 80% part-time basis for a two-year period that began June, 1985.

Kurtz, R. L.

Collaborating with Prof. V. E. Henrich and members of his group at Yale University in studies of the electronic structure and the influence of adsorbates on transition-metal oxide surfaces.

Collaborating (with R. Stockbauer) with Dr. V. Bermudez of the Naval Research Laboratory in a study of the influence of adsorbates in promoting phase transitions in the surface conductivity of oxides.

Collaborating (with R. Stockbauer) with Dr. A. Flodström of the Royal Institute of Technology, Stockholm, Sweden in studies of the mechanisms involved in stimulated desorption of ions and in studies of the influence of surface structure on ion angular distributions.

Collaborating (with T. E. Madey and R. Stockbauer) with Drs. W. R. Hunter, J. Rife, and M. Kabler of the Naval Research Laboratory and Dr. R. Williams of Wake Forest University in experiments at the x-ray ring of the Brookhaven National Light Source. This work includes the instrumentation of the double-grating monochromator designed by the NRL group and implementation of a surface science chamber that will be used for studies of the mechanisms of stimulated desorption of ions as well as extended-energy measurements of electron attenuation lengths in condensed molecular solids.

Collaborating (with T. E. Madey and R. Stockbauer) with Dr. J. L. Pena of the National Polytechnic Institute, Mexico City in studies of molecular chemisorption and ion desorption from TiO_2 surfaces.

Collaborating (with T. E. Madey and R. Stockbauer) with Prof. J. L. de Segovia of the Instituto de Fisica de Materiales, in Madrid, Spain in studies of the structure and reactivity in catalysis by metals and oxides. This work is conducted under the auspices of the U.S.-Spain Joint Committee for Technical Cooperation.

Madey, T. E.

Collaborating with Drs. I. Terzić, J. Vukanić and Z. Mišković 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.

Collaborating (with R. L. Kurtz and R. Stockbauer) with Drs. W. R. Hunter, J. Rife and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest University on the design and instrumentation for a beamline and chamber at the Brookhaven National Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating with Dr. N. Tolk of Vanderbilt University on studies of electron-stimulated desorption of excited-alkali neutral atoms from surfaces.

Collaborating 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.

Collaborating 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 Dr. J. L. de Segovia of the Instituto de Fiscia de Materiales, in 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 R. Kurtz and R. Stockbauer) with Prof. J. L. Pena of the National Polytechnic Institute, Mexico City in synchrotron studies of oxide surfaces.

Melmed, A. J.

Collaborating with Dr. W. A. Schmidt and Prof. J. H. Block of the Fritz Haber Institute, Berlin on properties of semiconductors in electric fields and effects due to metallic overlayers.

Collaborating with Dr. R. D. Arollia of the General Electric Company and Prof. H. Fraser of the University of Illinois to investigate atomic structure and chemical microcomposition for a series of nickel-based superalloys.

Collaborating with Mr. J. Smith and Prof. H. Fraser of the University of Illinois on studies of three related nickel-based superalloys using field ion microscopy, transmission electron microscopy, and atom-probe analysis.

Collaborating with Dr. M. J. Kaufman of the NBS Metallurgy Division on comparative studies with atom-probe field-ion microscopy and transmission electron microscopy of nickel-based superalloys and a series of Al-Li-Cu alloys.

Collaborating with Dr. N. Shinn of the Sandia National Laboratories on the growth of chromium crystal layers by expitaxy from the vapor phase.

Powell, C. J.

Collaborating (with S. Tanuma) with Dr. D. R. Penn of the NBS Electron Physics Group on calculations of inelastic mean free paths of low-energy electrons in solids.

Collaborating with Dr. M. P. Seah of the National Physical Laboratory, London 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

Stockbauer, R.

Collaborating (with R. L. Kurtz) with Drs. C. Kunz and F. Senf of the German Synchrotron Laboratory DESY, Hamburg and Drs. R. Nyholm and A. Flodström of the Royal Institute of Technology, Stockholm, Sweden in studies of the mechanisms of the photon-stimulated desorption of ions from surfaces.

Collaborating (with R. L. Kurtz) with Dr. A. Flodström of the Royal Institute of Technology, Stockholm, Sweden on experiments at the NBS Synchrotron Radiation Facility SURF-II to investigate (1) mechanisms of photon-stimulated desorption of ions from a non-maximal-valent oxide and (2) ions desorbing from adsorbates on semiconductors.

Collaborating (with R. L. Kurtz) with Dr. V. Bermudez of the Naval Research Laboratory on studies at the NBS SURF-II facility of the influence of adsorbates in promoting phase transitions in the surface conductivity of oxides.

Collaborating (with R. L. Kurtz and T. E. Madey) with Drs. W. R. Hunter, J. Rife, and M. Kabler of the Naval Research Laboratory and with Dr. R. Williams of Wake Forest University on the design and instrumentation for a beamline and chamber at the Brookhaven Synchrotron Light Source to study chemisorbed molecules on clean metal surfaces, mechanisms of photon-stimulated desorption of ions, and electron attenuation lengths in condensed molecular solids.

Collaborating (with T. E. Madey and R. L. Kurtz) with Dr. J. L. Pena of the National Polytechnic Institute, Mexico City in studies of molecular chemisorption and ion desorption from TiO_2 surfaces.

Collaborating (with T. E. Madey and R. L. Kurtz) with Prof. J. L. de Segovia of the Instituto de Fisica de Materiales, in Madrid, Spain in studies of the structure and reactivity in catalysis by metals and oxides. This work is conducted under the auspices of the U.S.-Spain Joint Committee for Technical Cooperation.

Collaborating with Dr. A. C. Parr of the NBS Radiation Physics Division and with Dr. D. Holland of Daresbury Laboratory, England on measurements of the fragmentation of molecules using photoelectron-photoion coincidence techniques.

Interacting with Drs. A. C. Parr, J. Hardis, and D. L. Ederer of the NBS Radiation Physics Division, Dr. J. L. Dehmer of Argonne National Laboratory, and Drs. J. B. West and D. Holland of Daresbury Laboratory, England on measurements of photoelectron angular distributions as a function of photon energy in gas-phase molecules.

10. VISITING SCIENTISTS

The Surface Science Division has been host during the past year to a number of scientists who have worked with the Division staff on problems of mutual interest.

Barak, D., Head of the Electronic Design Department of the Israeli Nuclear Research Center-Negev, worked at NBS for one year beginning August 1985. He interfaced an x-ray photoelectron spectrometer to a computer system and developed new software for this instrument and for a new digital ESDIAD system.

Bermudez, V. M., of the Naval Research Laboratory worked one month at NBS in early 1986 performing photoemission experiments on vanadium oxide surfaces at the SURF-II synchrotron radiation facility.

Chambers, G. P., a graduate student at the University of Maryland, has worked at NBS this past year under a cooperative agreement. He has been involved in the development of a data base system for the compilation of evaluated sputtering yield data and in quantitative sputter-depth-profiling of interfaces.

Chen, H.-H., of the National Science Council in Taiwan is spending a year at NBS, beginning in July 1986, working on applications of synchrotron radiation to the characterization of surfaces.

Clinton, W. L., of Georgetown University spent eight months at NBS on an intermittent basis performing theoretical studies related to electron- and photon-stimulated desorption of ions and neutrals from surfaces.

Einstein, T. L., of the University of Maryland worked at NBS for about five months on an Intergovernmental Personnel Assignment on studies of surface critical phenomena.

Hashiguchi, Y., of the Nippon Steel Corporation, Japan worked at NBS since March 1985 on a one-year assignment involving measurements of sputter-depth profiles of multilayer thin-film reference materials.

Holloway, S., of the University of Liverpool, visited NBS for two weeks during the winter of 1985-86 and one week during the summer of 1986 to work on theoretical modeling of reactive molecular processes at surfaces.

Hylden, J. L., of the Naval Research Laboratory spent one month at NBS in early 1986 performing photoemission experiments on vanadium oxide surface at the SURF-II synchrotron radiation facility.

Jansen, W. R., a graduate student of the Twente University of Enschede, The Netherlands worked at NBS for three months in the fall of 1985. He extended software for automated x-ray photoelectron spectroscopy measurements in a timesharing mode and for data reduction.

Larsson, C. U. S., of the University of Lund, Sweden, is spending about 4 months per year at NBS, starting December 1985, performing ESDIAD studies of the surface chemistry of silicon.

Marton, D., of the Technical University of Budapest, Hungary, is a Fulbright Scholar who is spending sixteen months at NBS, beginning September, 1985, on studies of the surface topography of ion-bombarded surfaces and characterizing multilayer thin-film structures.

Nicol, J. M., of the University of Maryland is spending two years at NBS, beginning November 1985, using neutron scattering methods to characterize adsorption on surfaces of high-area metallic and zeolite catalysts.

Polak, M., of the Ben Gurion University of the Negev, Isarel, is spending one year at NBS beginning August 1986, performing studies of molecular structure on semiconductor and metal surfaces using high-resolution EELS and ESDIAD.

Shinn, N. D., of Sandia National Laboratory, spent four months at NBS during the fall of 1985 performing synchrotron radiation studies of small molecules adsorbed on single-crystal chromium surfaces.

Tanuma, S., of the Nippon Mining Company is working at NBS on a two-year assignment that began in August 1985. He is participating in measurements of core-level binding energies by different electron-spectroscopic methods, in calculations of electron inelastic mean free paths in solids, and in analyses of algorithms for x-ray photoelectron spectroscopy.

Wei, J., a graduate student at the University of Maryland from the People's Republic of China, spent two months at NBS during the summer of 1986 performing studies of catalysis over well-characterized copper surfaces.

CHEMICAL KINETICS DIVISION

S. E. Stein, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1986

1. INTRODUCTION

A. Background

The goal of chemical kinetics is to understand the critical factors controlling chemical change and reactivity. To achieve this goal chemical change is interpreted in terms of individual molecular events and quantitative theoretical models are devised for these events. The societal importance and exciting scientific opportunities in this area are documented in the Pimentel Report to the National Academy of Sciences on "Opportunities in Chemistry" (National Academy Press, Washington, D.C., 1985). In this report chemical kinetics is listed as the first of seven "Intellectual Frontiers in Chemistry" where the greatest opportunities for major advances lie. Understanding chemical reactivity is given as the first of five priority areas where continued growth can "provide the basis for U.S. competitive advantage in development of new processes, new substances, and new materials". Moreover, chemical kinetics is an important part of each of the other four priority areas, especially "Chemistry Around Us" and "Chemical Behavior Under Extreme Conditions".

The breadth and vitality of this area were also evident in the proceedings of the first International Conference on Chemical Kinetics, recently published as an issue of the Journal of Physical Chemistry and spanning a wide range of chemical reaction systems and experimental methods. A sampling of areas represented were, *a priori* calculations of potential energy surfaces, rate measurements of organic and organometallic species in solution, state-to-state energy transfer determinations and ion-molecule rate measurements. Underlying this striking diversity was a common concern for transition states and for the basic molecular properties determining reactivity.

Exciting experimental breakthroughs and theoretical developments have been made over the last few years that have dramatically expanded the breadth and depth of the discipline. Experimentally, largely as a result of advances in laser and computer technology, a new array of instrumentation has been developed with improved precision and sensitivity which is now yielding increasingly varied and detailed kinetic information. Spurred on by practical concerns such as combustion, these new instruments, alongside more established techniques, have brought certain areas of kinetics to a high degree of development where practitioners are on the verge of devising reliable theories with broad predictive power. The development of these theoretical tools is of critical importance to the field, since they provide frameworks for interpreting as well as generalizing results of individual experiments.

While the number and diversity of reactions investigated by kineticists are increasing at a rapid pace, the area has actually become more cohesive as interrelations between formerly divergent areas become increasingly clear. For instance, concepts developed from the study of unimolecular reactions are being widely used to explain critical features of gas-phase ion-molecule chemistry. In a similar manner, results of gas-phase ion chemistry are beginning to provide a solid conceptual foundation for solution ion chemistry, a poorly understood area of immense practical importance.

B. Scope

Over the past several years the scope of research within the Chemical Kinetics Division has expanded significantly. Five years ago its primary emphasis was on gas-phase reactions of neutral species. Through recent additions of staff and changes in research direction, it is now roughly equally divided into groups studying ion and neutral reactions and on studies in the gas and condensed phases. In addition, the data centers (ion and neutral) are broadening their efforts in kinetic and thermochemistry data evaluation. Since predictive theories are required by both experimentalists and "data evaluators", advancement of these theories provides a key unifying factor for the diverse activities in the division. In fact, it is expected that the Division will ultimately be able to offer not only NBS evaluated data but also NBS "calibrated" predictive models for data not currently available.

C. Activities

Most activities within the Chemical Kinetics Division fall within one of two distinct, but closely interacting areas, kinetic measurement and data evaluation. In the former area we both develop new measurement techniques and determine rates and mechanisms of selected chemical processes. These new techniques either allow monitoring reaction intermediates not observable by existing techniques (two new techniques are multiphoton ionization and modular MS/MS spectrometry) or enable kinetic measurements to be made in unique, hard-to-study chemical environments (examples are studies of large species at high temperatures using heated shock tube, flow reactor and novel laser heating techniques). We measure rates, determine products and develop reaction mechanisms for selected simple processes needed for the interpretation of complex, practical processes. Special attention is given to those cases where a small number of measurements can yield a broad advance in predictive theory. A wide range of programs of this nature are underway including reactions of ions and neutral molecules in both the gas and condensed phases.

Other programs are devoted to the theoretical analysis of important reacting systems too difficult to fully analyze by experimental means. An example is our development of a chemical theory of graphite and very large polycyclic aromatic molecules.

Data center activities and associated theoretical studies are at the heart of the division's efforts. This work not only organizes a wide spectrum of kinetic data and thermodynamic properties of reactive intermediates, but also utilizes this data to extract general reactivity patterns and develop improved predictive theories. Major areas of uncertainty revealed in the course of evaluations often prompt studies in one of our experimental programs. Moreover, the considerable breadth of ongoing experimental work in the division ensures that insight needed for thorough data evaluation is available.

Several significant improvements in our instrumentation have been made over the past year. A state-of-the-art, optical multichannel analyzer has been purchased and optimized for real time detection of vacuum UV irradiation. This replaces detection by photographic plates, a much more laborious and less flexible procedure. A new heated shock tube has been constructed, enabling the study of even larger molecules. Construction of a unique, very high temperature (up to 2500 K) graphite flow reactor is near completion. This will enable the study of reactions at organic molecules at temperatures well above those normally employed in flow reactors.

This has been a highly productive year. Both the total number of research publications (60 published, 42 in press or submitted) and the number per research staff member (4.3, 3.0) are at an all-time high for our division. Viewed in another way, the net cost per published paper was $41,000, comparable to that for productive academic institutions and well below that for research institutes. Moreover, the cost per publication in terms of total NBS support was only $20,000. A major reason for this increased productivity was the very large number of guest workers attracted to our division (21 individuals, see Section 10). Another reason was the maturation of two programs begun several years as competence-development initiatives.

D. Services to Other Bureau Programs and Other Agencies

The Chemical Kinetics Division serves as a technical resource for a wide range of external programs. This activity is an integral part of our mission, and a key means of applying our scientific expertise to industrial, defense, and environmental problems. Moreover, these projects are directly related to, and strongly supportive of, the basic long-range scientific objectives of the division. In FY 86 we participated in the following NBS and other agency programs:

Office of Standard Reference Data

- The Chemical Kinetic Data Centers (ion and neutral) for data compilation and evaluation.

Department of Energy

- Compilation and evaluation of combustion chemistry data
- Chemistry of hazardous waste incineration
- Pulse radiolysis studies of electron transfer in solution
- High pressure mass spectrometric studies of ion kinetics and thermodynamics.

Department of Defense

- Chemical theory of carbon
- Kinetics of the decomposition of nitroaromatics
- Multiphoton ionization processes
- Tandem mass spectrometric studies
- Ion-cyclotron resonance studies of ion-molecule condensation processes in hydrocarbons.

National Aeronautics and Space Administration

- Elementary kinetic studies of stratospheric reactions
- Chemical kinetics of planetary atmospheres
- Evaluation of stratospheric chemical kinetic data

Environmental Protection Agency

- Acid rain chemistry

2. DATA CENTERS

R. F. Hampson, Jr., J. T. Herron, R. D. Levin,
S. G. Lias, W. G. Mallard, W. Tsang, and G. W. Zumwalt
R. J. Cvetanovic, F. Westly

Evaluated kinetic and thermochemical data are the most important output of the Chemical Kinetics Division. It is a responsibility of every member of the division. The focus for the data evaluation activities is in the two data centers within the division: the Chemical Kinetics Data Center (led by J. T. Herron) and the Ion Kinetics and Energetics Data Center (led by S. G. Lias). On an operational basis the two data centers work together closely through a sharing of operating procedures, data bases, and personnel.

A. Chemical Kinetics Data Center

(R. F. Hampson, Jr., John T. Herron, R. Levin, W. Tsang, G. W. Zumwalt, R. J. Cvetanovic and F. Westley,)

The goal of the Chemical Kinetics Data Center is to serve as the nation's primary source for evaluated chemical kinetic data. The emphasis is on gas phase processes for which there is a demonstrated need.

The approach is to compile all data on gas phase chemical kinetics, and to evaluate specific sub-sets of this general database. This allows us to concentrate our efforts on those areas of greatest practical interest, while maintaining the ability to move rapidly into new evaluation activities as the need arises. The evaluated and unevaluated databases are also available to outside users.

Evaluated chemical kinetic data is most needed in those areas of science and technology in which computer simulation studies are being used to predict the behavior of large scale, complex chemical systems. Thus,the focus of our evaluation program is in the area of the oxidation of organic compounds, particularly as related to combustion and atmospheric chemistry. This also constitutes the largest active area in experimental chemical kinetics.

1. Accomplishments

The most important accomplishments of the past year have been in redefining and setting new goals for the data center and in making major changes in the daily operations of the center in order to achieve these new goals. The coverage of the data center has been expanded to include the whole of gas kinetics. The entire backlog of evaluated data on combustion chemistry has been edited and reformatted, and will be published or submitted for publication by the end of 1986. The same is true for the backlog of unevaluated data. New projects have been initiated and new approaches to database management and dissemination explored.

Over the past year we completed the task of establishing an evaluated chemical kinetic database for combustion chemistry. This was a monumental undertaking that has been in preparation for almost five years. It is unique in providing complete coverage of all possible reactions of all possible species involved in the combustion of the C1 to C5 hydrocarbons. The evaluations were based on published experimental data, or where no data existed, on the basis of theory. In almost all cases the evaluation involved the extrapolation of data into pressure and temperature regions beyond the range of the experimental measurements. This work is a particularly good example of the application and power of predictive techniques in data evaluation. We fully expect that extension of the data base to alkanes greater in size than C5 will be accomplished through the use of predictive techniques based on the existing evaluated database.

The combustion database contains data on 563 elementary chemical reactions, and will be published in four parts:

"Chemical Kinetic Data Base for Combustion Chemistry. Part 1. Methane and Related Compounds", W. Tsang and R. F. Hampson, J. Phys. Chem. Ref. Data, 15, 1087 (1986)

"Chemical Kinetic Data Base for Combustion Chemistry. Part 2. Methanol", W. Tsang, submitted to J. Phys. Chem. Ref. Data

"Chemical Kinetic Data for Combustion Chemisty. Part 3. Propane, n-Propyl, and i-Propyl", W. Tsang, to be submitted to J. Phys. Chem. Ref. Data

"Chemical Kinetic Data for Combustion Chemistry. Part 4. t-Butyl, i-Butyl and i-Butane", W. Tsang, to be submitted to J. Phys. Chem. Ref. Data

In addition, two related papers concerned with the thermochemical and kinetic properties of free radicals have been published:

"The Stabilty of Alkyl Radicals", W. Tsang, J. Am. Chem. Soc., 107, 2872 (1985)

"Thermodynamic and Kinetic Properties of the Cyclohexadienyl Radical", W. Tsang, J. Phys. Chem., 90, 1152 (1986)

Work is in progress on the evaluation of data on the reactions of atomic oxygen. This will be published in three parts. The first part, "Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen O(3P) with Unsaturated Hydrocarbons", by R. J. Cvetanovic, has been submitted to J. Phys. Chem. Ref. Data. Parts 2 and 3, "Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen $O(^3P)$ with Sulfur Containing Compounds", by R. J. Cvetanovic and D. Singleton, and "Evaluated Chemical Kinetic Data for the Reactions of Atomic Oxygen $O(^3P)$ with Saturated Organic Compounds", by J. T. Herron, are in preparation.

The compilation of chemical kinetic data for combustion chemistry, which consisted of several distinct data sets set up at different times, has been put into a common format. This compilation of unevaluated data is a much larger database than the comparable evaluated database, listing data on upwards of 1984 elementary reactions. This is the core database that will be used for development of a general database containing data on all gas phase chemical reactions. This task involved the entry of data published between 1977 and 1982, and the reformatting and further annotation of data previously abstracted and published as NBSIR 81-2254 (1981), which covered the literature published between 1971 and 1977.

The center continues to provide support to the NASA stratospheric chemistry program. Robert Hampson was one of the authors of the recently released NASA report to Congress; "Present state of knowledge of the upper atmosphere. An assessment report. Processes that control ozone and other climatically important trace gases", which warned of the consequences of a global warming trend. The role of trace gases in promoting the greenhouse effect means that trace atmospheric constituent chemistry is of great importance. For that reason we are initiating a new program with NASA support to re-consider the existing database. This is described in more detail below.

In addition, evaluation activities in the area of halogen chemistry have continued including participation on the NASA Panel for Data Evaluation.

Plasma chemistry is of great practical importance in the fabrication of microelectronic components, the surface coatings industry and in the transmission and switching of electric power. There are, however remarkably few data available to carry out computer simulation studies of what are very complex chemically reactive systems. A part of that problem has been successfully treated through evaluation of both the thermochemical and kinetic databases for the species involved in the dielectric breakdown of sulfur hexafluoride, which is widely used in the power industry. By accompanying the data evaluation activities with computer simulation, the potential for hazards resulting from the formation of toxic breakdown products has been demonstrated.

Three papers have resulted from this work:

"Thermochemical Data on the Gas Phase Compounds of Sulfur, Fluorine and Oxygen Related to Pyrolysis and Oxidation of Sulfur Hexafluoride," J. T. Herron, J. Phys. Chem. Ref. Data, submitted.

"A Critical Review of the Chemical Kinetics of SF_4, SF_5, and S_2F_{10} in the Gas Phase," Int. J. Chem. Kinetics," J. T. Herron, accepted for publication

"S_2F_{10} Formation in Computer Simulation Studies of the Breakdown of SF_6," J. T. Herron, IEEE Transactions on Electrical Insulation, accepted for publication

A major undertaking of the data center was the organization and running of the International Conference on Chemical Kinetics which was held at the NBS Gaithersburg site. It was supported by OSRD and by AFOSR, GRI, NASA, and NSF. Our goal in holding this meeting was to strengthen the connections between theory and experiment. We see an increasing reliance on theoretical methods in data evaluation and want to encourage their development. The meeting program was designed to do this. The meeting proceedings were published as a special issue of the Journal of Physical Chemistry (Volume 90, #3, January, 1986).

The design of the database management system for the HP-1000 computer is complete. Work on providing unique descriptors for all chemical species in the system will be finished this year, at which point the kinetics data base can be loaded.In summary, the design of the system is complete, and our goals have shifted from design to implementation.

Work started this year on developing a stronger capability in the area of modeling complex reaction systems. A prototype modeling program has been prepared and tested. An associated graphics program has also been written. Walter Braun is responsible for developing these programs in collaboration with David Kahaner of the Scientific Computing Division.

2. Plans

(a) Compilation of Gas Phase Chemical Kinetic Data.

We will continue to identify, abstract, and enter chemical kinetic data for all types of gas phase reactions into the existing data base. This will be the starting point for future data evaluation projects both within the Data Center and by outside workers.

(b) Combustion Chemistry Database.

The expansion of this data base will continue to be a high priority activity of the Data Center. We will do this by including new classes of fuel type species such as the alkenes or alkynes, or reactive species such as oxygen atoms or alkyl peroxy radicals. The objective will be to evaluate the existing body of data and to use the evaluations as a basis for developing estimation methods for reactions for which there are no data. A start was made last year on the evaluation of data on oxygen atom reactions with unsaturated organic species. That will be extended this year to include reactions of oxygen atoms with organic sulfur compounds, and reactions with saturated organic species.

(c) Stratospheric Chemistry Database.

Our existing programs in support of the NASA Upper Atmosphere Research Program will continue. The Data Center will retain responsibility for the evaluation of stratospheric halogen chemistry. We will actively participate in the activities of the NASA Data Evaluation Panel and of the re-established CODATA Task Group on Gas Phase Chemical Kinetics. These activities will be augmented through a new program involving a re-evaluation of the chemical kinetic data base recommended for use in modeling stratospheric chemistry. The goal of this program will be to provide documentation for including or rejecting each of the possible reactions of the reactive species included in current models. It will involve the development and use of techniques for estimating thermochemical and chemical kinetic parameters.

(d) Plasma Chemistry Database.

This activity will continue at a modest level. The earlier work on the properties of S-F compounds will be extended to some of the organic analogues, the sulfoxides and the sulfones. The thermochemistry of these compounds will be reviewed and new group values derived for the S-O type groups.

(e) Database Management System.

With the loading of the chemical kinetics database onto the HP-1000 computer, the emphasis will shift to the development of database management systems for desktop computer systems. Wherever possible commercially available systems will be used. The goal is to make the various databases available to outside users through easily transportable disk or tape media. As an added service to users, we will continue to develop auxiliary program packages to assist in the use and extension of the databases.

(f) Data Evaluation and Application Programs.

The activity started this year on the development of a set of programs for modeling complex chemical reaction systems and graphically displaying the results will be pursued in collaboration with Walter Braun of this Division and David Kahaner of the Scientific Computer Division. The possibility of devising a sensitivity analysis for the modeling program will be explored. Other program packages under consideration include RRKM programs, BEBO and BSBL programs, and various associated programs for obtaining thermochemical properties.

B. Ion Kinetics and Energetics Data Center
(S. G. Lias and R. D. Levin)

The goals of this Data Center are to collect and maintain an up-to-date file of experimental data pertaining to the thermochemistry of ions (ionization energies, appearance potentials, and equilibrium constants as well as the heats of formation of positive and negative ions in the gas phase) and the kinetics of ion/molecule reactions, to make compilations of these data and to publish evaluations of the collected data for use by the scientific and technological communities.

The Data Center is closely associated with both the Ion Kinetics Group, from which it derives scientific support, and the Chemical Kinetics Data Center, with which facilities and expertise are shared.

1. Accomplishments

During the past year, efforts were concentrated on completing the comprehensive compilation of evaluated ionization energies and heats of formation of positive and negative ions in preparation for submission to the Journal of Physical and Chemical Reference Data. Accomplishments on this task included: (a) abstracting data for approximately 1400 additional species, which appeared in the literature in the years 1981-1986, and adding these data to the data base; (b) locating or estimating heats of formation for the newly-added compounds; (c) identification of compounds within this group for which structural drawings need to be made for the publication, preparation of rough drawings, and arranging for the preparation of the final ink drawings; (d) writing of a review of the field to be included as introductory textual material; (e) writing of software to sort the data base; (f) downloading the associated bibliographic data base from a microcomputer to the HP-1000; and (g) coordinating efforts of NBS and non-NBS collaborators in reviewing the evaluations and the textual material. At this writing, the sort software is being de-bugged, the contributions of non-NBS authors to the textual material are being incorporated, and the task of evaluating the need for drawings is being completed. It is anticipated that the publication will be submitted to the Journal of Physical and Chemical Reference Data on or before January 1, 1987, as "Gaseous Ion and Neutral Thermochemistry" (GIANT) by J. E. Bartmess (University of Tennessee), J. L. Holmes (University of Ottawa), R. D. Levin, S. G. Lias, J. F. Liebman (University of Maryland, Baltimore County Campus), and S. E. Stein.

The data base for the 1984 Data Center publication of 780 evaluated gas basicities/proton affinities of neutral molecules was brought up to date by the addition of all the data which had appeared in the literature since the cut-off date of the original publication (1984). New data for 234 species were added, and some of the values of proton affinities were re-evaluated as a result of the appearance of better experimental or theoretical data. Work on this up-date continues.

With the collaboration of S. Stein, the entire ion energetics data base (containing heats of formation of more than 5000 neutral and ionic species) has been stored on disks for a microcomputer, where it is searchable using commercial software. This accomplishment represents a feasibility study by S. Stein for the possible future use of such systems for routine Data Center tasks.

2. Plans

During the first months of the coming year, top priority will be given to completing the major publication which is in progress, as described above.

As mentioned above, an up-date was prepared during the past year concerned with the data base of evaluated gas phase basicities and proton affinities of molecules. Since the data represent an extensive thermochemical ladder, maximum utility is obtained when they are presented in a sorted version according to proton affinity; it is anticipated that the data included in the original publication will be merged with the newer information and a publication will be prepared during the coming year. This small data base is ideal for distribution on disk for use with microcomputers; exploratory work on accomplishing this is beginning.

R. E. Huie and P. Neta, in collaboration with the Radiation Chemistry Data Center, Notre Dame University, are preparing an evaluated compilation of rate constants of inorganic radical reactions with organic and inorganic compounds in aqueous solutions. A publication will be prepared to be submitted to the Journal of Physical and Chemical Reference Data.

Discussions have begun with Drs. Vincent Anicich (Jet Propulsion Laboratory), Albert Viggiano (Air Force Geophysics Laboratory) and Jean Gallagher (JILA) on the possibility of collaborating on an comprehensive compilation and evaluation of ion/molecule rate constant data.

3. KINETICS OF NEUTRAL SPECIES

W. Braun, R. L. Brown, J. W. Hudgens, M. J. Kurylo, R. I. Martinez,
S. E. Stein and W. Tsang

R. Chen, J. P. Cui, S. Dheandhanoo, A. Fahr, Y. Z. He,
R. D. Johnson, III, S. Kafafi, A. H. Laufer, G. R. Long, H. Okabe,
M. D. Scheer, V. Senthilnathan, M. Suryan, T. Wallington, J. A. Walker,

A. Overview

The focus of the activities of this group is the study of the chemical kinetics of neutral species, with special emphasis on free radicals and excited state molecules. Our goals are to develop methods for the detection and quantification of transient reaction intermediates, to measure rate constants for processes involving these species and their precusors, and to determine the mechanisms of reactions in which these species are reactants or products. Individuals in this group interact strongly with our data evaluation program by providing key measurments, theoretical concepts and through direct involvement in evaluation activities. The past year has been an exceedingly succesful one for this group. By all the usual measures, productivity is at an all time high. Even more important, the ground work has been laid for increasingly significant contributions in future years.

The fundamental quantities of interest to this group remain elementary rate constants. They are a measure of the rate of change of the chemical constituents in a system where the molecules have a Boltzmann distribution. We regard this as the key interface between more detailed scientific information at the state-to-state level and the technological marketplace where kinetic information is used in predictive models. These measurements are also direct inputs into our data center. Furthermore, from these numbers one can derive data on molecular properties such as bond energies, enthalpies and entropies of formation, and transition state structures and energetics, that are necessary for our data evaluation activities in that they lead to algorithms for prediction and define the boundaries for the evaluation of existing data.

The range of problems under study by this group is very broad. They range from studies of reactions of atoms and small radicals and biradicals in the gas phase to the chemistry of large polynuclear aromatic hydrocarbons. In the following, the activities of the group are given very roughly in the order of the complexity of the molecular system under study. This ordering illustrates the fact that progress in studying complex chemistry depends on data on the kinetics of simpler systems. That is, although new factors are introduced with molecular complexity, the chemistry of atoms and small radicals is always an essential component for the understanding of the total system. Thus our background in the chemistry of atomic and small radical chemistry has been a major factor in the developement of our newer programs on the transformation of complex organic compounds. Indeed, at the present time much of the quantitative work at a fundamental level on the stability and reactivity of aromatic systems at high temperatures is coming from our laboratories.

B. Multiphoton Ionization Detection of Reactive Intermediates
(J. W. Hudgens, G. R. Long, and R. D. Johnson, III)

Resonance enhanced multiphoton ionization (REMPI) spectroscopy has become a popular optical technique because it can sensitively detect reactive intermediates not suitably detected using laser induced fluorescence (LIF), Raman, or CARS spectroscopies. REMPI selection rules also allow investigation of molecular states that are forbidden in conventional one photon experiments. The objective of this project is to develop and use REMPI to explore the spectroscopy and reaction dynamics of reactive intermediates.

In a REMPI experiment an intense laser beam irradiates molecules with laser light. When the frequency of the laser light becomes equal to either one-half or to one-third of the energy separation between two electronic molecular states and selection rules permit, the molecules absorb photons until they ionize. A mass spectrometer analyzes the ions.

Major improvements of the laboratory facilities which have benefitted the research program occurred during the year. Laboratory space was remodeled to suppy improved power and utility services for lasers, and a crane was installed to handle heavy vacuum components. In February, lasers and vacuum equipment were moved into this space. The new laboratory has provided a safer and more advantageous layout of equipment.

During FY85 significant effort was invested to design and procure components for a new mass spectrometer system designed specififcally for the needs of REMPI experiments. During the past year these components arrived and we assembled the apparatus and optimized its performance for experiments that involve molecular beams, effusive ovens and flow reactors.

The new multiphoton ionization apparatus is built with the vacuum system integrated into an optical table. This design allows precise and stable laser beam alignment. The vacuum system consists of a large chamber where molecular beams and laser beams interact, two sidearms where pulsed molecular beams of radicals are generated, and a chamber which houses a Reflectron time-of-flight mass spectrometer. The system has demonstrated excellent sensitivity and ion throughput efficiency.

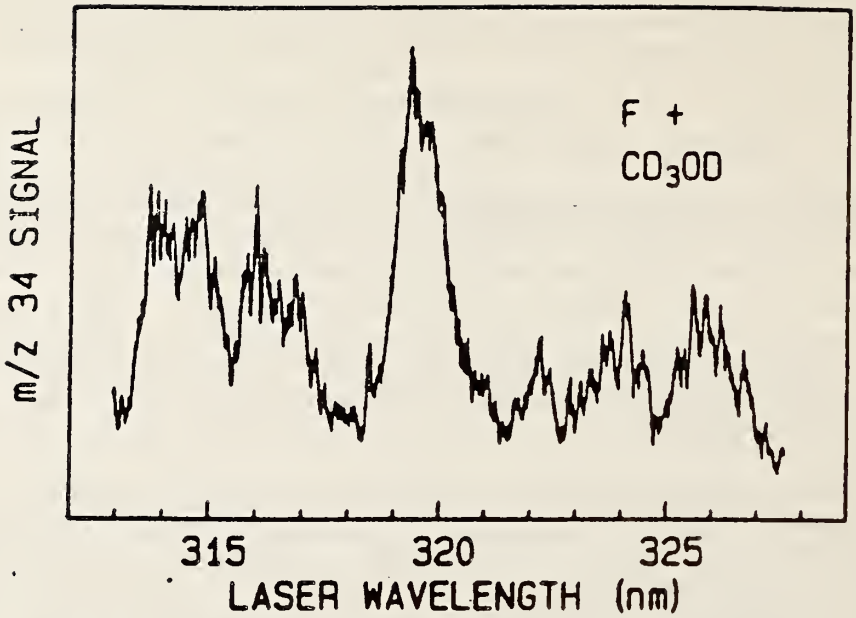


Fig 3.1. The m/z 234 REMPI spectrum observed from the perdenterated methoxy radical produced by the reaction F+CD_3OD.

In the inaugural study employing this new apparatus, we discovered the first REMPI band systems of methoxy radicals. During a second study which involved the development of an oxygen atom source, we observed the first REMPI bands of transient $O_2('\Delta)$ molecules. We believe that this REMPI detection method for $O_2('\Delta)$ molecules exceeds the sensitivity of any other optical technique. In addition, these experiments revealed previously unreported electronic states of O_2 molecules which reside between 67,000-73,000 cm^{-1}.

1. Spectroscopy of methoxy and hydroxymethyl radicals during the reaction of fluorine atoms with methanol.

Methoxy radicals, CH_3O, and hydroxymethyl radicals, CH_2OH, play important roles in a wide variety of chemical systems including the atmosphere, flames, interstellar space, and catalytic surfaces. During our REMPI studies these radicals were generated in a flow reactor by reacting fluorine atoms with methanol and isotopically substituted methanols, e.g.

$$CH_3OD + F \longrightarrow HF + CH_3O \quad (m/z\ 31) \quad (1a)$$
$$\longrightarrow HF + CH_2OD \quad (m/z\ 32) \quad (1b)$$

Methoxy radical REMPI spectra (Fig. 3.1) appeared as bands of dense rotational lines between 313-328 nm. Mass spectra of each isotopic analog showed that the molecular ions do not fragment. An isotopic substitution study proved that the chemical structure of the laser ionized species was that of methoxy radical.

The fact that methoxy ions do not fragment is significant. The ground state of the methoxy cation is unstable, but its lowest triplet state is bound. Thus, to produce unfragmented molecular ions, REMPI ionization must specifically prepare the triplet $\tilde{a}\ ^3A$ state methoxy cation. Additional work is underway to resolve the REMPI mechanism and the identity of the resonant electronic state which generates the spectrum.

Besides methoxy radicals reaction (1) also generates hydroxymethyl radicals, CH_2OH. Currently, REMPI spectroscopy is the only laser method that can detect the CH_2OH radical. This year we published an extensive analysis of REMPI spectra observed from four isotopically substituted hydroxymethyl radicals. The electronic bands observed between 420-495 nm (Fig. 3.2) were shown to originate from a 3p Rydberg state.

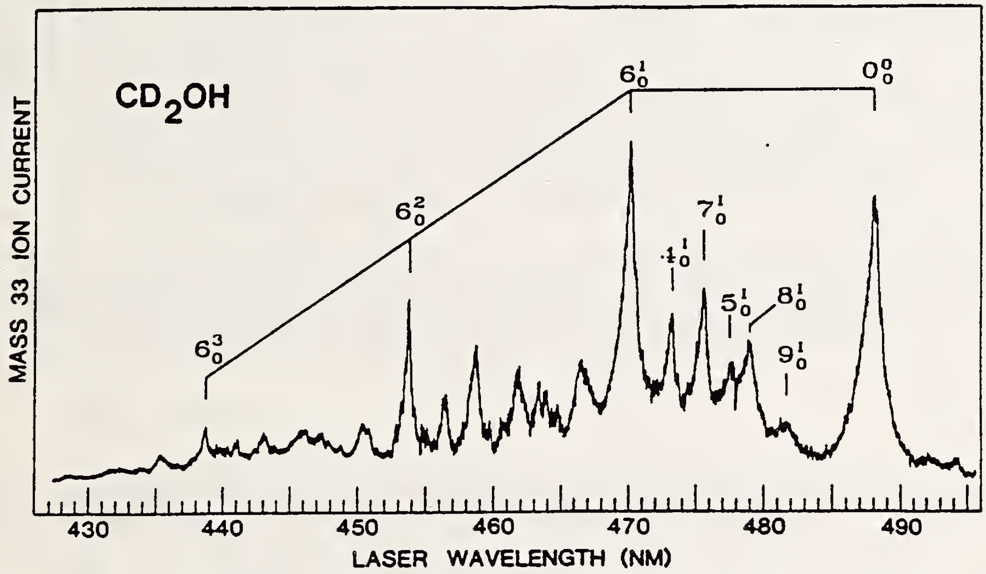


Fig. 3.2. Multiphoton ionization spectrum of the CD_2OH radical.

A normal mode analysis of the REMPI spectra enabled assignments of six active vibrational modes in the excited state. As a result 85% of the 130 vibrational bands observed between 420-495 nm were assigned. The normal mode assignments enabled a comparative analysis of electronic structure and bonding of the ground and Rydberg state hydroxymethyl radicals. Among other points this analysis showed that the hydroxymethyl ion is more strongly bound than the ground state radical. The methoxy to hydroxymethyl radical isomerization rate was directly measured and found to be slower than 2.9 sec^{-1} at 300K.

We note that as a result of these studies REMPI spectroscopy can now optically measure each transient species (F, CH_3O, and CH_2OH) produced and consumed in reaction (1). No other optical spectroscopy can accomplish such measurements.

2. REMPI studies of the F + Ketene reaction.

We have also applied REMPI spectroscopy successfully to the previously uncharacterized reaction of fluorine atoms with ketene and ketene-d2. The exothermic allowed channels are:

$$\begin{aligned} \mathrm{F + CH_2CO} &\longrightarrow \mathrm{HF + HCCO} && \Delta H = -27\ \mathrm{kcal/mol} && \text{(2a)}\\ &\longrightarrow \mathrm{CO + CH_2F} && \Delta H = -35\ \mathrm{kcal/mol} && \text{(2b)}\\ &\longrightarrow \mathrm{H + FHCCO} && \Delta H = -11\ \mathrm{kcal/mol} && \text{(2b)} \end{aligned}$$

The reaction was conducted in a flow reactor and mass resolved REMPI spectroscopy characterized the reaction products.

REMPI signals from fluoromethyl radicals, CH_2F and CD_2F, were observed between laser wavelengths of 270-380 nm. Besides showing the activity of reaction (2b) for the first time, these spectra are also the first spectra of any excited electronic state of the fluoromethyl radical. The REMPI spectra originate from two photon resonances with 3p and 4p Rydberg states. Absorption of a third photon ionizes the radicals. The spectra show vibrational progressions of the CF and CH_2 scissors modes.

During the study unexpected signals from CH and CF appeared. At ~311 nm a 2+1 REMPI band from CH radicals was observed. We determined that the CH radical was generated by the two-step photolysis of ketene:

$$\begin{aligned} \mathrm{CH2CO} + h\nu &\longrightarrow \mathrm{CH2 + CO} && (3)\\ \mathrm{CH2} + h\nu &\longrightarrow \mathrm{CH + H} && (4) \end{aligned}$$

CF radical m/z 31 REMPI bands were observed at 345 and 356 nm. Although we did not directly determine that HFCCO was produced by reaction (2), CF radicals are probably symptomatic of this reaction product. In this view CF radicals would originate via two-step photolysis of HFCCO:

$$\begin{aligned} \mathrm{FHCCO} + h\nu &\longrightarrow \mathrm{CFH + CO}\\ \mathrm{CFH} + h\nu &\longrightarrow \mathrm{CF + H} \end{aligned}$$

Halocarbenes are known to have predissociative states over the study wavelength.

3. Future Work

During the next year we will be continuing our search for free radicals of importance to combustion, photochemistry, and catalysis. Some of the targeted radicals are the phenyl, phenoxy, vinoxy, HO_2, ethynal propargyl, and vinyl radicals. We will conduct experiments that determine REMPI excitation mechanisms and state identities of the new detection schemes we discover.

The new multiphoton ionization apparatus enables us to generate reactive specie by laser photolysis in molecular beams. Because molecular beams enhances the control of experimental conditions during studies, we expect that a significant fraction of our future work will feature this synthetic approach. The new apparatus has facilities to support two molecular beams. During the next year and after initial studies which use molecular beam radical generation, we plan to try some crossed beam bimolecular reactive studies and probe for the nascent products with REMPI mass spectrometry.

C. Reactivity of Small Radicals

(M. J. Kurylo, P. A. Ouellette, and T. J. Wallington)

In this research program, spectroscopic measurement techniques are applied to the detection and chemical kinetic characterization of small gas phase free radicals in a controlled reactive environment. A major goal is to provide a quantitative data base for developing of theory of association reactions. Such studies also have direct applicability in the understanding of tropospheric acid rain formation, stratospheric ozone depletion and other important technological areas. In the area of chemistry we have seen on impressive application of fundamental chemical kinetic information for the solution of societal problems. Increasing emphasis is being placed on high accuracy rate measurements. The Chemical Kinetics Division has long been a participant in this program, with our data center playing a key role. One of us (MJK) is a member of the NASA Stratospheric Kinetics Data Panel. Our choice of problems is thus influenced by the needs of this community. However, these high accuracy measurments also provide important information with regard to fundamental energy exchange effects in unimolecular decompositions.

1. HO_2 Chemistry

During the past year, detailed measurements have been completed which describe the temperature dependence of the reaction

$$HO_2 + NO_2 + N_2 \qquad HO_2NO_2 + N_2 \tag{1}$$

as a function of pressure. This work, supported by the NASA Upper Atmospheric Research Program, utilized the technique of flash photolysis kinetic absorption spectroscopy. Reaction (1) is the primary source of pernitric acid in the atmosphere and plays an important role in the catalytic reaction cycles describing stratospheric ozone depletion. The temperature dependence work is a follow-up to our earlier room temperature investigations from which we were able to calculate the fall-off parameters which relate the pressure dependence of the reaction rate constant. The data from the present work were fit to this same fall-off equation

$$k([M],T) = \{k_{o,M}(T)[M]/(1 + k_{o,M}(T)[M]/k\ (T))\}F_c^{1/\tilde{a}} \tag{I}$$

$$a = 1 + \{(1/N)\log(k_{o,M}(T)[M]/k\ (T))\}^2$$

and

$$N = 0.75 - 1.27\log(F_c)$$

with the temperature dependence of the fall-off parameters given by

$$k_{o,M}(T) = k_{o,M}(300K)\{T/300\}^{-n} \tag{II}$$

and

$$k\ (T) = k\ (300K)\{T/300\}^{-m} \tag{III}$$

The room temperature (300K) values of the fall-off parameters could be determined from the equation (I) analysis of our earlier results. For data evaluation purposes, our results have been fitted jointly with the one other existing temperature study reported in the literature to give (in molecular units)

$$k_{o,N2}\ (300K) = 1.8 \times 10^{-31}$$
$$k_{o,O2}\ (300K) = 1.5 \times 10\text{-}31$$

$$k_{inf}\ (300K) = 4.7 \times 10\text{-}12$$
$$n = 3.2\ q$$
and $$m = 1.4\ q$$

These results support current recommendations which have been based on a limited data set coupled with theoretical computations. A manuscript giving full details of the measurements and data reduction has been prepared for submission to the Journal of Physical Chemistry.

2. OH Reactivity

In addition to the hydroperoxy radical studies, we have initiated a series of experiments directed at the determination of the rate parameters for the reaction of OH radicals with a series of halogen-substituted benzenes. The kinetic parameters derived from this work will lend themselves to mechanistic interpretations and will yield important information about substituent effects in aromatic oxidation reactions thereby assisting our understanding of more complex transformations. This work is nearing completion and a manuscript will be prepared for submission to the International Journal of Chemical Kinetics.

3. Plans

Next year, the HO_2 kinetic studies will be extended to the investigation of reaction (2).

$$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2 \qquad (2)$$

This reaction is important in the atmospheric oxidation of methane and other hydrocarbons as well as in low temperature combustion systems. Laboratory experiments designed for the study of reaction (2) do not lend themselves to standard first or second order kinetic analyses due to complications caused by the self reaction of the two radicals. Instead, the experimental radical concentration vs. time profiles must be compared to concentration profiles produced via computer modeling over a range of experimental conditions for determination of the rate constants. During the previous year we completed work on the computer analysis routines which will be employed in the data reduction and conducted modeling experiments to indicate the experimental conditions which will be most sensitive to the determination of the rate constant.

Future OH studies will be extended to include other substituents (for the aromatic systems) and/or reactions with various reduced sulfur compounds. The former systems will extend the data base for the development of predictive models, while the latter have more direct applicability to atmospheric oxidation and should yield important information regarding the role of Coulombic effects in free radical reactions.

Over the next several months, we also plan to initiate the design and construction of an apparatus suitable for studying reactions of the NO_3 radical. Although this species plays a major role in the chemistry of the troposphere and stratosphere, considerable rate constant and mechanistic data are still needed. A few kinetic studies can be performed for NO_3 using flash photolytic generation. These, however, are limited due to reaction interference of the precursors. For this reason we plan to utilize discharge flow technology coupled with detection via absorption spectroscopy to investigate a series of oxidation reactions involving this important free radical.

D. Reactions of Biradicals and Unsaturated Free Radicals
(W. Braun, A.Fahr and A. Laufer)

The objectives of this program are to produce and chemically characterize biradicals and unsaturated free radicals through flash photolysis using vacuum ultraviolet kinetic spectroscopy to follow species concentrations. Gas chromatography is used for end-product analysis. Isotopic substitution is used to clarify mechanistic processes.

Our recent efforts, supported by the NASA Planetary Atmospheres Program, are directed towards understanding the mechanism of formation and the chemistry of the vinylidene biradical. This species, the smallest of a large class of unsaturated biradicals, was initially identified by us on the basis of its characteristic absorption in the vacuum ultraviolet. We have determined that the particular state of vinylidene under observation is the lowest lying excited triplet, about 40 kcal/mol above the ground singlet state. The particular excited state is metastable with respect to the ground singlet as there is a 45 kcal/mol barrier to its isomerization to acetylene. The intermediate is quite stable requiring about 10^4 collisions to quench.

Triplet vinylidene has been identified as an important intermediate in several photochemical and reactive processes. Although directly observed from the vacuum ultraviolet photolysis of C_2H_4 and C_2H_2, a more convenient source has proven to be the be flash photolysis of vinyl chloride, C_2H_3Cl. The photodecomposition has been previously studied and may be described as follows,

$$C_2H_3Cl \rightarrow H_2C{=}CH_2 + HCl \qquad (1)$$
$$\rightarrow C_2H_2 + HCl \qquad (2)$$
$$\rightarrow C_2H_3 + Cl\ (^2\Pi_{3/2,1/2}) \qquad (3)$$

Aside from C_2H_3 radicals all the decomposition products could readily be monitored by their VUV absorptions. Channel (1) is the primary process and the initial temporal profiles of $H_2C{=}C$ and HCl are identical. They are thus formed in the same reaction. HCl is a non-transient whose concentration could be directly deduced from its absorption. At times short compared to the collisionally induced isomerizaton of the triplet vinylidene, the concentration of $H_2C{=}C$ and HCl are equal. This leads to an extinction coefficient for the former of 694 cm-1 atm-1 at 137 nm. This permits a direct determination of the quantum yield of triplet vinylidene in the photolysis of other systems.

In an earlier study it was shown that He quenched the deuterated vinylidene ($D_2C{=}C$) about 5.5 times slower than the protonated moiety. The observation has been utilized to examine the quenching of vinylidene by a series of non-reactive molecules; Ar, N_2, H_2, CO, and CH_4. To improve the accuracy of the experiments, the study was carried out with deuterated vinylidene rather than protonated which allows for longer time profiles. The rate constants are the sum of all removal processes, including chemical reaction. In the two cases where reaction were possible, H_2 and CH_4, there was no evidence of chemical reaction. The observation agrees with our earlier bond strength-bond length theoretical prediction of slow abstraction rate parameters for the triplet vinylidene radical. The rate constants were of the order of 10^{-14}-10^{-15} cm^3 molec^{-1}s^{-1}. We were able to measure quenching parameters for only a limited number of molecules of interest. To provide an approximation scheme for estimation of physical quenching rate parameters for other species we fit our data to a model using the potential well-depth that has proven to be remarkably useful.

This past year we were able to obtain the first definitive measurement of a chemical process involving triplet vinylidene, i.e., the reaction with molecular oxygen. The reaction, written as

$$D_2C = C + O_2 \rightarrow D_2CO + CO \qquad (4)$$

was found to proceed through a cyclic intermediate comparable to that found in the reaction of several other unsaturated radicals such as C_2H, C_2H_3, C_3H_5, and in the present work D_2CC, with O_2. The striking feature of the reaction was the 1:1 correspondence between the formation of the two products, D_2CO and CO. Nevertheless it was difficult to determine the kinetic parameters in the presence of competing CO producing reactions such as reaction of O(3P) with product acetylene or with C_2H_3Cl reactant remaining following photolysis. All the competing processes were considered and the rate constant for (4), 1.5×10^{-13} cm^3 molecule^{-1}s^{-1}, was obtained from a model.

We have obtained a commercial array detector with which preliminary experiments are in progress to optimize the vacuum ultraviolet response. The commercial device is designed to maximize the output over a wavelength region from the ultraviolet through to the infra-red. Our requirement, however, is limited to the up-conversion from the vacuum ultraviolet to a wavelength observable by the photosensitive device. Initial efforts to improve the response are underway. A factor of 2-3 improvement in sensitivity seems feasible. A critical factor is maintenance of instrumental resolution as it is planned to join the detector to the exit plane of the 2-m Eagle vacuum spectrograph in a configuration that will permit simple conversion from array detection to vacuum ultraviolet sensitive plates which have certain advantages. Our interest is to record a large number of spectral elements, the unique advantage of plate technology, with photomultiplier sensitivity and speed without loss of spectral resolution.

E. Energy Transfer from Vibrationally Excited Molecules

(W. Braun and M. D. Scheer)

We have developed a new method for determining rapidly changing translational temperatures in a gas that has been heated by such transient phenomena as the passage of a shock wave or the absorption of sub-microsecond pulses of radiation from an infrared laser. The method depends upon the use of trace amounts of Hg vapor and its absorption of radiation in the neighborhood of the 253.7 nm isotopic and hyperfine multiplet. As the Hg atoms sense changes in the translational temperature of the host gas, the absorption of 253.7 nm radiation also changes by virtue of the Doppler and Lorentz broadening of the multiplet lines. Emission spectra of a Hg discharge light source in the neighborhood of 253.7 nm were shown to be readily simulated by a two zone computer model even at large optical densities. The same lamp parameters that were used in these calculations could also be used to simulate the experimental pressure and temperature dependence of the total integrated absorption. This provided a means for obtaining the temperature calibration curves needed to monitor the changing translational temperature of a gas undergoing rapid heating or cooling.

This detection method has been directly applied to the measurement of v-r,t energy transfer of vibrationally excited gases. Use was made of a CO_2 TEA laser tuned to P_20 (10.6um) lines to excite SF_6 into some initial distribution of vibrational states. The degree of excitation was systematically varied by attenuating the laser beam with partially absorbing CaF_2 windows. The relaxation was measured by monitoring the time resolved absorption of a 254nm beam by a 500:1 SF_6-Hg mixture. The final temperature, Teq, (i.e. the T after complete equipartition of the excitation energy but before the beginning of significant cooling by thermal conduction) was obtained from the above mentioned Hg absorption vs. temperature calibration.

The experimental results were analyzed as follows: The Hg absorption data (Δ absorption vs time) were converted to ΔT or ΔE vs time curves and the relaxation time constants (τ) were determined from the initial slopes. To obtain the average energy transferred per collision, $\langle \Delta E \rangle$, it is necessary to calculate the energy change during the relaxation process, which is equal to the energy per model of SF_6 required to bring its translational and rotational degrees of freedom from 298K to Teq. It follows then that $\langle \Delta E \rangle = (\tau)/(Z)$, where X is the SF_6 collision frequency and $\langle \Delta E \rangle$ is the average vibration energy transferred to rotation and translation per collision between two vibrationallly excited SF_6 molecules. A decadic plot of log <ΔE> versus log <E> (where <E> is the energy required to bring the SF_6 from 298K to Teq). Shows that <ΔE> increases as the square of the excitation energy <E>.

In a second series of experiments, a trace of toluene (instead of Hg) was added to SF_6 and its absorption of the Cd 228nm resonance line monitored the vibrational energy transfer from the SF_6* into the internal degrees of freedom of the toluene. The time constants obtained with toluene (for v-v transfer) were almost identical to those obtained with Hg as the tracer (for v-v, t transfer) suggesting that toluene may acquire internal energy via the route SF_6(v)-SF_6(r,t)-toluene(v,r,t).

We plan to apply the Hg tracer technique in future experiments to molecules that are larger and more complex than SF_6 and to study how the rates of energy transfer are affected by the structure of the colliding molecule and whether it is a net donor or net acceptor of energy in the relaxation process.

F. MS/MS Tandem Mass Spectrometry

(R. I. Martinez and S. Dheandhanoo)

1. Goals

The focus of this study is the use of MS/MS tandem mass spectrometry to monitor in real time reactive polyatomic species in complex reacting mixtures. The time dependence of the concentrations of all reactants and products provides unique insights into the mechanisms of complex physicochemical systems. Our instrument has been operational since the beginning of the year and we have successfully developed a generic transferable target thickness standard for the common target gases Ar and N_2. This goes a long way towards eliminating one of the major impediments blocking the measurement of standardized MS/MS spectra for characteriza-tion of unknown species. There is a pressing need for quality assurance in this area and the work is supported by the Air Force.

2. Instrumental Approach

Tandem mass spectrometry (MS/MS) exploits the ion fragmentation patterns which are characteristic of the structure of a compound. Thus the ion-fragmentation mapping obtained in the MS/MS by collision-induced dissociation (CID) of ions allows one to uniquely identify any component in a complex mixture. These characteristic profiles ["breakdown curves"] of ion abundance vs. target density (or collision energy) correspond uniquely to the sequence:

(granddaughter)i <-- (daughter)j <-- (parent)k

thus allowing the "genealogical tree" of CID fragmentation to be reconstructed, and the structure of an unknown species to be assigned.

3. Critical Parameters

To permit the characterization of unknown compounds in complex reacting mixtures, it is essential to analyze their CID "breakdown curves". There are several critical parameters which can significantly alter the observed CID spectra. However, one of the most important is the effective gas target thickness. The effective target thickness of the CID gas is defined as: (actual path length traversed by the ion through the CID gas target) x (effective number density of the CID target gas). A recent international round robin test indicated that the effective target thickness of a CID gas was in error by estimated factors of 2-4. More importantly, there has been no direct way to measure the effective target thickness actually perceived by the ions undergoing CID in either molecular beam target or collision chamber instruments. Because of the complex oscillatory trajectories of ions within a quadrupole mass filter, the actual path length traversed by the ion through the CID gas can be significantly longer than the nominal gas target length. Hence, our first task was to develop an absolute target thickness standard. In this we have succeeded.

Knowledge of effective target thicknesses is also essential for the development of CID spectral libraries generated in different types of instruments. On the order of 150 commercial triple quadrupole MS/MS instruments are in operation worldwide, being used as analytical tools for rapid, direct speciation of complex multicomponent mixtures (gas, liquid, or solid). Nonetheless, effective utilization is hindered by instrumental artefacts which have prevented the use of reference spectral libraries. The generation and interchange of reference libraries of CID spectra necessitates standardized operating conditions for the various designs of these instruments.

4. Accomplishments

We have developed a new measurement method which permits in situ calibration of effective target thickness. It involves determination of the cross-section $\sigma(E)$ versus energy (E) curve of the simplest of ion-molecule charge transfer reactions $A+ + B \rightarrow B+ + A$ under pseudo-first order conditions. Since,

$$\mathrm{Ln}\ Y = \sigma E\ L_{eff}\ [B] = \beta\ P_B,$$

where $Y=[A+]0/[A+]$, σE is the reaction cross-section at a collision energy E, Leff= effective path length traversed by projectile ion through CID target gas, Leff [B]= effective target thickness for A+ in B, B= proportionality constant, and PB= pressure of target gas B corresponding to [B], measurement of Ln Y provides in-situ calibration of the effective target thickness if σE is known. Moreover, if we monitor B+, from the relation

$$\mathrm{Ln}\ W = \sigma E\ L_{eff}\ [B] = \beta\ P_B$$

where W= [B+]/{ [B+] - [B+] } = [A+]0/{ [A+]0 - [B+] }, obtaining the same results from Ln Y and Ln W measurements provides strong assurance that the instrument is well behaved.

We have thus obtained the $\sigma(E)$ vs. E relation for the symmetric (resonant) charge transfer reaction $^{22}Ne^+(^{20}Ne,^{22}Ne)^{20}Ne^+$. This reaction was selected to validate instrument performance because the theory of resonant charge transfer is reasonably well established, and because the natural abundance of ^{22}Ne (9.22%) is sufficient to permit the measurement (with good signal-to-noise ratios) of the projectile ion decay (Ln Y measurements) and product ion growth (Ln W measurements). Figure 1 shows our $\sigma(E)$ for collision energies from ca. 5-60 eV (LAB) and summarizes the experimental and theoretical results reported for this reaction by several investigators. Prior to our work, it was not clear from the limited number of experimental studies which theoretical model one could or should use to obtain reliable estimates of $\sigma(E)$ for use in target thickness calibrations. Our results from Ln Y and Ln W measurements provide new $\sigma(E)$ which are in excellent agreement with the Rapp-Francis theory as corrected by Dewangan (see Fig. 3.3 - solid line labelled D). Moreover, our review of work in the field of charge transfer reactions, as summarized in Figs. 1 and 2, indicates quite a disparity among different workers. Similarly, Figure 3.4 shows our results for Ar+(Ar,Ar)Ar+, showing equally good agreement with the Dewangan theoretical line for this reaction (labelled D in Fig. 3.4). Hence, since our instrument is kinetically well behaved, it should be possible to readily determine for polyatomic CID gases the branching ratios $\alpha(E)$ for different reactive channels i. This work has been submitted for publication.

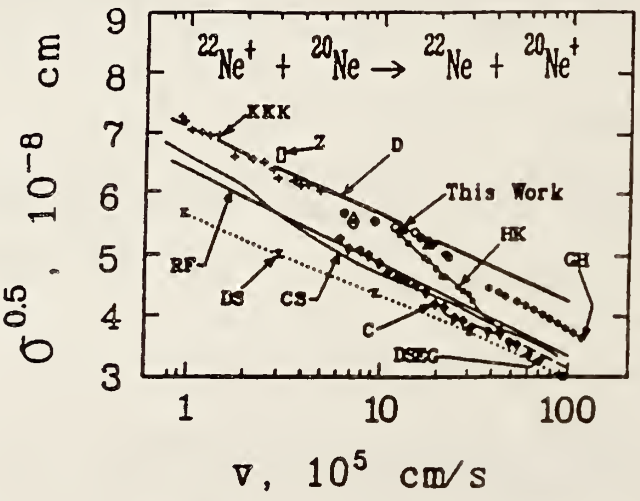


Fig. 3.3. Plot of σ1/2 (reaction cross-section)1/2 vs. projectile ion velocity v. Ne+(Ne,Ne)Ne+ Comparison of our results with other workers and with theoretical models. o,o - our projectile decay experiments; the two symbols correspond to two different sets of experiments. - our product growth experiments

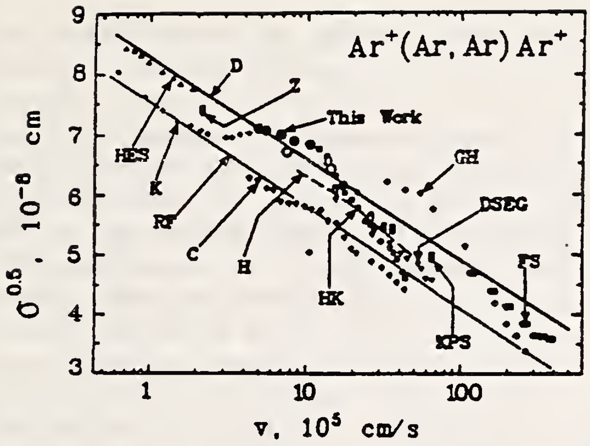


Fig. 3.4. Plot of σ1/2 (reaction cross-section)1/2 vs. projectile ion velocity v. Ar+(Ar,Ar)Ar+ Comparison of our results with other workers and with theoretical models. o - our projectile decay experiments o - our product growth experiment

Other workers can now perform in-situ target thickness calibrations in their instruments by using our measurement protocol with our $\sigma(E)$ vs. E results for the appropriate CID target gas. Since Ar and N_2 are commonly used as CID target gases, our measurements of $\sigma(E)$ for $Ar+(N_2,Ar)N_2+$ and Ar+(Ar,Ar)Ar+ allow one to calibrate in-situ the target thickness of N_2 or Ar gas targets.

5. Plans

Interlaboratory round-robin testing of our kinetic method in various types of instruments is essential to confirm its reliability as a generic target thickness standard. Consequently, we will soon initiate collaborative round-robin experiments with academic, industrial, and government laboratories. Several investigators have agreed to participate to establish the degree of variability one encounters when using a standardized protocol with different operators on the same and/or different instruments of several types. We will also be measuring $\sigma(E)$ for CH_4 targets. Then we will use our kinetic protocol to correct for mass discrimination within the MS/MS between the parent and fragement masses. This is essential to standardize the CID spectra independent of instrument parameters. We will then measure absolute breakdown curves for selected compound classes.

G. Single Pulse Shock Tube Studies on Thermal and Chemical Stability of Aromatic Compounds

(W. Tsang., W. G. Mallard, J. A. Walker, Y. Z. He, and J. P. Cui)

The focus of our work continues to be the behavior of aromatic systems under extreme conditions. This has been a neglected area in chemical kinetics as evidenced by the lack of quantitative data. Our approach has been to study the fundamental aspects of the reactivity of aromatic structures and thereby establish quantatively the scientific basis for future advances. During the past year we have concentrated on defining and resolving a number of uncertainties in the decomposition of nitrotoluene compounds and in exploiting our technique for studying the mechanisms and rates of hydrogen atom attack on substituted aromatic compounds where there is the possibility of multiple reaction channels. The heated single pulse shock tube has worked extremely well and has in fact been in continuous use for the entire year. We are in the process of putting together another instrument. Details of our experiments are given in the following sections. We are particularly interested in extending our data base for the transformation of aliphatic hydrocarbons to cover aromatic systems. This will then permit the full use of the powerful techniques of chemical kinetics modeling for the understanding and optimization of the full range of processes in which aromatic compounds are of key importance.

1. Nitroaromatic Decomposition

Nitroaromatic compounds are important industrial chemicals. Their most important use is as explosives. The stability of such compounds is of great importance for safety as well as a determinant for ignition behavior. As a result there has been much past interest and controversy on the rates and mechanisms of the initial decomposition process. In our report last year we discussed some unexpected results in the decomposition of o-nitrotoluene. We noted that toluene and cresol, the expected products, amount to less than one-half of the total o-nitrotoluene that disappeared. We have now resolved this problem and discovered a remarkable new mechanism for its decomposition. Specifically, it involves the formation and disappearance of anthranil as a key reaction intermediate. The conversion of o-nitrotoluene to anthranilic acid in strong base was first reported by Preuss in 1900. Subsequent isotopic labeling work has established that the reaction proceeds through the initial formation of anthranil. In our shock tube, reactions can only occur in the gas phase and there is no possiblility of base catalysis. It appears that at sufficiently high temperatures a reaction channel has been opened which leads to the same product as the base catalyzed reaction. Our conclusions are based on detection of trace quantities of anthranil in steady state concentration, the determination of its rate of formation and decomposition and the identification of a common product of anthranil and o-nitrotoluene decompositon (which we believe to be cyanocyclopentadiene). Fig. 3.5 is a plot of the larger stable products found during o-nitrotoluene decomposition. Fig. 3.6 shows the effect on the mass balance when anthranil formation and decomposition is taken into account. It is clear that we have accounted for all the decomposition channels of o-nitrotoluene.

The rate expressions that we have found for anthranil formation and destruction are

$$k(\text{o-}CH_3C_6H_4NO_2 \Rightarrow \text{anthranil}) = 1.2\times10^{13}\,\text{Exp}(-26020/T)/s$$
$$k(\text{anthranil} \Rightarrow \text{products}) = 4.0\times10^{15}\,\text{Exp}(-25800/T)/s$$

These rate expressions are compatible with the mechanisms as outlined in Fig. 3.7 and 3.8. A paper on these findings has been submitted to the Journal of the American Chemical Society.

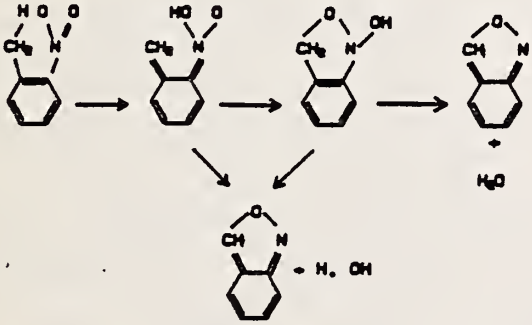


Fig. 3.5. Reaction Products from o-Nitrotoluene Decomposition as a function of C-NO2 bond cleavage rate constants

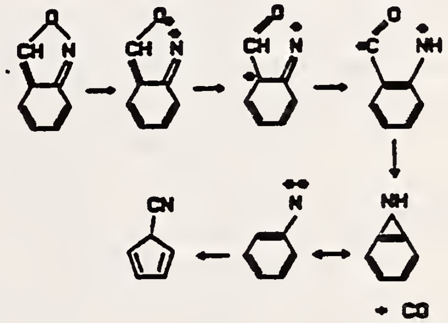


Fig. 3.6. Mass Balance for o-Nitrotoluene Decomposition

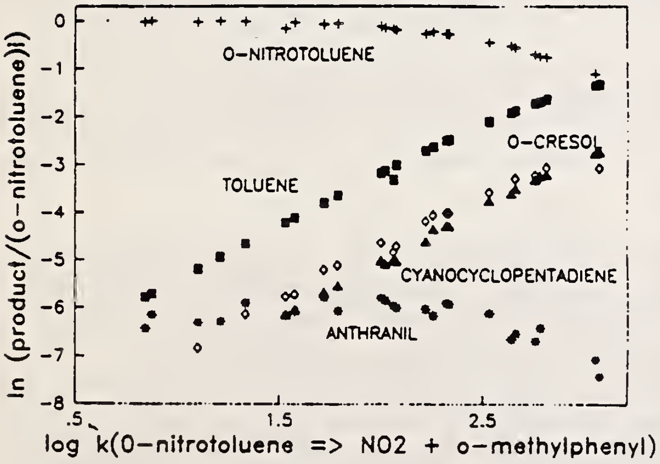


Fig. 3.7. Mechanism for Anthranil Formation from o-Nitrotoluene Decomposition

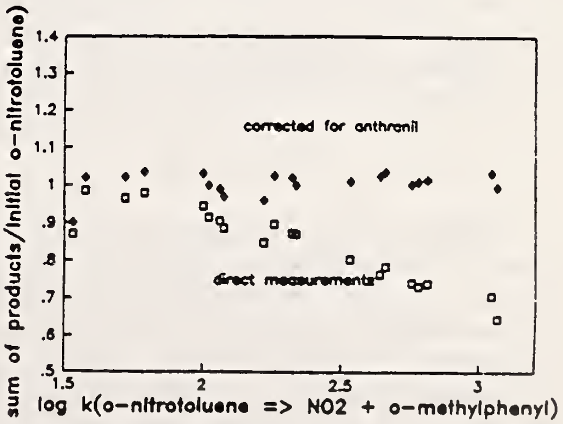


Fig. 3.8. Mechanism for Anthranil Decomposition

We have completed and published in the Journal of Physical Chemistry a paper dealing with $C-NO_2$ bond cleavage in the decomposition of nitroaromatic compounds. This is the main decomposition channel for all except the compounds with a methyl grouping ortho to the the nitro group. The rate expressions are,

$$
\begin{aligned}
k(C_6H_5NO_2 &\Rightarrow C_6H_5 + NO_2) = 1.9\mathrm{x}10_{15}\mathrm{Exp}(-33026/T)/s \\
k(o\text{-}CH_3C_6H_4NO_2 &\Rightarrow o\text{-}CH_3C_6H_4 + NO_2) = 6.4\mathrm{x}10_{14}\mathrm{Exp}(-30888/T)/s \\
k(p\text{-}CH_3C_6H_4NO_2 &\Rightarrow p\text{-}CH_3C_6H_4 + NO_2) = 7.7\mathrm{x}10_{14}\mathrm{Exp}(-32305/T)/s
\end{aligned}
$$

In addition, we estimate that the rate expression for the isomerization of the nitro compounds to the nitrite is approximately $10_{13}\mathrm{Exp}(-27600/T)/s$.

The general trend of these rate expressions is in accord with thermokinetic expectations. It can be seen that the A-factors for $C-NO_2$ bond breaking are very close to each other. Thus, transition state structures for similar processes do not vary greatly. In conjunction with the thermochemistry we obtain a combination rate between phenyl type radicals and NO_2 of approximately 10_9 l/mol-s. This is somewhat lower than combination rates involving organic radicals and is due to the possibility of nitrite formation as an alternative reaction channel. The relative rate constants for $C-NO_2$ bond breaking are of the order of 2.4:1:.8 for o-nitrotoluene: nitrobenzene: p-nitrotoluene at the reaction temperature of approximately 1050K. Thus the effect of methyl substitution is seen to be relatively small under our conditions. The degradation of o-nitrotoluene ultimately to form anthranil is characterized by a relatively small pre-exponential factor. This is expected on the basis of a concerted process similar to the retroene reactions that we are familiar with in hydrocarbon chemistry. In the course of conversion to anthranil either OH and H atom or H_2O is formed. From the yields of the light hydrocarbons which are the result of the induced decomposition of cyclopentane by active radicals we conclude that both channels must make some contribution. The relatively large A-factor for anthranil decomposition is in line with the large entropy of activation to be expected with the breaking of the five membered ring. Finally, the formation of cyanocyclopentadiene suggests the presence of nitrene as an intermediate.

Methyl substitution ortho to the nitro moiety leads to the opening of a new preferred reaction channel. This pathway releases radicals into the system. At temperatures lower than that utilized here, where ignition of nitroaromatic explosives occurs, this will be strongly preferred in comparison to simple $C-NO_2$ bond cleavage or NO_2 isomerization. Note that the rate expressions given here provide to minimum values of the rate constants since in the condensed phase catalysis can occur. These results are in accord with the detection of substantial quantities of dinitroanthranil in TNT decomposition in the condensed phase. Our results are in quantitative disagreement with recent work on the same systems using laser pyrolysis. We attribute this difference to the uncertainty in the reaction conditions in laser pyrolysis. A comparison of the two set of results leads us to suspect that the temperatures may be much higher than claimed. This work has been supported by the Army Research Office.

The results of this study are indicative of the interesting new reaction channels that become available as one goes to more complicated molecules. At the present time we have no basis for predicting how and when such processes will occur. Nevertheless organic chemists have for many years used high temperature pyrolysis as a preparative tool. We believe that we have now the means of systematically examining the details of such processes and placing the kinetics for decomposition into a quantitative frameworks.

2. Hydrogen Atom Attack on Substituted Aromatics:

We continue to exploit the technique discussed last year for the determination of the mechanisms and rates of hydrogen attack on substituted aromatic compounds. These processes are characterized by a multiplicity of reaction channels and at the present time there are no other methods that are capable of determining the kinetic characteristics of these very interesting processes. These include the effect of resonance energy on hydrogen atom abstraction reactions and the controlling factors affecting displacement processes. A paper on hydrogen atom reaction with toluene has recently been published. We have now completed work on the reactions with phenol, aniline and several chlorinated toluenes. Phenol is a key intermediate in the oxidation of aromatic structures, while chlorinated aromatics represent the most pressing issue in the incineration of hazardous wastes.

For the phenol study we have also determined the rate constants for OH attack on phenol and H-atom combination with phenoxy radical. A paper has been submitted for publication in the Journal of Physical Chemistry. In the following we summarize briefly the salient points in this work.

The experiments involve decomposing hexamethylethane in the presence of sufficiently large excesses of phenol. Hydrogen atoms, formed through the reaction

$$C_8H_{18} \Rightarrow 2\ t\text{-}C_4H_9 \Rightarrow C_4H_8 + H$$

react with phenol via abstraction of the phenolic hydrogen and displacement of OH. From the isobutene and benzene that is formed we find,

$$k(H+C_6H_5OH \Rightarrow C_6H_5O+H_2)/k(H+C_6H_5OH \Rightarrow C_6H_6+OH) = 16\text{x}\mathrm{Exp}(-3366/T)$$

over the temperature range 950-1100K and between 2.5 to 5 atms. In the presence of added methane, the benzene yield is depressed due to the reaction of hydrogen atoms with methane. Using a rate expression of $k(H+CH_4 \Rightarrow CH_3+H_2) = 2.4\text{x}10^{11}\ \mathrm{Exp}(-7000/T)$ l/mol-s, we find

$$k(H+C_6H_5OH \Rightarrow H_2+C_6H_5O) = 1.15\times10^{10}\ \exp(-3289/T)\ \text{l/mol-s}$$
$$k(H+C_6H_5OH \Rightarrow C_6H_6+OH) = 1.8\times10^{11}\ \exp(-6655/T)\ \text{l/mol-s}$$

The substitution of large quantities of carbon monoxide in place of methane leads to increased yields of benzene. This is due to the conversion of the displaced hydroxide radicals to hydrogen atoms and its reaction with phenol. On the basis of $k(OH+CO \Rightarrow CO_2+H) = 7 \times 10_7 \exp(.00092T)$ l/mol-s, we find

$$k(OH+C_6H_5OH \Rightarrow C_6H_5O+H_2O) = 6\times10_9\ \text{l/mol-s}$$

at 1032K. From the equilibrium constant the rate expression for the displacement of a hydrogen atom by hydroxyl radical is

$$k(OH+C_6H_6 \Rightarrow H+C_6H_5OH) = 6.5\times10_9\ \exp(-4430/T)\text{l/mol-s}$$

Comparison with OH disppearance rates in high temperature benzenes systems indicates that the primary process is the abstraction of a ring hydrogen. Finally, from results of experiments which lead to high yields of phenoxy radicals, we find

$$k(H+C_6H_5O \rightarrow C_6H_5OH) = 2 \times 10_{11}\ \text{l/mol-s}$$

Through detailed balance this leads to

$$k(C_6H_5OH \rightarrow C_6H_5O + H) = 4 \times 10_{15}\ \exp(-86000/RT)/\text{s}$$

The results of these and earlier study demonstrate that we have now a unique methodology for studying the reactions of hydrogen atoms with molecules where there are multiple reaction pathways. We plan to systematically exploit the possibilities and therebye build up an internally consistent set of rate constants for all high temperature reactions involving hydrogen atoms and organic substrates.

H. Substituent Effects on Bond Strengths

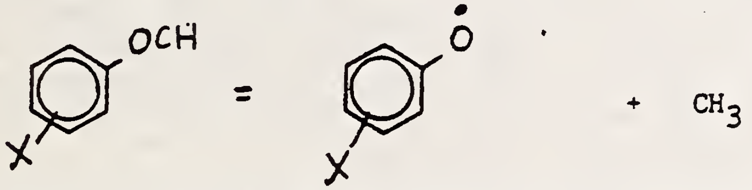
(S. E. Stein and M. Suryan)

In the simplest terms, rates of elementary chemical reactions in gases and non-polar environments depend on properties of the reaction center (atoms directly involved in bond making and breaking) and on effects of substituents. The nature of the reaction center defines the type of reaction and is generally the dominant factor. However, substituents can be very important and have long been of interest as a means of perturbing chemical reactions in a controlled and variable manner. One way in which substituents influence reactions is through their effects on bond strengths. However, remarkably little information of this nature is available. Moreover, most of the available data does not provide accurate differences in bond strengths because of the divergent experimental techniques used and the different treatments of the data. We have therefore undertaken a program for measuring accurate relative bond strengths for a variety of substituents of general chemical interest.

Our focus has been on substituents attached to methyl, benzyl and phenoxyl groups. We have measured rates of bond breaking for a large number of 2-substituted ethylbenzenes, anisoles (methoxybenzenes) and ring-substituted ethylbenzenes (reactions 1-3) using our very low pressure flow reactor. Differences in decomposition rates of substituted compounds yield differences in bond strengths.

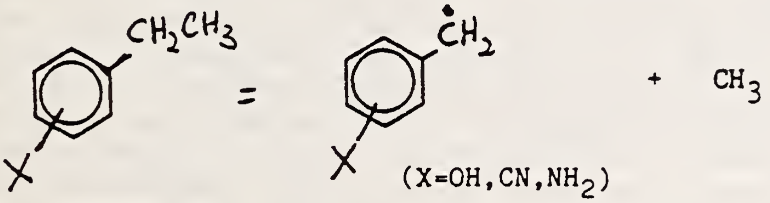
$$PhCH_2\text{-}CH_2X \; = \; PhCH_2^{*} \; + \; CH_2X \qquad (1)$$

($X=CH_3, COCH_3, OH, CN, CHO, NH_2, NHCH_3, C_2H, C_2H_3, Ph$)



(2)

($X=CH_3, COCH_3, OH, OCH_3, CN, CHO, NH_2, NO_2, C_2H_3, F, Cl, Ph, C_4H_4$)



(3)

($X=OH, CN, NH_2$)

Studies of reaction 1 led to the determination of accurate relative bond strengths for bonds of wide chemical interest (those forming substituted methyl radicals upon dissociation). While bond strengths of the majority of these bonds have been reported in the literature, accurate relative values are not available because of the wide variety of precursor molecules and experimental systems used. Preliminary values for lowering of Gibbs dissociation energies (in kcal/mol relative to ethylbenzene at 1000K) by X in $PhCH_2\text{-}CH_2X$ are, $X=CH_3$, 3; $COCH_3$, 3; OH, 4; CN, 5; CHO, 5; NH_2, 6; $NHCH_3$, 7; C_2H, 9; C_2H_3, 11; Ph, 11.

Effects of substituents on the second reaction type were surprisingly large for electron "donating" groups ($X= NH_2$, CH_3, OH, and OCH_3) and strongly dependent on the position of substitution. For such groups bonds were weakened by ortho- and para-substitution and slightly strengthened by meta-substitution. To illustrate, relative to the unsubstituted compound (X=H, anisole), for $X=OCH_3$ rates were 10, 1.7, and 7 (at 1000 K) in the ortho, II meta and para position. A particularly large effect was found for substitution at the ortho position for X=OH and NH_2. In these cases rates for ortho,meta,para substitution (again, relative to anisole) were 40, 0.7, 12 (X=OH) and 50, 0.7, 11 ($X=NH_2$). The origin of this ortho effect is unclear and is under further study. Polar electron withdrawing groups (X=CN, $COCH_3$, CHO and NO_2) have effects on bond strengths opposite those of donating groups, although the magnitudes of their effects are much smaller. Phenyl, benzo- and vinyl-groups significantly weakened bonds. Fluorine and chlorine substitution had a smaller effect. Relative rates closely parallel published electron spin densities in substituted phenoxyl radicals (W. T. Dixon et al. J. Chem. Soc., Faraday Trans I, 1713 (1974) and roughly follow available substitutent constants for electrophilic reactions in solution (the Hammett sigma+ constant). The large effect observed for electron donating groups is apparently due to the combined effect of destabilization of the anisole molecule by the substituent and stabilization in the product phenoxyl radical. Electron withdrawing groups presumably stabilize both the molecule and the radical and therefore have less effect. These ideas are being tested by theory.

The effects of substituents in the ring-substituted ethylbenzenes (reaction 3) were far smaller (a factor of ca. 5 less) than for substituted anisoles and both electron donating and withdrawing groups weakened the benzylic C-C bond. This again is in agreement with trends observed in ESR experiments. Along with the above results, these findings enable the parameterization of ESR data for the quantitative prediction of bond strengths not readily measured in a direct manner.

Over the next year we will examine these reactions using both ab initio and semi-empirical theory to gain further insight into the origin of these substituent effects. We will also use these values to separate so-called polar and thermodynamic effects on available rate constants for reactions involving these substituents. We will then turn our attention to the measurement of bimolecular rate constants at high temperatures using both our conventional low pressure flow reactor and a new, very high temperature graphite Knudsen cell reactor now under construction. Specifically, we will attempt to measure rates of reaction of vinyl radicals with unsaturated molecules. No data of this nature are available despite the widespread use of these reactions in combustion models. The possibility that these reactions may involve chemically activated isomerization steps make these reactions very interesting at a fundamental level.

I. Chemical Theory of Graphite

(S. E. Stein, R. L. Brown and S. A. Kafafi)

Graphite and many carbonaceous substances consist primarily of large polyaromatic molecules of varying size, shape, and edge composition. An understanding of the chemistry of graphite is hampered by the inability to isolate these large molecules for individual study. As a result, the chemistry of graphite is often treated phenomenologically. Reactivity is thought to involve edges, defects and other "active" sites, although the chemical nature of these is a matter of speculation.

To develop this understanding we have been engaged in a program which focusses on the fundamental chemical properties of very large polyaromatic structures. Graphite and nearly all carbonized organic materials are composed primarily of these structures. Early in this program we discovered that the atomic orientation at the edges of these structures and their overall size were critically important factors in determining the reactivity of these structures. Our work has therefore concentrated on separating and examining individually these two variables.

Our major recent finding has been that a modified version of classical Huckel theory is both qualitatively reliable and quantitatively accurate when applied to large polyaromatic species. In addition, we found that both the simpler theories (PMO, structure-resonance theory and other perturbation methods) and the more computationally involved SCF-methods make serious errors in their extension to very large molecules. We now have a predictive theory that we feel is not prone to major errors. Fortunately, this theory is sufficiently simple to allow calculations for molecules as large as we wish (up to several thousand carbon atoms). One important result of this application is that attack of interior carbon atoms in graphitic sheets results in a significant loss of resonance energy and is thus not likely to be an important process in graphitic systems. Another finding is that large differences in reactivity between different edge sites remains even in the limit of an arbitrarily large graphite structure. Simpler theories incorrectly predicted that all sites become equally reactive in the limit of very large cluster size. More sophisticated theories incorrectly predict a finite, edge- dependent band gap in very large clusters as well as an unreasonable bond alteration. We have also discovered that this modified Huckel method accurately predicts heats of formation of pi-radicals. This technique has not previously been thoroughly applied to these species, so that this observed accuracy strongly supports the reliability of this theoretical approach.

In general terms, edge carbon atoms behave very much like those of normal polynuclear aromatic molecules, with properties depending strongly on the local structure. Phenanthrene-like edges are rather unreactive and thermodynamically stable. They are as susceptible to free radical and electrophilic attack as are structurally related positions in naphthalene and phenanthrene. Anthracene-like edges are thermodynanamically unstable and highly reactive, with properties comparable to those of the linear polyacenes. Regardless of edge structure, interior carbon atoms situated only several bond lengths from an edge have properties (bond orders, free valence) not far from those of the interior carbon atoms in cata-condensed polyaromatic molecules like coronene. A significant general finding for the molecules studied is that there is only a weak relation between the position of the highest occupied molecular orbital and the reactivity of the most reactive position. For instance, while very large Series 3 molecules (phenanthrene-like edges, see Fig. 3.9) will have higher HOMO energies than small Series 1 molecules (anthracene- like edges, see Fig 3.9), they will be far less reactive (cf., Figs. 3.10 and 3.11). This HMO method predicts that thermodynamic stability is strongly influenced by edge type. In contrast, because they utilize local properties only, group additivity methods do not predict significant edge effects.

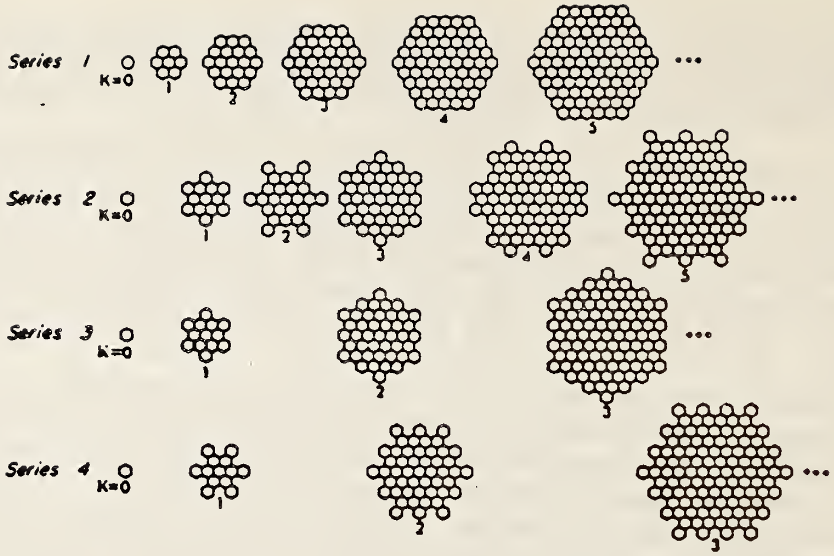


Fig. 3.9. Homologous series of hexagonally symmetric molecules.

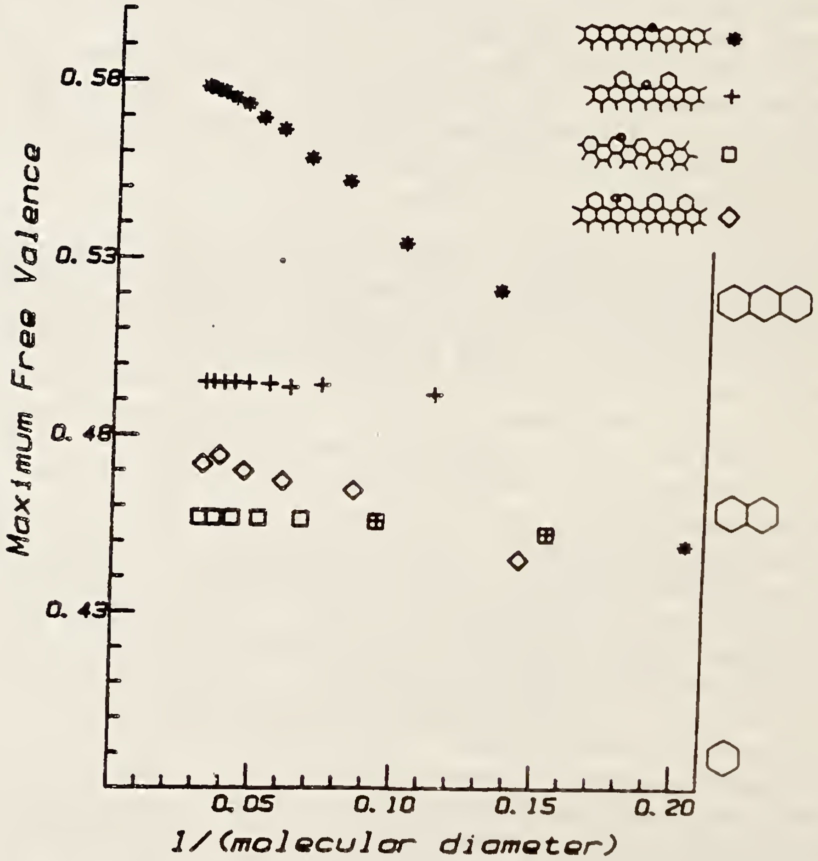


Fig. 3.10. Maximum free valence for each molecule in the four homologous series as a function of molecular size.

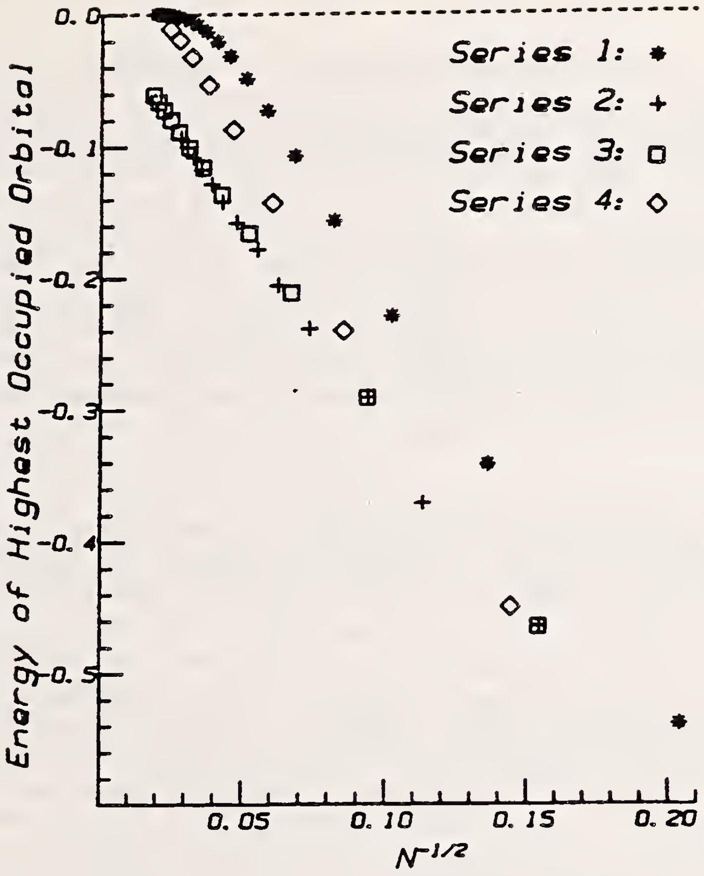


Fig. 3.11. Energy of highest occupied molecular orbital (HOMO) as a function of molecular size. The reciprocal of the square root of the number N of Pi-electrons in the molecule was used for the abscissa. This was done to expand the scale near the origin (i.e., where N goes to infinity). Energy is in units of β.

Wave functions, which describe overall molecular properties, separate into two distinct classes for molecules with reactive edges. Those of a more stable variety are qualitatively similar to those of an infinite plane and of the molecules with stable edges. Those of a less stable variety correspond to orbitals whose electron density are located primarily at the edges. The latter variety lead to a near zero band gap, and the associated spectroscopic and electronic properties, for molecules of relatively small size. For example, a molecule with reactive edges containing 60 carbon atoms has the same band-gap as a molecule of the stable variety containing between 2000 and 2500 carbon atoms.

4. ION KINETICS

R. E. Huie, R. D. Levin, S. G. Lias, M. Mautner, P. Neta, L. W. Sieck,
N. Altstein, A. Harriman, and S. Mosseri

A. Overview

Research of the Ion Kinetics Group is concerned with the mechanisms and rates of chemical reactions of charged species in the gas and condensed phases. The group was originally associated with the competence-building program, "Kinetic Studies of the Effects of Ionizing Radiation" which investigated the chemical effects of ionizing radiation on matter. While this highly successful initiative expires in October, 1986, an important part of the research of the group remains in the field of radiation chemistry. The radiation chemistry studies primarily address the kinetics and mechanisms of reactive intermediates generated in the liquid phase by high energy pulses of electrons. Related studies in the gas phase examine the bimolecular chemical reactions and thermochemistry of positive and negative ions using kinetic mass spectrometry as a research tool.

The broad interest of the program is illustrated by the diversity of Other Agency support granted to members of the group. The liquid phase radiation chemical studies of electron transfer processes are supported by the Chemical Sciences Division, Department of Energy, because of applications of the results to solar energy conversion. A grant from the Environmental Protection Agency has been given for the studies of the chemistry of aqueous inorganic solutions for understanding the mechanism of formation of acid rain. Some aspects of the gas phase ion chemistry program are supported by the Department of Energy, which is interested in developmental work on the analytical technique known as chemical ionization mass spectrometry. The Air Force Office of Scientific Research also gives support to the kinetic mass spectrometry work because an understanding of the reactions and photochemistry of small hydrocarbon ions is of concern for spacecraft survivability.

The group also has been historically affiliated with the Ion Kinetics and Energetics Data Center, with members of the scientific staff collaborating on compilations and evaluations of data necessary for the understanding of the chemistry of ions and the effects of ionizing radiation on matter. The activities of the Data Center are described in Section 2.

The individual tasks included in the program of the Ion Kinetics group are summarized as follows:

Kinetics of the Interactions between Ions and Molecules

Fundamental investigations of the chemistry of ions, including determination of reaction rates, mechanisms and thermochemistry.

Energetics of Solvation and the Chemistry of Solvated Ions

Studies of the link between the kinetics and thermochemistry of ions in the gas phase and in the liquid phase; the prediction of liquid phase thermochemical parameters from the results of gas phase mass spectrometric studies.

Radiation Chemistry of Organic and Biochemical Solutions

Pulse radiolysis investigations into energy transfer and radiation damage mechanisms in biologically important substances.

Kinetics and Radiation Chemistry of Aqueous Inorganic Solutions

The study of electron transfer reactions in aqueous solutions of inorganic salts, with particular emphasis on the kinetics of reactions involving SO_3^-, SO_5^-, and HSO_5^-.

Ion Kinetics and Energetics Data Center

The maintenance of an up-to-date evaluated data base on the thermochemistry of ionization processes and the kinetics of ionic reactions, and the publication of related compilations.

B. Gas Phase Ion Kinetics

The program aims at achieving a fundamental understanding of unimolecular and bimolecular reactions of positive and negative ions in the gas phase, and further, at examining the kinetics and thermochemistry of ion/molecule clustering, i.e. of solvation. Experimental work is carried out using two kinetic mass spectrometers, a pulsed ion cyclotron resonance spectrometer (ICR), ideal for establishing reaction mechanisms and for accurate rate constant determinations, and a unique pulsed high pressure mass spectrometer which is particularly adapted for studies of the thermochemistry of ion/molecule clustering processes.

1. Kinetics of Ion/Molecule Reactions: Thermochemical Kinetics of Ions (S. G. Lias, M. Mautner, and L. W. Sieck in collaboration with P. J. Ausloos, 540, and T. J. Buckley, 543)

This task involves the elucidation of the bimolecular chemistry of ions generated in the gas phase, including an examination of reaction mechanisms and measurements of rate and equilibrium constants as a function of temperature. The latter experiments lead to quantitative information about the thermochemistry of proton transfer, charge transfer, and other ionic reactions. The scientific emphasis of the work ties in directly with the data evaluation efforts of the Ion Kinetics and Energetics Data Center. Accomplishments of the past year are discussed below.

(a) Rate Constants of SF_6- Reactions

A collaborative study is in progress with R. J. Van Brunt of the Electrosystems Division (NBS) and I. Sauers (ORNL). This project involves measurements of the rate constants for reactions involving SF_6-and various neutral species such as SOF_4, SOF_2, SO_2F_2, SO_2, SiF_4, etc., which are known to be major long-lived stable by-products of the decomposition of SF_6 in the presence of trace oxygen and water vapor. The temperature dependences of the various rate constants are under investigation here, while the ORNL measurements involve the dependence of k on electric field strength (E/N). Some of the reactions, including $SF_6^- + SOF_4 \rightarrow SOF_5^-$ and $SF_6^- + SO_2 \rightarrow$ products, are found to exhibit rate constants which show strong negative temperature coefficients (see Fig. 4.1). The information derived from these studies is being used to generate a computer model which predicts the behavior of oxy-fluoride production during corona discharge in high pressure SF_6, which in turn will provide new insight on the processes occurring in vapor-insulated high voltage systems and during plasma etching, both of which incorporate SF_6 as the gaseous dielectric.

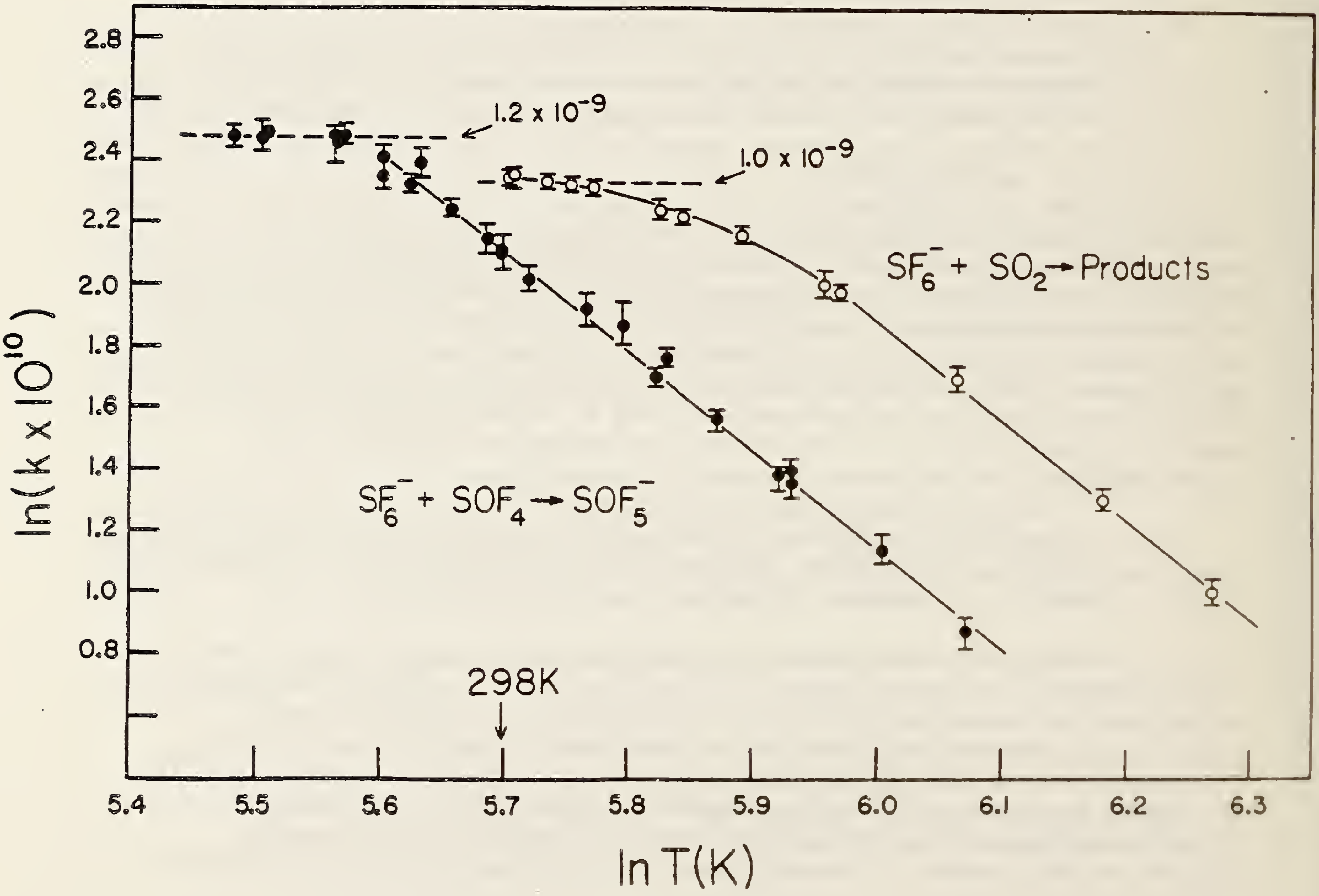


Fig. 4.1.

(b) Proton Affinities of Hydrazines

In spite of the wealth of data which exists concerning the gas phase basicities and proton affinities of organic compounds, no information is available for relatively complex alkyl-substituted hydrazines. This class of molecules is of special interest due to its biological importance, and because of the large geometry changes which occur upon ionization. The individual proton affinities of 16 cyclic and acyclic hydrazines were measured relative to monoamine standards. As expected, the values were found to be quite high, ranging from 224.4 kcal/mol for tetramethyl- to 231.6 kcal/mol for bis-piperidine and 2,3-diaza-2,3-dimethylbicyclo[2.2.2]octane. Variable temperature equilibrium constant measurements verified that entropies of protonation are smaller than 1 cal/deg-mol. The proton affinities were combined with adiabatic ionization energies (also measured in this laboratory) to give the (N+-H) bond dissociation energies, which can then be used to quantitate the stabilization conferred on a hydrazine cation radical by its 3 electron pi bond. The accumulated data indicate approximately 20 kcal/mol stabilization in the tetraalkylhydrazines. These studies were collaborative efforts with the laboratory of Professor Steve Nelsen, University of Wisconsin.

(c) Structures and Kinetics of $C_6H_5^+$ Ions

A comprehensive examination of the structures and reaction kinetics of $C_6H_5^+$ ions has been carried out on the NBS ion cyclotron resonance spectrometer (ICR). It was found, in agreement with previous work, that $C_6H_5^+$ ions generated as fragment ions in aromatic compounds, from dissociative proton transfer to halobenzenes, or as products of ion/molecule condensation reactions such as:

$$C_4H_3^+ + C_2H_2 \rightarrow C_6H_5^+$$

dsplay two or more structures. Ions which unambiguously have the phenyl structure were formed by irradiating $C_6H_5Cl^+$ ions with an argon ion laser; dissociation of the molecular ion results in the formation of phenyl ions in a two-photon process. An examination of the bimolecular reactions (and rate constants for these reactions) of the phenyl ions and the various $C_6H_5^+$ isomers formed in different systems, revealed that structural assignments made in collision-induced dissociation studies in the literature had were erroneous. The isomerization mechanisms were mapped as a function of energy. These results were used in the Ion Kinetics and Energetics Data Center evaluation of the thermochemistry of $C_6H_5^+$ species.

(d) Comparison Standard for Acidity Scale: The Acidity of Methanol

An existing scale of gas phase acidities of molecules, which had been established by ion/molecule equilibrium constant determinations in ICR instruments in a number of laboratories, suffered from the fact that absolute values assigned to acidities at the high end of the scale were unreliable, particularly for aliphatic alcohols, acetylene derivatives, and aromatic compounds. This unreliability was linked to the acidity of a key compound, methanol, which could not be directly determined by ICR spectroscopy relative to a reference standard such as H_2O for which an absolute acidity value is available; because of the large difference in their respective acidities the proton transfer equilibrium constant for the reaction:

$$OH^- + CH_3OH \Leftrightarrow CH_3O^- + H_2O$$

is too large to be determined by ICR. However, the equilibrium constant associated with this process was readily accessible to measurement by the pulsed high pressure mass spectrometer because that instrument has a much greater dynamic range than ICR. Taking advantage of the variable temperature capability of the instrument, the equilibrium constant was determined as a function of temperature, leading to reliable enthalpy and entropy changes for the equilibrium. From these results, it was determined that the acidity of methanol is 381.6+-0.7 kcal/mol. Experimental re-evaluation of acidities of compounds in the range 370-410 kcal/mol is in progress.

2. Solvation Thermodynamics and the Kinetics of Solvated Ions
(M. Mautner and L. W. Sieck)

Ionic species such as those generated in acidic or basic environments or by radiation are ubiquitous intermediates in biochemical and organic reactions. The stabilities and reactivities of ionic intermediates are affected by their intrinsic molecular properties (studied in the gas phase as described above), and by interactions with the condensed phase environment. This task utilizes the high pressure mass spectrometer to bridge the gap between the understanding of ionic chemistry attained in the gas phase studies and that required for understanding and predicting processes occurring in irradiated liquids, acid catalyzed reactions, and enzyme catalyzed processes. In the high pressure mass spectrometer, it is possible to generate a given ion in the presence of a solvent molecule (such as H_2O, for example) to determine the thermochemistry of solvation by an examination of equilibria such as:

$$A^+ + M \rightarrow [A^+.M]$$

$$[A+M] + M \rightarrow [A^+.M_2]$$

and to study the kinetics and mechanisms of reactions of the solvated ions. These data can then be used to interpret liquid phase data on ionic processes in terms of intrinsic molecular properties.

In the fall of 1985, a comprehensive study of the kinetics and thermochemistry of clustering reactions initiated by anions of the type RO-and RCO_2- (where R is an alkyl group or H) was initiated. The goal of this project is: (1) to provide the first-ever information concerning the thermochemistry (stabilities) of association ions incorporating organic ligands where the bonding is of the type RO-...H-O- and RCO_2-...H-O-; and (2) to use the information derived from model systems to generate predictive schemes (correlation lines) which define the relationship between the dissociation energy of the cluster ion and the gas phase acidity of the ligand. Related work involving determinations of the acidities of organic compounds has been described above. This is an ongoing project which continues as of this writing. Work has been carried out during the past year on the following problems:

(a) Dissociation Energies of RO-...H-O- and RCO_2-...H-O Bonds

Dissociation energies of RO-HOR, RCOO-HOR, and RCOO-HOOCR complexes were measured and found to range from 14 to 29 kcal/mol. High values (28.8 and 29.3 kcal/mol) were found for the symmetric dimers CH_3O-$HOCH_3$ and CH_3COO-.$HOOCCH_3$. The binding energy was found to decrease as the difference between the acidities of the components increase. For 13 dimers, it was found that the relationship between the differences in gas phase acidity of the complexed molecules and the binding energy of the complex could be expressed as a linear correlation. However, data for some dimers were found to deviate substantially from the correlation, suggesting structural effects. For example, the large binding energy value of 36.8 kcal/mol found for HCOO-HOOCH suggests double hydrogen bonding involving a CH...O- type bond. On the other hand, the data indicate that only one hydrogen bond is formed in RCOO-.H_2O association ions. Comparison between anionic and cationic hydrogen bonded systems shows that the bonding energies are similar for RO-B and ROH_2+.B complexes involving the same ligand, B, suggesting primarily electrostatic interactions in both, while RCOO-.B is weaker by 4 - 6 kcal/mol than $RCOOH_2$+.B, possibly due to charge delocalization in RCOO-. The weakening of O-...HO hydrogen bonds to charge delocalized anions was also observed in CH_2=CHO-.H_2O, where the binding energy is 15.3 kcal/mol. Additional measurements involving a variety of delocalized anions are currently in progress.

(b) Thermochemistry of Mixed Water-Methanol Cationic and Anionic Clusters

The thermochemistry of mixed water-methanol cationic clusters, $(H_2O)n(CH_3OH)mH$+, and anionic clusters, $[(H_2O)n(CH_3OH)m$ -H]-(i.e. clusters containing OH- or CH_3O-) was measured. It was found that the total hydrogen-bonded network in as given positive cluster was more stable by 3 - 6 kcal/mol than that in the corresponding negative cluster. The variations of the stabilities of the cationic and anionic clusters with number of components (n + m) show remarkable similarities. For example, both $H_3O^+.nH_2O$ and $OH^-.nH_2O$ exhibit effects of solvent shell filling at n = 3. The neat methanol clusters were found to be more stable than neat water clusters, and the difference varied only slightly with n. This was found to be true for both the anionic and cationic systems. The thermochemistry suggests that the favored topology in mixed water-methanol clusters is one which places the methanol molecules near the charge center and water molecules at the periphery.

(c) Structures of Ionic Clusters

Another study involved evaluation of attachment energies for successive solvation of cations in order to determine at which step a distinct solvent shell is filled. Thermochemical criteria were developed and applied to data on clustering about metal ions and onium ions. Satisfactory evidence for the distinct filling of shells was found in 14 systems, and tentative evidence was found in another 15 out of the 59 systems evaluated.

(d) Heats of Hydration of Protonated Oxygen and Nitrogen Bases

In a related project, gas phase clustering data were used to predict heats of hydration of protonated oxygen and nitrogen bases. Using simple empirical relations, the ionic heats of hydration were found to be predictable within -+2 kcal/mol on the basis of just one parameter, the gas phase proton affinity of the base. The model which was developed demonstrates the use of gas phase data in analyzing the factors which influence ion solvation in solution.

C. Liquid Phase Ion Kinetics

The program aims at achieving a fundamental understanding of the chemistry of reactive intermediate species generated in liquids by pulses of high energy electrons. Experimental work is carried out using two electron accelerators, a Febetron and a pulsed Van de Graaff, coupled with optical detection techniques. The scientific emphasis of the work also leads to data evaluation efforts, described under the write-up for the Kinetics Data Center. Accomplishments of the past year are discussed below.

1. Radiation Chemistry of Organic and Biochemical Solutions
(P. Neta, A. Harriman, M. Mautner, and S. Mosseri)

Pulse radiolytic techniques are used to characterize the chemical properties of short-lived species in irradiated solutions. Particular attention is given to the chemistry of reactive transients which have been implicated as intermediates in a variety of chemical and biological systems. An important aspect of this program is the study of inter- and intramolecular electron transfer processes aimed at understanding similar phenomena in biological systems, as well as in photochemical systems of interest for possible use in solar energy conversion; this aspect of the work is supported by the Department of

Energy. By studying the kinetics and mechanisms of the various transient species and by understanding the parameters that control them, one can hope to be able to predict the behavior of these species in more complex systems.

(a) Photogeneration of Oxygen or Hydrogen from Water: Laboratory Studies of Solar Energy Storage

Photogeneration of oxygen from water is an integral part of green plant photosynthesis and many laboratory models aimed at the storage of solar energy have tried to mimic this natural process. In this problem area, an experimental examination of the catalytic oxidation of water to oxygen by metalloporphyrin pi-radical cations has been carried out. In the ideal case, a metalloporphyrin (synthetic analogue of chlorophyll) absorbs light and forms an excited state which then donates an electron to another compound in the system. The electron acceptor then reacts with a catalyst to form hydrogen from water. The metalloporphyrin radical cation (formed after donating an electron) should react with another catalyst that will produce oxygen. Thus the overall process is the decomposition of water by sunlight to hydrogen and oxygen with no net change in the other components of the system. For this purpose, it is necessary to find the proper catalyst, the best metalloporphyrin, and the optimal experimental conditions. This was done using pulse radiolysis and monitoring the rate of reaction of various porphyrins and catalysts to determine the factors that influence these rates.

Previous work in this laboratory, which was concentrated on zinc porphyrins, examined the effects of variations in porphyrin structure and solution conditions on the oxidation of water to oxygen by the porphyrin radical cation, catalyzed by RuO_2. During the past year, the effect of variations in the metal center was examined, with attention given to Mg, which is also the metal center of chlorophyll. Comparing Mg to Zn and other metals (Pb, Cd, Pd, Cu, Fe, In) correlations between the electronegativity of the metal, the oxidation potential of the porphyrin, and the lifetime of the metalloporphyrin radical cation are found. Increased electronegativity pulls electrons from the porphyrin ligand to the metal center, raising the oxidation potential and making water oxidation more thermodynamically favorable. On the other hand, increased electronegativity promotes hydroxylation of the radical cation which results in shorter lifetime and thus a lower probability of reaction with the RuO_2 catalyst. Thus, the electronegativity of the metal exerts two opposing effects on the processes leading to oxygen products and necessitates optimization of conditions.

In examining variations in the metal center, attention has also been given to metalloporphyrins in which the metal is oxidized, rather than the ligand. Certain Mn(III) porphyrins were found to undergo oxidation to the Mn(IV) state, which is unstable in neutral solutions. The Mn(IV) is reduced back to Mn(III) but without oxidizing water to oxygen. The RuO_2 catalyst has a pronounced effect on the decay kinetics and some oxygen is evolved in the process, but the yield is very poor. Therefore, studies have been initiated on other transition metal porphyrins that may form higher oxidation states. Preliminary examination of ruthenium and osmium porphyrins indicates that the former produce radical cations while the latter are oxidized at the metal center.

Related work is aimed at improving the properties of the RuO_2 catalyst. Preparations have been attempted using radiolytic reduction of RuO_4^- without the polymer. (The usual procedure involves chemical reduction of RuO_4^- with H_2O_2, followed by stabilization with a short water-soluble polymer). The product formed appears to have smaller size particles and to be more stable over long periods. Its exact structure and its efficiency in oxygen production are under study.

Some attention was also given during the past year to hydrogen production through the photodecomposition of water. Preliminary studies on Au(III) porphyrins indicate formation of stable radical anions which react on the surface of colloidal platinum catalyst to reduce water to hydrogen. The kinetics of reaction of Pt catalyst with several reducing radicals is under study.

(b) Study of the Reactions of Peroxy Radicals

The toxicity of halogenated alkanes (such as carbon tetrachloride and the anaesthetic agent halothane, $CF_3CHClBr$) is believed to originate from cytochrome-P_{450}-mediated generation of peroxyl radicals with subsequent attack on biological targets, especially unsaturated lipids. The feasibility of this proposed mechanism was demonstrated in this laboratory in a pulse radiolytic study of the reactions of peroxyl radicals with iron porphyrins and with fatty acids.

During the past year, the rate constants for oxidation of zinc-tetraphenylporphyrin by CCl_3O_2 radicals were determined. They are found to be strongly solvent-dependent (two orders of magnitude). This dependence was found to be due to complexation of certain organic solvents at the axial position of the zinc porphyrin, which affects the redox potential to a certain extent but has a dramatic effect on the rate of reaction of CCl_3O_2 in hydrogen abstraction reactions is being studied with cyclohexane, cyclohexene, and hexamethylbenzene. The rate constants for these reactions can not be followed directly by kinetic spectrophotometry and are, therefore, determined by competition kinetics.

Because CF_3Br is widely used as a fire extinguisher and a refrigerant, experiments were carried out which were designed to examine its possible toxicity by determining the reactivity of the peroxyl radical that may be produced from it, the CF_3O_2 radical. This radical is more reactive than CCl_3O_2 by a factor of approximately 10 in oxidation reactions. The peroxyl radical formed from CBr_4 has also been studied; surprisingly, this radical displays a higher reactivity than CCl_3O_2. This discrepancy is under investigation. The probability of formation of these damaging radicals in biological systems is being examined by a collaborator (Brault) using model systems.

The common peroxyl radicals produced in biological systems are less reactive than the halogenated analogues and can be best represented by CH_3O_2, the simplest organic peroxyl radical. The reactivity of this radical as a one-electron oxidant was determined with several molecules and found to be generally about 100 times less than the rate constants for CCl_3O_2. The redox potential for CH_3O_2 was estimated to be in the range 0.6-0.7 V.

(c) Temperature Dependence of Rates and Equilibria of Electron Transfer Processes

In order to determine the enthalpy and entropy changes that contribute to the electron affinities of organic and biological molecules in aqueous solution, the temperature dependences of charge transfer rate and equilibrium constants in the pulse radiolysis of liquids was studied using the temperature-controlled radiolysis cell. These studies may be divided into two parts: (1) kinetics of electron transfer from nitroaromatic radical anions and (2) electron transfer equilibria between nitro compounds, quinones, and oxygen.

Rate constants for electron transfer from various nitroaromatic radical anions to other nitroaromatic compounds in aqueous solutions were found to increase from $\sim 10^5$ to $\sim 10^8$ $M^{-1}s^{-1}$ upon increase in driving force from 0 to -300 mV, while the activation energies decrease from ~6 to ~3 kcal/mol. Nitro compounds with ortho substituents exhibit lower electron affinities due to rotation of the nitro group away from the ring plane. Anion radicals of such compounds transfer their electron much more slowly (k down to $\sim 10^6$ $M^{-1}s^{-1}$) despite the apparent increase in driving force (to ~550 mV). This behavior is rationalized by an increase in solvent reorganization energies around these radical anions caused by localization of the charge. In general, nitroaromatic radical anions donate electrons much more slowly than other radical anions, in reactions with similar driving forces, due to low self-exchange rates for $ArNO_2/ArNO_2^-$.

Temperature effects on electron transfer equilibria:

$$A^- + B \Leftrightarrow A + B.^-$$

were studied for the cases: (1) A = nitro compound, B = quinone; (2) A and B are both quinones; (3) A = quinone, B = oxygen.

The question of interest here is whether the redox potentials obtained at room temperature, which are known for many quinones and nitroaromatics, reflect differences in the heats of one-electron reduction of the aqueous compounds, or whether entropy effects are also significant. The results show that, in fact, the entropy contributions to the Gibbs free energy change can be significant.

The entropy changes in the present equilibria are most likely due to changes in solvation, and in particular, the solvation of the ions. In both of the reactions of the type (AQS-)- + B <=> B- + AQS-, the entropy change is negative. This is reasonable, since the reaction proceeds from a one-ion to a two-ion system, and increased ion solvation can lead to more structured solvent.

By using the known enthalpy and entropy of hydration of O_2- we can calculate the corresponding values for the semiquinones and nitroaromatic radical anions (if the values for the neutral compounds are known). These studies are still in progress.

2. Kinetics and Radiation Chemistry of Aqueous Inorganic Solutions
(R. E. Huie and P. Neta)

This program includes research in two related areas: the chemistry of small free radicals, and the aqueous phase chemistry of the atmosphere. The work on small free radicals, supported by a contract with DOE, is focussed on deriving basic information (e.g. redox potentials, self-exchange rates) about simple free radicals in aqueous solutions. These experimental results have application to understanding other redox systems. For example, a study of the effects of substituents on the one-electron oxidation of phenols was carried out using radical reactants chosen so that their reactivity would be sufficiently great to allow determination of the rate constants, but not so reactive that substituent effects would be small.

The work on the aqueous phase chemistry of the atmosphere is focussed on the chemistry of free radicals likely to enter or be formed in atmospheric droplets, especially their reactivity toward other possible constituents of the droplet. These results have direct application to modelling of the chemistry of the atmosphere, particularly for understanding the acidification of precipitation.

(a) Reactions of Oxidizing Radicals

Based on results from earlier work in this laboratory on the chemistry of small free radicals, a study has been completed of the effect of substituents on the rate of one-electron oxidation of phenol. The rate constants for reactions of ClO_2, NO_2, and SO_3- with phenol varied from immeasurably slow ($<10^{-1}$ $M^{-1}s^{-1}$) to values almost as great as the diffusion controlled limit ($>10^9$ $M^{-1}s^{-1}$), and depended on the redox potential of the phenol or phenoxide ion and that of the inorganic radical. The results showed that these one-electron oxidation reactions could be correlated with the Hammett substituent constants and that the reactivity, in general, could be correlated with the difference in redox potentials.

(b) Reactions of Reducing Radicals

During the past year, a study of some one-electron transfer reactions involving the couple SO_2/SO_2^- has been carried out. Both pulse radiolysis and voltammetry (in collaboration with A. Harriman of the Royal Institution, London) were employed. At a pH of 2, the one-electron redox potential of SO_2 was measured to be −0.31 V. This value increased somewhat at lower pH. From the rate constants for the reduction of SO_2 by the methyl viologen radical cation, and the reduction of several metal complexes by SO_2, we have calculated self-exchange rates for SO_2/SO_2^-. The values span four orders of magnitude (ignoring one very low value for IrCl6-). Apparently, the SO_2/SO_2^- couple behaves like the O_2/O_2^- couple, possibly because of the great difference in solvation between the charged and uncharged halves of the couple.

(c) Reactions of Methylperoxy Radicals

Under Section C.1., above, studies of the reactivity of methylperoxyl and substituted methylperoxyl radicals were described, primarily in relationship to their importance in biological chemistry. Alkylperoxyl radicals are also of considerable importance in atmospheric chemistry, and would be expected to play a role in the chemistry of atmospheric droplets, possibly initiating the autoxidation of sulfite.

$$RO_2 + SO_3^{2-} \rightarrow RO_2^- + SO_3^-$$

Therefore, information was sought on the reactivity of these peroxyl radicals toward sulfite. The carboxymethylperoxyl radical was found to react with a rate constant of $<10^5\ M^{-1}s^{-1}$. Since the reactivity of this radical toward other reductants was found to be similar to that of methylperoxyl, this limiting value can be assumed to be applicable to the latter radical also. The trichloromethylperoxyl radical is known to be a stronger oxidant than the methylperoxyl radical, and the rate constant for its reaction with sulfite was found to be $9 \times 10^6\ M^{-1}s^{-1}$.

(d) Reactions of Atmospheric Interest

In the literature of atmospheric chemistry, papers dealing with the role of radicals in droplet chemistry have begun to appear. These reactions may be very critical in determining atmospheric aqueous chemistry. As a result, rate constants have been determined for the oxidation of sulfite by several radicals in aqueous solution, notably for the reaction of OH with HSO_3^-/SO_3^{2-}, which is an important process in atmospheric chemistry. The rate constant determined for reaction with SO_3^2 was in good agreement with a value reported previously, but the value for the reaction with $HSO_3^-$was lower than the previously-accepted value by about a factor of two.

The chloride ion is a significant trace species found in atmospheric droplets. This ion can scavenge strong oxidants producing the dichloride radical, Cl_2^-. A value of the rate constant for the reaction of this radical with bisulfite which was about a factor of ten greater than that reported previously has been determined. The earlier work may have been complicated by the occurrence of a chain reaction which regenerated Cl_2^-.

The reaction of SO_4^- with S(IV), in which radicals are produced by reduction of $S_2O_8^{2-}$, was also investigated. The results led to values for the rate constants which were much lower than expected from comparison with similar systems. It was suggested that a chain reaction takes place in this system involving the reduction of the peroxydisulfate by the sulfite radical to regenerate SO_4^-.

An additional reaction of direct atmospheric significance is the chain propagating reaction of SO_5^- with S(IV). In earlier work from this laboratory, a rate constant for this reaction at pH 6.8 was determined. During the past year, measurements were made at pH 8.7 and 1.9, to allow the rate constants for reaction with SO_3^{2-} and HSO_3^- to be separated. A rate constant of 1.3 x 107 $M^{-1}s^{-1}$ was obtained for the reaction of SO_5- with SO_3^{2-}. For the reaction with HSO_3^-, an upper limit of $<3 \times 10^5$ $M^{-1}s^{-1}$ was derived.

Related computer modelling studies have been carried out to determine the sensitivity of simple models of the aqueous-phase atmospheric oxidation of SO_2 to these kinetic results. An important conclusion is that when one uses these new values for the rate constants in the model, the effect of added chloride on the chemistry is not great. Because of the slowness of the SO_5^- + HSO_3^- reactions, secondary reactions of this radical, including self-reaction and reactions with other radicals, will be important. Some of these reactions will be investigated in the coming year.

(e) Development of the Van de Graaff System

The additional pulse radiolysis work generated by the new EPA contract has put further pressure on the experimental capabilities at NBS. Therefore, additional effort has been given to making the NBS Van de Graaff accelerator into a working tool for kinetics studies. While this has involved some instrument- and software-development, most of the work has been concerned with solving a number of small problems expected with such a complex apparatus.

In addition to taking pressure off the Febetron, the use of the Van de Graaff for pulse radiolysis studies affords some important advantages. First, the high repetition rate permits signal averaging, so that radicals with weak absorptions, such as NO_2, can be monitored. Second, the shorter overall optical train and the greater penetration depth of the electrons permits measurements further into the UV, down to 220 nm. This allows one to monitor radicals directly which previously could be followed only indirectly, if at all. For example, the rate constant for the reaction:

SO2- + O2 -> SO2 + O2-

($k = 2.4 \times 10^9$ $M^{-1}s^{-1}$) has been measured by monitoring SO_2- at 260 nm.

The solution handling and data collection procedures on the Van de Graaff have been automated. In the coming year, procedures will be developed to transfer the data from the Tektronix computer (which is also used to control the experiment) to a separate computer for data analysis.

5. PUBLICATIONS

A. Publications of Past Year

Alfassi, Z. B., Huie, R. E. and Neta, P., "Substituent Effects on Rates of One-Electron Oxidation of Phenols by the Radicals ClO_2, NO_2 and SO_3^-", J. Phys. Chem. 90, 4156 (1986).

Ausloos, P. and Lias, S. G., "On the Mechanism of the Reactions of Alkyl Ions with Alkylamines: Competing Proton Transfer and Condensation Reactions", J. Am. Chem. Soc. 108, 1792 (1986).

Billmers, R., Griffith, L. L., and Stein, S. E., "Hydrogen transfer Between Anthracene Structures" J. Phys. Chem., 90, 517, (1986).

Billmers, R. L., Griffith L. L., and Stein, S. E., "Hydrogen Transfer Between 9,10 Positions in Anthracene and Phenanthrene" Preprint Paper, Fuel Sciences Division American Chemical Society, 283 (1985).

Brault, D. and Neta, P., "Oxidation of Fe(III)-Porphyrins by Peroxyl Radicals Derived from 2-Propanol and Methanol. Evidence for Acid Dependent and Acid Independent Pathways", Chem. Phys. Letters 121, 28 (1985).

Brault, D., Neta, P. and Patterson, L. K., "The Lipid Peroxidation Model for Halogenated Hydrocarbon Toxicity. Kinetics of Peroxyl Radical Processes Involving Fatty Acids and Fe(III)-Porphyrins", Chem. Biol. Interact. 54, 289 (1985).

Christensen, P. A., Harriman, A., Neta, P. and Richoux, M. C., "Photooxidation of Water Using Prussian Blue as Catalyst", J. Chem. Soc., Faraday Trans. 1, 81, 2461 (1985).

Deakyne, C. A., Meot-Ner (Mautner), M., Campbell, C. L., Hughes, M. G., and Murphy, S. P., "The Proton in Multisolvent Clusters. 1. The Acetonitrile-Water System", J. Chem. Phys., 90, (1986).

Dixon, D. A. and Lias, S. G., "Absolute Values of Gas Phase Proton Affinities and Basicities of Molecules: A Comparison between Theory and Experiment", in "Molecular Structure and Energetics" (J. F. Liebman and A. Greenberg, editors), VCH Publishers, Inc.: Deerfield Beach, FL (1986).

Dulcey, C. S. and Hudgens, J. W., "Multiphoton Ionization Spectroscopy and Vibrational Analysis of a 3p Rydberg State of the Hydroxymethyl Radical" J. Chem. Phys., 84, 5262, (1986).

El-Shall, M. S., Kafafi, S. A., Meot-Ner (Mautner), M., and Kertesz, M., "Ionic Charge Transfer Complexes. 2. Comparative ab initio and Semiempirical Studies on Cationic Complexes of Aniline+", J. Am. Chem. Soc., 108, 4391 (1986).

Fahr A., and Laufer, A. H., "Quantum Yield of Vinylidine(3B2) for the Vacuum UV Photolysis of Acetylene and Ethylene ", J. Photochemistry 34, 261, (1986).

Frenklach, M., Clary, D. W., Gardiner W. C., and Stein, S. E., "Shock Tube Pyrolysis of Acetylene: Sensitivity Analysis of the Reaction Mechanism for Soot Formation" in"Shock Waves and Shock Tubes, Proceedings of the 15th International Symposium on Shock Waves and Shock Tubes" (D. Bershader and R. Hanson, ed) Stanford University Press, Stanford CA. 285, (1986).

Hampson, R., et.al., "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation Number 7," JPL Publication 85-37, July 1, 1985.

Hampson, R., et.al., "Present State of Knowledge of the Upper Atmosphere. An Assessment Report", NASA Reference Publication 1162, May 1986.

Harriman, A., Neta, P., and Richoux, M. C., "Reactions of Magnesium Porphyrin Radical Cations in Water. Disproportionation, Oxygen Production and Comparison with Other Metalloporphyrins", J. Phys. Chem., 90, 3444 (1986).

Harriman, A., Neta, P., and Richoux, M. C., "Catalyzed Decay of Oxidizing Radicals" in "Homogeneous and Heterogeneous Photocatalysis" (E. Pelizzetti and N. Serpone, editors), D. Reidel Publ. Co., 123, (1986).

Herron, J. T., Tsang, W., Stein, S. E., and Golden, "International Conference on Chemical Kinetics," J. Phys. Chem., 90, 343 (1986).

Herron, J. T., and Tsang, W., "Chemical Kinetics - Theory and Experiment," J. Res.NBS, 389 (1986).

Hoffbauer, M. A., and Hudgens, J. W., "Multipnotn Ionization Detection of Gas Phase Benzyl Radicals" J. Phys. Chem., 89, 5152, (1985).

Huie, R. E., "Chemical Kinetics of Intermediates in the Autoxidation of SO_2", Fossil Fuels Utilization: Environmental Concerns, ACS Symposium Series 319, 284 (1986).

Huie, R. E. and Neta, P., "Rate Constants for One-Electron Oxidation by Methylperoxyl Radicals in Aqueous Solutions", Int. J. Chem. Kinetics,

Huie, R. E. and Neta, P., "Kinetics of One-Electron Transfer Reactions Involving ClO_2 and NO_2", J. Phys. Chem. 90, 1193 (1986).

Jovanovic, S. V., Neta, P., and Simic, M. G., "One-Electron Redox Reactions of Pyrasozlin-5-ones. A Pulse Radiolysis Study of Antipyrine and Analogues", Mol. Pharmacol., 28, 377 (1985).

Karpas, Z., Stevens, W. J., Buckley, T. J., and Metz, R., "The Proton Affinity and Gas Phase Ion Chemistry of Methyl Isocyanate, Methyl Isothiocyanate and Methyl Thiocyanate, J. Phys. Chem ., 89, 5274 (1985).

Karpas, Z., "The Proton Affinity of H_2Se, SeCO and H_2CSe and Reactions of Positive Ions with H2Se", Chem. Phys. Lett. 120, 53 (1985).

Karpas, Z. and Jasien, P. G., "The Proton Affinity of Hydrogen Telluride", Int. J. Mass Spectrom. Ion Proc., 69, 115 (1986).

Kurylo, M. J., Ouelette, P. A., and Laufer, A. H., "Measurements of the Pressure Dependence of the HO_2 Radical Self Disproportionation Reaction at 298 K" J. Phys. Chem., 90, 437, (1986).

Kurylo, M. J. and Ouelette, P. A., "The Pressure Dependence of the Rate Constant for the Reaction HO_2 +NO_2+ M = HO_2NO(M=N_2, O_2 at 298K," J. Phys. Chem., 90, 441, (1986).

Langley, R., Hambright, P., Alston, K., and Neta, P., "Kinetics of the Reduction of Manganese(III)-Myoglobin by Dithionite", Inorg. Chem., 25, 114 (1986).

Lias, S. G., Karpas, Z., and Liebman, J. F., "Halomethylenes: Effects of Halogen Su I. Thermochemistry and Structural Implications and Role in Ion Solvation", in "Molecular Structure and Energetics" (J. F. Liebman and A. Greenberg, editors), VCH Publishers, Inc.: Deerfield Beach, FL, 71, (1986).

Meot-Ner (Mautner), M.and El-Shall, M. S., "Ionic Charge-Transfer Complexes. 1. Cationic Complexes with Delocalized and Partially Localized Pi Systems", J. Am. Chem. Soc., 108, 4386 (1986).

Meot-Ner (Mautner), M., Karpas, Z., and Deakyne, C. A., "Ion Chemistry of Cyanide and Isocyanides. 1. The Carbon Lone Pair as Proton Acceptor: Proton Affinities of Isocyanides", J. Am. Chem. Soc., 108, 3913 (1986).

Meot-Ner (Mautner), M. and Karpas, Z., "Ion Chemistry of Cyanides and Isocyanides. 2. Alkylation of HCN and Cyanides by Oxygen and Sulfur Compounds. Gas-Phase Synthesis and Reactions of Protonated Isocyanides", J. Phys. Chem., 90, 2206 (1986).

Meot-Ner (Mautner), M. and Neta, P., "Kinetics of Electron Transfer from Nitroaromatic Radical Anions in Aqueous Solutions. Effects of Temperature and Steric Configuration, J. Phys. Chem., 90, (1986).

Meot-Ner (Mautner), M., Neta, P., Norris, R. K., and Wilson, K., "Temperature Effects on Rates of Dehalogenation of Aromatic Anion Radicals", J. Phys. Chem., 90, 168 (1986).

Meot-Ner (Mautner), M. and Sieck, L. W., "The Ionic Hydrogen Bond and Ion Solvation. 4. SH+...O and NH+...S Bonds. Correlations with Proton Affinity. Mutual Effects of Weak and Strong Ligands in Mixed Clusters", J. Phys. Chem., 89, 5222 (1985).

Neta, P., Richoux, M. C., Harriman, A., and Milgrom, L. R., "Resonance Stabilization of Zinc Porphyrin Pi-Radical Catioins", J. Chem. Soc. Faraday Trans. 2, 82, 209 (1986).

Neta, P., Silverman, J., Markovic, V., and Rabani, J., "Radiation-Induced Reactions of Polymer Radicals with Ruthenium tris-Bipyridyl OH Adduct in Aqueous Solutions Studied by Pulse and Gamma Radiolysis", J. Phys. Chem., 90, 703 (1986).

Richoux, M. C., Neta, P., Christensen, and Harriman, A., "Formation and Decay of Zinc Tetrakis(N-methyl-3-pyridyl)porphine Pi-Radical Cation in Water", J. Chem. Soc. Faraday Trans. 2, 82, 235 (1986).

Richoux, M. C., Neta, P., and Harriman, A., "One- and Two-Electron Oxidation of Lead(II) Tetrakis(N-methylpyridyl) Porphyrins in Aqueous Solution", J. Chem. Soc. Faraday Trans. 2, 82, 201 (1986).

Richoux, M. C., Neta, P., Harriman, A., Baral, S., and Hambright, P., "One and Two-Electron Reduction of Metalloporphyrins. Radiation Chemical, Photochemical and Electrochemical Studies. Kinetics of the Decay of Pi-Radical Anions", J. Phys. Chem., 90, 2462 (1986).

Robaugh, D. A., Tsang, W., Fahr A., and Stein, S. E., "Ethylbenzene Pyrolysis: Benzyl C-C or C-H Bond Homolysis" Ber. Bunsenges. Phys. Chem., 90, 77, (1986).

Robaugh, D. and Tsang, W., "Mechanisms and Rate Constants for Hydrogen Atom Attack on Toluene" J. Phys. Chem., 90, (1986).

Robaugh, D. and Tsang, W., "Shock Tube Study on the Stability of Iodobenzene and o-Iodotoluene" J.Phys. Chem., 90, (1986).

Robaugh, D. A. and Stein, S. E., "Stabilties of Highly Conjugated Radicals from Bond Homolysis Rates" J. Amer. Chem. Soc., 108, 3224, (1986).

Sieck, L. W., "Thermochemistry of Solvation of NO_2- and $C_6H_5NO_2$- by Protic and Aprotic Dipolar Molecules in the Vapor Phase. Comparison with Cl- and Variation with Ligand Structure", J. Phys. Chem., 89, 5552 (1985).

Speller, C. V. and Meot-Ner (Mautner), M., "The Ionic Hydrogen Bond and Ion Solvation. 3. Bonds Involving Cyanides. Correlations with Proton Affinities", J. Phys. Chem., 81, (1985).

Stein, S. E., "Free Radicals in Coal Conversion" in "Chemistry of Coal Conversion" (R. H. Schlosberg,ed) Plenum Publishing, 13, (1985).

Stein, S. E. and Fahr, A., "High Temeprature Stabilities of Hydrocarbons" J. Phys, Chem., 89, 3714, (1985).

Stein S. E. and Brown, R. L., "Pathways to Graphite. Properties of Very Large Benzenoid Hydorcarbons" in "Moleuclar Structure and Energetics" (J. F. Leibman and A. Greenberg, ed.) VCH Publishers, Deerfield Beach, FL, (1986).

Tsang, W., "The Stability of Alkyl Radicals," J. Am. Chem. Soc., 107, 2872 (1985).

Tsang, W., "Thermodynamic and Kinetic Properties of the Cyclohexadienyl Radical," J. Phys. Chem., 90, 1152 (1986).

Tsang, W. and Hampson, R. F., "Chemical Kinetic Database for Combustion Chemistry. Part 1. Methane and Related Compounds," J. Phys. Chem. Ref. Data, 15, 1087 (1986).

Tsang, W., "Single Pulse Shock Tube Study on the Stability of Perfluorobromethane", J. Phys. Chem., 90, 414 (1986).

Tsang W., and Robaugh, D., "Single Pulse Shock Tube Studies on the Stability of Aromatic Compounds" in "Shock Waves and Shock Tubes, Proceedings of the 15th International Symposium on Shock Waves and Shock Tubes" (D. Bershader and R. Hanson, ed) Stanford University Press, Stanford CA. 319, (1986).

B. Publications in Progress

Alfassi, Z. B., Harriman, A., Mosseri, S. and Neta, P., "Rates and Mechanisms of Oxidation of ZnTPP by CCl_3O_2 Radicals in Various Solvents", Int. J. Chem. Kinetics, in press.

Braun, W., Scheer, M., and Kaufman, V., "Measurement of Transient Gas Temperature by Broadening of the Hg 61S0 - 63S1 Line", J. Res. NBS in press

Braun, W., Scheer, M., and Cvetanovic, R. J., "Use of the Doppler Broadening of the 254 nm Hg Absorpton Line as a Measure of V-RT Transfer in Vibrationally Excited Gases, J. Chem. Phys., submitted

Cvetanovic, R. J., "Evaluated Chemical Kinetic Data for the Reactions of O(3P) Atoms with Unsaturated Hydrocarbons", J. Phys. Chem. Ref. Data, submitted

Deakyne, C. A., Meot-Ner (Mautner), M., Buckley, T. J., and Metz, R., "Proton Affinities of Diacetylene, Cyanoacetylene, and Cyanogen. Experimental and ab initio Studies", J. Chem. Phys., submitted.

El-Shall, M. S. and Meot-Ner (Mautner), M., "Ionic Charge Transfer Complexes. 3. Delocalized Pi Systems as Electron Acceptors and Donors. Dimer Cations of Naphthalene Derivatives", submitted to WERB.

Fahr, A. and Laufer, A. H., "Collisional Quenching of Excited Vinylidine (3B2), J, Phys. Chem., in press

Frenklach, M., Gardiner, W. C., Clary, D., and Stein, S. E., "Effects of Fuel Structures on Soot Formation Mechanisms" 21st Symposium on Combustion, in press

Hambright, P., Neta, P., Richoux, M. C., Abu-Gamra, Z., and Harriman, A., "Redox Chemistry of Water Soluble Vanadyl Porphyrins", J. Photochem., in press.

Harriman, A., Christensen, P. A., Porter, G., Morehouse, K., Neta, P., and Richoux, M. C., "Decay of High Valent Manganese Porphyrins in Aqueous Solution and Catalyzed Formation of Oxygen", J. Chem. Soc. Faraday Trans. 1, in press.

Herron, J. T., "Thermochemical Data on the Gas Phase Compounds of Sulfur, Fluorine and Oxygen Related to Pyrolysis and Oxidation of Sulfur Hexafluoride," J. Phys. Chem. Ref. Data, submitted.

Herron, J. T., "A Critical Review of the Chemical Kinetics of SF_4, SF_5, and S_2F_{10} in the Gas Phase," Int. J. Chem. Kinetics, in press

Herron, J. T., "S_2F_{10} Formation in Computer Simulation Studies of the Breakdown of SF_6," IEEE Transactions on Electrical Insulation, in press

Huie, R. E., and Neta, P., "Rate Constants for the Oxidation of Sulfite Radicals in Aqueous Solutions", Atmos. Environ., submitted.

Karpas, Z. and Lias, S. G., "On the Mechanism of Formation of Dialkylhalonium Ions in Alkyl Halides", J. Org. Mass Spectrom., submitted.

Karpas, Z. and Meot-Ner (Mautner), M., "Alkyl Transfer Reactions between Protonated Alcohols and Ethers. The Gas Phase Alkylation of Formaldehyde", J. Phys. Chem., submitted.

Kurylo, M. J. and Ouelette, P. A., "Rate Constants for the Reaction HO_2NO_2+ N_2 = HO_2NO_2 + N_2: The Temperature Dependence of the Fall off Parameters", J. Phys. Chem.,(submitted to WERB)

Lias, S. G., "Ion Kinetics and Energetics: The Physical Chemistry of Ions in the Gas Phase", The Encyclopedia of Physical Science and Technology (R. A. Meyers, editor), Academic Press: New York, in press.

Martinez, R. I. and Dheandhanoo, S., "Validation of Absolute Target Thickness Calibrations in a QQQ Instrument by Measuring Absolute Total Cross-Sections of Ne+(Ne,Ne)Ne+", Int. J. Mass Spectrom. Ion. Processes, submitted.

Martinez, R. I. and Herron, J. T., "Stopped flow Studies of the Mechanisms of Ozone-Alkene Reactions in the Gas Phase: Tetramethylethylene", J. Phys. Chem., submitted.

Meot-Ner (Mautner), M., "Multicomponent Cluster Ions. 2. Comparative Stabilities of Cationic and Anionic Hydrogen Bonded Networks. Mixed Clusters of Water-Methanol", J. Am. Chem. Soc., in press.

Meot-Ner (Mautner), M. and Deakyne, C. A., "The Ionic Hydrogen Bond and Ion Solvation. 5. Predictive Relation for Heats of Hydration. Hydrophobic Solvation of Ions", J. Phys. Chem., in press.

Meot-Ner (Mautner), M., Rumack, D. T., and Nelsen, S. F., "Slow Organic Electron Transfer Reactions", J. Am. Chem. Soc., submitted.

Meot-Ner (Mautner), M. and Sieck, L. W., "Relative Acidities of Water and Methanol and Stabilities of the Dimer Anions", J. Phys. Chem., in press.

Meot-Ner (Mautner), M. and Sieck, L. W., "The Ionic Hydrogen Bond and Ion Solvation. 5. OH...O- Bonds. Gas-Phase Solvation and Clustering of Alkoxide and Carboxylate Anions", J. Am. Chem. Soc., in press.

Meot-Ner (Mautner), M. and Speller, C. V., "The Filling of Solvent Shells in Cluster Ions: Thermochemical Criteria and the Effects of Isomeric Clusters", J. Phys. Chem., in press.

Neta, P., "Reactions of Radicals with Biologically Important Molecules", Chapter in a CRC book on Organic Radicals, in press.

Neta, P., "Radiation Chemistry of Quinonoid Compounds", in "The Chemistry of the Quinonoid Compounds" (S. Patai and Z. Rappoport, editors), Wiley, in press.

Neta, P., Huie, R. E., and Harriman, A., "One-Electron Transfer Reactions of the Couple SO_2/SO_2^- in Aqueous Solution. Pulse Radiolytic and Cyclic Voltammetric Studies", J. Phys. Chem., submitted.

Neta, P. and Huie, R. E., "Rate Constants for Some Reactions of NO3 in Aqueous Solutions, J. Phys. Chem., in press.

Neta, P. and Ross, A. B., "Representative Rate Constants for Radical Reactions of Biologically Important Molecules", in a CRC book on Organic Radicals, in press.

Okabe, H. and Glicker, S., "Photochemistry of Diacetylene", J. Phys. Chem., accepted.

Sieck, L. W., "Thermochemistry of Solvation of SF_6^- by Simple Polar Organic Molecules in the Vapor Phase", J. Phys. Chem., in press.

Stein, S. E., Fahr A., and Mallard, W. G., "Phenyl Radical Reaction with Ethane, Ethnye and Benzene," 21st Symposium on Combustion" in press.

Stein, S. E., Griffith, L. L., Billmer, R. L., and Chen, R., "Anthracene Pyrolysis" J. Org. Chem., submitted.

Stein, S. E., Brown, R. L., and Manka, M., "Rate Constants for Hydrogen Transfer by Diphenylmethyl and Fluorenyl Radicals" J. Phys. Chem., submitted.

Tsang, W., "Chemical Kinetic Data Base for Combustion Chemistry. Part 2. Methanol," J. Phys. Chem. Ref. Data, submitted.

Tsang, W. and Herron, J. T., "Chemical Kinetics Data Base for Combustion Modeling", Proceedings of the 10th International Codata Conference, in press.

Tsang, W. "Fundamental Aspects of Key Issues in Hazardous Waste Incineration" ASME Publication, in press.

Tsang, W., Robaugh, D., and Mallard, W. G., "Single Pulse Shock Tube Studies on $C-NO_2$ Bond Cleavage During the Decomposition of Some Aromatic Compounds" J. Phys. Chem., in press.

6. TALKS

Brown, R. L., "Chemical Theory of Graphite" Carbon Conference Lexington, Ky, April, 1986.

Brown, R. L., "Chemical Theory of Graphite" AFOSR Contractors' Meeting Alburquerque, NM, Mar., 1986.

Brown, R. L., "Huckel Molecular Orbital Theory Applied to PAH" 1st Symposium on the Quantum Chemistry of Polynuclear Aromatic Compounds, NRL, Washington DC, June, 1986.

Cvetanovic, R. J., "Reaction of Oxygen Atoms with Olefins", Catholic University of America, Washington, D.C., April, 1986.

Herron, J. T., "The National Bureau of Standards Chemical Kinetics Data Base," International Symposium on Gas Kinetics, Bordeaux, France, July, 1986.

Herron, J. T., "A Chemical Kinetics Data Base for Combustion Chemistry," International Symposium on Combustion, Munich, West Germany, August 1986.

Hudgens, J. W., "Spectroscopy of Free Radicals Using Resonance Enhanced Multiphoton Ionization" Symposium Theoretical and Experimental Studies of Transient species" 190th ACS Meeting, Chicago, Ill. Sept., 1985.

Hudgens, J. W., "Multiphoton Ionization of Free Radicals" Chemistry Dept. University of Illinois, Urbana, Illinois, Sept. 1985.

Hudgens, J. W., "Multiphoton Ionization of Free Radicals" Chemistry Dept. Yale University, New Haven Conn., Jan, 1986.

Hudgens, J. W., "Multiphoton Ionization of Free Radicals" Ballistics Research Laboratory, Aberdeen Proving Grounds, Jan., 1986.

Hudgens, J. W., "Resonance Enhanced Multiphoton Ionization Spectroscopy of Reactive Intermediates" Gordon Conference on Multiphoton Processes, June, 1986.

Hudgens, J. W., "Multiphoton Ionization Spectras of BrO and ClO Radicals" Gordon Conference on Molecular Electronic Spectroscopy, August, 1986.

Huie, R. E., "Reactions of Intermediates in the Autoxidation of SO_2", Department of Chemistry, University of the District of Columbia, March, 1986.

Huie, R. E., "Radical Intermediates in the Autoxidation of SO_2", Argonne National Laboratory, March, 1986.

Huie, R. E., "Radical Intermediates in the Autoxidation of SO_2", Radiation Laboratory, University of Notre Dame, South Bend, Indiana, March, 1986.

Huie, R. E., "Aqueous Phase Reactions of NO_3", Symposium on Acid Rain, 191st National Meeting, American Chemical Society, New York, N. Y., April, 1986.

Kurylo, M. J., "Flash Photolysis Kinetic Absorption Spectroscopy Applied to the Study of Gas Phase HO_2 Reactions, Dept. of Chemistry, Catholic University of America, October 1985.

Kurylo, M. J., "Rate Constants for the Reaction $HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$: The Temperature Dependence of the Fall-off Parameters", XVIth Informal Conference on Photochemistry, University of Colorado, June, 1986.

Lias, S. G., "Structures and Reactivities of $C_6H_5^+$ Ions", Seventh East Coast Symposium on Ion/Molecule Chemistry, University of Delaware, Newark, Delaware, October, 1985.

Lias, S. G., "Competing Proton Transfer and Condensation Reactions", 191st National Meeting, American Chemical Society, New York, N. Y., April, 1986.

Martinez, R. I., "Ozone-Alkene Reactions: Dimethyl Dioxymethylene", 191st ACS National Meeting, New York, NY, April, 1986.

Martinez, R. I. "Methodology for the Determination of the Absolute Total Cross-Sections in a QQQ Instrument" 34th ASMS Annual Conference on Mass Spectrometry and Allied Topics Cincinnati, OH, June, 1986.

Martinez, R. I., "Dioxymethylenes: A Source of Oxygen Atoms in Alkene Ozonolysis?" 17th Informal Conference on Photochemistry, Boulder CO, June 1986.

Martinez, R. I., "Methodology for the Determination of Absolute Total Cross-Sections in a QQQ Instrument and Its Application to In-Situ Target Thickness Calibrations" 17th Informal Conference on Photochemistry" Boulder CO, June,1986.

Martinez, R. I., "Research Opportunities in Mass Spectrometry" Office of Naval Research, Arlington, VA, July , 1986.

Mautner, M., "The Ionic Hydrogen Bond", Department of Chemistry, University of Maryland, Baltimore County Campus, December 17, 1985.

Mautner, M., "The Ionic Hydrogen Bond and Cluster Ions", Molecular Spectroscopy Division Seminar, National Bureau of Standards, January, 1986.

Mautner, M., "The Ionic Hydrogen Bond", Department of Chemistry, University of Southern Illinois, March 19, 1986.

Neta, P., "Pulse Radiolysis Studies of Porphyrins. Application to Solar Energy Conversion Systems", Radiation Chemistry Symposium, First Pan American Chemical Congress, San Juan, Puerto Rico, October, 1985.

Stein, S. E., "Chemical Fundamentals of Coal Char formation" Contractors' meeting Gas Research Institute, Chicago, Illinois, June, 1986.

Stein, S. E., "Molecular Orbital Theory of PAH" Contractor's Meeting, Gas Research Institute, Chicago, Illinois, June, 1986.

Stein, S. E., "Chemistry of Polynuclear Aromatic Hydrocarbons,Chemistry Department, West Virginia University, Morgantown WVA., May, 1986.

Stein, S. E., "Phenyl Radical Reaction with Ethane, Ethnye and Benzene," 21st Symposium on Combustion, Munich, Germany, July, 1986.

Tsang, W., "The Reaction of Hydrogen Atoms with Phenol" 191st ACS Meeting, New York, NY, June, 1986.

Tsang, W., "The Stability of Nitroaromatic Compounds" ARO Workshop on Nitramine Decomposition" Livermore, California June, 1986.

Tsang, W., "Evaluated Kinetics Database for Combustion Chemistry," International CODATA Conference, Ottawa, Canada, July, 1986.

Tsang, W., "Chemical and Thermal Stability of Aromatic Compounds" Catholic University, Sept., 1986.

7. CHEMICAL KINETICS DIVISION SEMINARS

Ross, D. S., Stanford Research Center, Palo Alto, CA, "A New View of Nitration Chemistry", November, 1985.

Platz, M. S., Department of Chemistry, Ohio State University, Columbus, OH, "Photochemistry and Photobiology of Aromatic Azides", November 1985.

Lowe, J. P., Department of Chemistry, Penn State University, State College, PA, "MO Theory of Substitution in Polymers and Chemisorption on Surfaces", Frebruary 1986

Niki, H., Ford Motor Company, Detroit, MI, "FTIR Spectroscopic Study of the Mechanisms for Atmospheric Reactions of Olefins", April 1986

Dewar, M. J. S., Department of Chemistry, University of Texas, Austin, TX, "Chemistry by Molecular Simulations", May 1986

Len, M. C., Naval Research Laboratory, "Application of Lasus to Chemistry, May 1986

Henglein, A., Hahn-Meitner Institute, Berlin, "Extremely Small Colloidal Semiconductor Particles: Electron Transfer Reactions and Size Quantization Effects", June 1986

Gimarc, B., University of South Carolina, Columbia, "Topological Charge Stabilization", June 1986

Burrows, J. P., Max-Plank Institute, Germany, "Chemical Dynamics of Atmospheric Reactions", July 1986

Bartmess, J. E., University of Tennesse, Knoxville, TN, "Gas Phase Ion Chemicstry", July 1986

Plumb, I. C., CSIRO Division of Applied Physics, Sydney, Australia, "Gas-Phase Reactions in Plasma Etching Systems", August 1986

Traeger, J. C., University of Ottawa, Ottawa, Canada, "Studies of Thermochemistry of Ions", August 1986.

Heicklen, J., Department of Chemistry, Pennsylvania State University, College Park, PA"

Wallington, T. J., "The Role of the NO_3 Radical in Atmospheric Chemistry: Laboratory Kinetics and Field Measurements", September 1986

8. TECHNICAL AND PROFESSIONAL COMMITTEE PARTIPATION AND LEADERSHIP

Hampson, R. F.

Member, NASA Panel for Data Evaluation

Member, CODATA Task Group on Chemical Kinetics

Huie, R. E.

Member, Environmental Protection Agency Grant Review Panel

Member, Atmospheric Chemistry Working Group, Subcommittee for Atmospheric Research

Kurylo, M. J.

Member, NASA Panel for Data Evaluation

Lias, S. G.

Member, Organizing Committee of NATO ASI on "Structure/Reactivity and Thermochemistry of Ions", June 29-July 11, 1986, in Les Arcs, France

Member, Editorial Board of the series, "Molecular Structure and Energetics", VCH Publishers, Inc.

Member, Editorial Board of the NBS Journal of Research

Program Manager, Office of Standard Reference Data, NBS

Neta, P.

Member, International Commission on Radiation Units and Measurements (Committee on Chemical Dosimetry)

Regional Editor, "Radiation Physics and Chemistry"

Sieck, L. W.

Member, Panel for Small Business Innovative Research Program of the U. S. Department of Energy

Stein, S. E.

Member, Editorial Advisory Board, International Journal of Chemical Kinetics

Tsang, W.

Committee of the 21st Symposium on Combustion

9. PROFESSIONAL INTERACTIONS, CONSULTING AND ADVISORY SERVICES

Herron, J. T.

collaborated with R. VanBrunt of the Electrosystems Division on dielectric breakdown phenomena

collaborated with David Kahaner of the Scientific Computing Division on computer modeling programs (with Walter Braun)

consulted with J. Troe and D. Baulch on international co-operative efforts in data evaluation for combustion chemistry

Hudgens, J. W.

collaborated with D. Bogan (Catholic University of America) on studies of fluorine reactions with ketene.

collaborated with J. Leibman (University of Maryland, Baltimore county) detection of small free radicals.

consultative services to Ole Krogh (Tegal Corp., Novato, CA) on the REMPI detection of CF_3 during the plasma etching of surfaces.

Huie, R. E.

consulted with Dr. G. Mills of Argonne National Laboratory on the chemistry of sulfite derived radicals.

consulted with Dr. D. J. Jacob of Harvard University on the Mechanism of SO_2 oxidation in clouds.

Kurylo, M. J.

consultative services to R. B. Timmons (U. of Texas, Arlington) on HO_2 kinetics.

consultative services to D. Bogan (Catholic University of America) on HO_2 kinetics.

Lias, S. G.

collaborated with Drs. John L. Holmes (University of Ottawa), John E. Bartmess (University of Tennessee), and Joel F. Liebman (University of Maryland, Baltimore County Campus) on production of an evaluated compilation of heats of formation of ions and related neutrals, ionization potential, appearance potential, and electron affinity data.

collaborated with Drs. Vincent G. Anicich (Jet Propulsion Laboratory), Albert Viggiano (Air Force Geophysics Laboratory), and Jean Gallagher (JILA) to organize compilation of data on ion/molecule rate constants.

Levin, R. D.

serves as NBS EEO Counselor.

Martinez, R. I.

provided technical information and consultation regarding the Martinez-Herron Desulfurization Process (US Patent No. 4,351,810) to several international corporations.

collaborated with S. Kafafi, Cairo University (Egypt) on thermochemistry of dioxiranes (and their isomers) and of alkenoxy radicals.

initiated collaboration with several investigators who will participate in interlaboratory round robin experiments designed by us to evaluate the general utility of our kinetic method as a generic standard for target thickness calibrations in QQQ instruments.

consulted with D. Stone and Maj. K. Den Bleyker of the US Air Force regarding standardization of QQQ operating parameters for speciation of unknowns by MS/MS analysis.

consulted with P. Dawson, NRC-Ottawa on ion trajectories within quadrupole mass filters, especially as it relates to QQQ instruments.

consulted with J. Futrell (U. of Utah), C. Ng (Ames Laboratory), K. McFee (Bell Labs), G. Dunn (JILA), and A. Phelps (JILA) regarding the relative reactivities of the states of the Ar ion.

consulted with E. K. Lee, U. C. Irvine, on the mechanism for the Photooxidation of matrices, and the probable involvement of dioxymethylenes.

consulted with J. Sodeau (University of East Anglia) on experimental desig to validate the formation of hyroxy-substituted methylene and dioxymethylene during the photolysis of H_2CO and H_2CO/O_2 matrices, respectively.

consulted with H. J. Akimoto (Japan Environment Agency) on the chemistry of dioxiranes (and their isomers).

consulted with S. Trevino, US Army, on trajectory calculations and associated kinetics related to simulation of detonation of highly energetic materials.

consulted with H. Guard, D. Nelson, and K. Wynne of ONR on research opportunities in real-time mass spectrometry.

consulted with M. Dixon and J. Gray of Galileo Electro-Optics regarding design of novel high-mass detector.

consulted with P. S. Berger, President of Teknivent Corp., on requisite design and operational characteristics for an MS/MS system controller and data system.

Mautner, M.

collaborated with Dr. C. A. Deakyne, Air Force Geophysics Laboratory, on studies of ion clustering energetics.

collaborated with Professor S. Nelsen, Department of Chemistry, University of Wisconsin, on ion chemistry of hydrazines.

Neta, P.

collaborated with A. Harriman, Royal Institute, London, England, on kinetics of redox reactions of porphyrins.

collaborated with P. Hambright, Chemistry Department, Howard University, on porphyrin reactions.

Sieck, L. W.

collaborated with the Analytical Mass Spectrometry Group of the Organic Analysis Division, Center for Analytical Chemistry, NBS concerning adduct ion formation in MS/MS.

collaborated with R. Van Brunt of the Electrosystems Division, NBS, concerning electron transport mechanisms in SF_6.

collaborated with Professor S. Nelsen, Department of Chemistry, University of Wisconsin, on ion chemistry of hydrazines.

collaborated with I. Savers, Health and Safety Research Division, Oak Ridge National Laboratory, on joint studies involving reactions of SF_6^-.

Stein, S. E.

collaborated with M. Frenklach, Louisiana State University on soot formation thermochemistry.

collaborated with W. R. Moore, West Virginia University on synthesis of polynuclear aromatic compounds.

collaborated with K. Kishore, IIS, Bangalore, India, on pyrolysis of polymers.

Tsang, W.

collaborates with A. Lifshitz (Hebrew University, Jeruslaem) under an Israeli-American Binational Foundation grant on studies dealing with the thermal stability of organic molecules.

collaborates with F. Tully (Combustion Research Facility, Sandia National Laboratory) on the interpretation of OH reactions with olefins.

provided consultative services to Dan Chang (UC, Davis), G. Hahn (KWU, Erlangen, Germany), M. MacIntosh (Argonne National Laboratory) on various aspects of hazardous waste incineration.

provided consultative services to G. Zimmerman (Zentralinstitute for Organische Chemie, DDR) on the thermal stability of organic molecules.

10. VISITING SCIENTISTS

Alfassi, Z., of Ben Gurion University returned to Division and has spent two months at NBS as a guest scientist working on pulse radiolysis.

Altstein, N., of the Weizman Institute of Science, Israel, is spending two years at NBS as a guest scientist working on pulsed electron sources.

Bai, J., of Dalian Institute of Cehmical Physics, Dalian, Liaoming, People's Republic of China, is spending one year at NBS as a guest scientist working on Photochemistry of planetary atmospheres.

Behar, D., of Soreg Nuclear Research Center, Israel spent six weeks at NBS working on Pulse radiolysis studies of electron transfer reaction and the effects of polyelectrolytes on such reactions.

Chen, R., of West Virginia University has spent eighteen months at NBS as a guest scientist working on free radical chemistry.

Dheandhanoo, S., of Georgetown University, has spent 10 months at NBS as a guest scientist working on obtaining and analyzing CID spectra of selected target molecules.

Fahr, A., has spent one year at NBS under a cooperative agreement with Georgetown University, working on thermolysis of aromatic compounds.

Harriman, A., of The Royal Institution, London, has spent one year at NBS as a guest scientist working on pulse radiolysis.

He, Yu Zhong, of the Institute of Mechanics Academia Sinica, Beijing, has spent one year at NBS as a guest scientist working on shock tube studies on thermal stability of molecules.

Kafafi, S., of the University of Cairo has spent one year at NBS as a guest scientist working on polynuclear aromatic hydrocarbons.

Kishore, K., of Indian Institute of Science, Bangalore, India spent six weeks at NBS as a guest scientist working on polymer pyrolysis.

Laufer, A., of the Department of Energy has spent one day a week at NBS working on free radical species.

LeMotais, B., of the University de Paris-Sud, France spent one year at NBS working as a guest scientist working on studies of electron transfer processes carried out using the technique of pulse radiolysis.

Manka, M., of Catholic University has spent one year at NBS as a guest scientist working on thermolysis of organic compounds.

McNesby, J. R., of the University of Maryland has spent five months at NBS as a guest scientist working on high temperatues and non-equilibrium chemical kinetics involving organic compounds relevant to combustion and potential industrial chemical processes.

Mosseri, S., of Ben Gurion University of the Negev has spent one year at NBS as a guest scientist working on pulse radiolysis.

Price, I. W., is working on electronics design projects.

Richoux, M.-C., of The Royal Institution, London, spent one year at NBS as a guest scientist working on pulse radiolysis experiments.

Rumack, D., of the University of Wisconsin has spent one month at NBS as a guest scientist working on mass spectrometry of hydrazine derivatives.

Senthilnathan, V., of West Virginia University has spent seven months at NBS as a guest scientist working on free radical reactions on high temperature fluids.

CHEMICAL THERMODYNAMICS DIVISION

S. Abramowitz, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1986

1. INTRODUCTION

A. Objectives

Chemical Thermodynamics provides measurement techniques, concepts and data on the energetics and equilibria of chemical processes. Chemical thermodynamics is used to predict equilibria in chemical reactions, thermodynamic properties of high temperature refractory materials and gases, activities of aqueous solutions used in technologies varying from power generation and electrorefining to biotechnology. This division develops the models necessary for correlating structure with thermodynamic properties, develops the science of calorimetry in order to obtain precise data from the microwatt to megawatt levels, carries out precise thermodynamic measurements, including those on Standard Reference Materials, develops the measurement capabilities for molecular structure determinations and critically evaluates thermodynamic data in all phases for the use of industry, government and academia. A current emphasis is directed towards the needs of the emerging biotechnology industry. In particular, this division is developing the measurement and computational techniques for obtaining biomolecular structures of proteins, enzymes, enzyme-substrate complexes and DNA species using x-ray and neutron diffraction. The thermochemistry of generic processes of interest to biochemistry and biotechnology are being studied in order to develop standards and provide key data, to develop quantitative models for the energetics of these processes and estimation schemes of demonstrated reliability for the concomitant thermodynamic properties. A new effort is being launched in the coming year aimed at correlating structure and function for proteins. This research will coordinate with the biothermodynamics and biomolecular structure efforts in order to develop structure-function-energetics correlations.

The objectives of the Chemical Thermodynamics Division include:

- Application of the science of calorimetry to the needs of existing and new technologies through the design of novel calorimeters and the development of improved procedures to obtain enhanced measurement precision and accuracy.

- Development and certification of Standard Reference Materials for the use of existing and emerging technologies.

- Measurement of the thermochemical properties of key chemical species and processes including bioprocesses and phase transitions of aqueous biomolecular species.

- Provision of critically evaluated compilations of the thermodynamic properties of inorganic, organic and bioorganic compounds in the gaseous, liquid, solid and aqueous phases.

- Development of estimation schemes for the prediction of thermodynamic properties of organic, inorganic, and bioorganic species in the gaseous, liquid, solid and aqueous phases.

- Development of measurement and computational methodology for the determination of the structure of biomacromolecular species using the techniques of x-ray and neutron diffraction.

In achieving these objectives Division scientists are encouraged to be aware of and to respond to the needs of industry, government and academic institutions for measurement standards, accurate data and concepts in the field of thermodynamics.

B. Organization and Staff

The Chemical Thermodynamics Division has four groups. An additional group has been organized, this year, under the leadership of Alex Wlodawer to guide the growth in the biomolecular structure group. Malcolm Chase has assumed the leadership of the Chemical Thermodynamic Data Centers Group, which includes the Chemical Thermodynamics Data Center and Electrolyte Data Center. Dr. Chase has extensive industrial experience in the evaluation of chemical thermodynamic data for both industrial and military technologies. He brings to this position an awareness of the needs of these technologies and will make the products of this group more responsive to those needs. Dr. Chase will also continue his activity as the director of the JANAF Thermochemical Data Project. This change in leadership will allow David Garvin to devote all his energies to the evaluation of chemical thermodynamic data in support of national and international data evaluation programs. The group structure is

- Biothermodynamics, S. Abramowitz, Group Leader

- Biomolecular Structure, A. Wlodawer, Group Leader

- Chemical Thermodynamics Measurements, E.S. Domalski, Group Leader

- Chemical Thermodynamic Data Centers, M.W. Chase, Group Leader

The division has 26 full-time staff, 1 part-time employee, 6 guest workers, 7 students, 5 contractors and 1 consultant. This fiscal year two additional members have joined the Biomolecular Structure Group. Dr. Gilliland will be continuing work he began elsewhere on the maintenance and development of a computer based database for the crystallization of biomolecular species and will conduct research in biomacromolecular structure and on means to systemize the crystallization of proteins and other biomolecular species. Dr. Weber will conduct research on evaluating the effects of selected mutations on the structures of proteins and protein-substrate complexes. In addition the group has a postdoctoral associate, three guest workers and a technician. Funds for one guest worker and the technician are being provided by the Center for Advanced

Within NML we are cooperating with the Center for Analytical Chemistry on several programs in the area of biotechnology including the thermodynamics characterization of monoclonal antibody antigen interactions and the use of NMR in speciating carbohydrates. We are also collaborating with the Center for Basic Standards on temperature measurements in combustion studies. We are cooperating in the planning and carrying out of a research program in support of AFOSR needs in cooperation with both IMSE and NEL.

Our staff has many interactions with voluntary standards organizations and international societies such as ASTM, ANSI, ASME, CODATA, IUPAC, and IAEA etc. This past year staff members participated in the planning and formations of a new ASTM committee on Biotechnology. Staff members hold memberships on diverse committees ranging from environmental and health concerns to energy utilization and database management. Members of the Biomolecular Structure Group organized a three-day Mid-Atlantic Protein Cystallography Workshop at NBS in May 1986. The workshop was attended by about 80 scientists.

We are actively planning for the maintenance of a protein crystallization database. Computing expertise for the necessary programming for this task will be provided by the Chemical Thermodynamics Data Centers Group. The differential scanning calorimetry effort has been successfully integrated into the biothermodynamics efforts in this past year. This laboratory is documenting standard procedures for calibrating differential scanning calorimeters that have been designed for use with biochemical samples. Work has continued in the measurement of the thermodynamics of enzyme catalyzed reactions. The work on the five and six membered monosaccharides has been completed and efforts will be made, in the coming year, to construct estimation schemes for the prediction of the thermodynamic formation properties for this class of compounds. Efforts have begun in other areas including the measurement of the thermodynamics of the reactions of monoclonal antibodies with antigens and the use of microcalorimetry to characterize the rates of enzyme catalyzed reactions and to measure enzyme activity.

Work will also continue on the determination of enthalpies of formation of key phosphorus compounds and other biomolecular building blocks including the development of predictive schemes for these compounds. Benzoic acid will be recertified during this fiscal year. Research to characterize the chlorinated organic species present in the effluents resulting from the combustion of municipal solid waste will also be continued.

Biotechnology (CARB) to support research of mutual interest. This group has acquired state-of-the-art computing and x-ray detector equipment in the last year. It also has access to additional equipment through its collaboration with others including CARB and Genex.

Additional expansion is planned for FY87 in the area of protein structure-function studies. A laboratory will be refurbished for molecular biology work and will be used for protein synthesis and for the investigation of the effect of changes in protein structure on function. It is expected that this new activity will involve close collaboration with the biothermodynamics and biomolecular structure programs.

The division participates in the work of the Office of Standard Reference Data and the Office of Standard Reference Materials. In support of the Standard Reference Data program, the Chemical Thermodynamics Data Centers group evaluates thermochemical data for organic and inorganic species, develops database management systems for chemical thermodynamics, and develops critically evaluated data and reliable estimation schemes for organic and biochemical species. In support of the Standard Reference Materials program, the Thermodynamics Measurements Group maintains standards for oxygen bomb and heat capacity calorimetry and develops new standards as needed. Benzoic acid is a best seller of the Standard Reference Material Program. It is responsible for converting the chemical system of measurements to the electrical system and is used to calibrate combustion bomb calorimeters for the fuel industry, power generation industry and in bomb calorimeter research laboratories.

The research needs of two federal agencies and one industrial trade association are being addressed by the division. We receive funding from the Department of Energy for determining the chlorine content of municipal solid waste and optimizing conditions for the formation and destruction of chlorinated organic species, and for the development of thermodynamic data for flue gas clean-up in fossil fuel technology. Programs being pursued for the Department of Defense include the provision of combustion calorimetric data and estimation methods for the thermodynamic and related properties of organic phosphorus compounds and development of thermodynamic functions for species of importance to high temperature technologies including rocketry, reentry, and energy production. We are developing computer algorithms for aqueous thermodynamics and providing annotated bibliographies for the sources of the data for the Design Institute for Physical Property Data (DIPPR), which is sponsored by AIChE. We have finished the revision of a previous publication on the thermodynamic data for biomass and waste incineration in cooperation with the Solar Energy Research Institute (SERI).

In addition to the interactions which we have with other NBS programs and federal agencies the division cooperates with other NBS units. Within CCP we have a joint program with the Chemical Kinetics Division on database managment systems, with both the Chemical Kinetics and Spectroscopy Divisions in developing and carrying out a research program in support of the high temperature technology needs of AFOSR and with the Surface Science Division in developing computer algorithms for the interpretation of sputtering depth profiles.

2. BIOTHERMODYNAMICS

S. Abramowitz, E. Gajewski, R.N. Goldberg, W.H. Kirchhoff,
F.P. Schwarz, D. Steckler, Y.B. Tewari

A. Biochemical Thermodynamics
(R.N. Goldberg, E. Gajewski, D. Steckler, Y.B. Tewari)

The long term goals of this research are to provide understanding of the thermodynamics of the key processes and interactions relevant to biochemistry and biotechnology. This understanding is needed to predict the feasibility of biochemical processes, optimization of product yields and elimination of side reactions in industrial processes. The data are necessary to construct estimation schemes to reliably predict the thermochemical properties of substances and processes for which measurements are not available. The goals are realized by development of measurement and computational methodology, determination of reliable thermodynamic values, and establishment of the relationship between molecular structure and the formulation of predictive methods.

The thermodynamic investigations include, where feasible, both equilibrium composition and calorimetric measurements on carefully characterized biochemical systems. Independent measurements of enthalpy and equilibrium composition as a function of temperature enable the reliable modelling of reactions outside of the temperature range of the measurements. The effects of pH, metal ion concentration, ionic strength and temperature on the equilibrium and enthalpy measurements are also investigated. An equilibrium model of the system allows one to account for the experimentally determined values and to predict these quantities under a variety of possible conditions. The calculations require identification of the individual molecular processes, activity coefficient models to account for nonideality, and numerical solution of the equilibrium equations which describe the system. The final set of thermodynamic parameters makes possible the prediction of the thermodynamic behavior of a system under a wide range of conditions beyond those used for the measurements. The combined approaches of equilibrium measurements, calorimetry and computer modelling is believed to be unique to NBS.

Written descriptions of the microcalorimeters, procedures and software used in the studies of biochemical systems have been prepared. The documentation includes a detailed description of the construction, calibration, operation, performance and use of these calorimeters. The software allows for the acquisition and treatment of data from three microcalorimeters simultaneously. Software for the acquisition and treatment of data from an isoperibol solution calorimeter, using a quartz thermometer, is also described. Procedures for obtaining kinetic parameters such as enzyme activity and rates of conversion of substrate to product are also described with accompanying examples using glucose isomerase.

Summaries of the accomplishments of the individual projects follow:

1. Thermodynamics of the Hydrolysis of Adenosine 5'-Triphosphate

The enthalpy of the hydrolysis of the enzyme catalyzed conversion of adenosine 5'-triphosphate (ATP) to adenosine 5'-diphosphate (ADP) and inorganic phosphate was investigated using microcalorimetry. There are five measurements of this equilibrium in the literature. Four of these are in agreement. All of them involve the use of coupled reactions to obtain the Gibbs energy change, which is known to ± 1.5 kJ mol^{-1}. These results are sufficiently accurate for our needs. Enthalpies of reaction were measured as a function of ionic strength (0.05 to 0.66 mol kg^{-1}), pH (6.4 to 8.8) and temperature (25 to 37 °C) in Tris/HCl buffer. The measured enthalpies were adjusted for the effects of proton ionization and metal ion binding, protonation, interaction with the Tris buffer and ionic strength effects to obtain a value of $\Delta H = -20.5 \pm 0.4$ kJ mol^{-1} at 25 °C for the process:

$$ATP^{4-} + H_2O = ADP^{3-} + HPO_4^{-} + H^{+}$$

Since earlier investigations did not systematically investigate the effects of pH, ionic strength or temperature the results obtained are currently the best value for the enthalpy change for this biochemical process. The result of $\Delta C_p^o = -237 \pm 30$ J mol^{-1} K^{-1} is the only direct determination of this thermodynamic quantity.

2. Thermodynamics of Carbohydrate Isomerization Reactions

The thermodynamics of the enzymatic conversion of aqueous D-psicose to D-allose was investigated using high pressure liquid chromatography. The reaction was carried out in phosphate buffer at pH 7.4 over the temperature of 44.1 to 76.1 °C. From the temperature dependency of the equilibrium constants, the following results were obtained for the conversion process at 25 C: $\Delta G^o = -1.41 \pm 0.09$ kJ mol^{-1}, $\Delta H^o = 7.42 \pm 1.7$ kJ mol^{-1} and ΔC_p^o was estimated to be 67 ± 50 J $mol^{-1}K^{-1}$. An approximate equilibrium constant of 0.3 was also obtained at 60 °C for the conversion of D-psicose to D-altrose. The kinetics of these reactions are not rapid enough to permit a direct calorimetric determination of the enthalpy changes.

This study is a continuation of earlier studies of carbohydrate isomerization reactions using the enzyme, glucose isomerase, which included isomerizations of glucose to fructose, xylose to xylulose and ribose to ribulose and arabinose. The possibility of other isomerization reactions involving sorbose, galactose, tagatose and talose were also investigated. Isomerization was not observed for the above carbohydrates.

The available information on the thermodynamics of the aldo/keto isomerization of hexoses and pentose is summarized in Table 1. With the exception of the mannose/fructose system, all the results were determined in this laboratory using both HPLC, for the determination of equilibrium constants, and where feasible, microcalorimetry to determine both the enthalphy and heat capacity changes. This represents the most complete set of information on the thermodynamics of carbohydrate isomerization reactions.

The observed thermodynamic data for the hexoses and pentoses will be coupled with other thermodynamic data such as enthalpies of combustion and solution and heat capacities to estimate the thermodynamic formation properties of the hexoses and pentoses. Available NMR and polarimeteric data will be used, where appropriate, to obtain speciation information for the solutions.

Table 1

Thermodynamics of isomerization reactions involving D-aldohexoses and D-aldopentoses in aqueous solution 298.15K

Process	ΔG^{o} (kJ mol^{-1})	ΔH^{o} (kJ mol^{-1})	ΔS^{o} (J mol^{-1} K^{-1})	ΔC_p^{o} (J mol^{-1} K^{-1})
Ribose-arabinose	-3.44 ± 0.30	-9.8 ± 3.0[a]	-21.3	
Ribose-ribulose	2.85 ± 0.14	11.0 ± 1.5[a]	27.3	
Xylose-xylulose	$4.38_9 \pm 0.031$	16.09 ± 0.67[a]	39.2	40 ± 23[a]
Arabinose-ribulose	6.29 ± 0.34	20.75 ± 3.4[a]	48.5	
Allose-psicose	-1.41 ± 0.09	$7.4_2 \pm 1.7$[b]	29.6	$67 + 50$[d]
Psicose-altrose	≈ 3.4			
Allose-altrose	≈ 2.0			
Glucose-fructose	0.349 ± 0.053	2.78 ± 0.20[a]	8.15	76 ± 30[c]
Mannose-fructose	-2.72	0.0[b]	9.12	
Glucose-mannose	3.07	2.78	$+0.97$	

[a] Based on direct calorimetric measurements.
[b] Calculated from the temperature dependency of equilibrium constants.
[c] Calculated from the temperature dependency of enthalpies of reaction.
[d] Based on both an estimate and the temperature dependency of equilibrium constants.

3. Equilibrium Studies of the Conversion of Trans-Cinnamic Acid and Ammonia to L-Phenylalanine

The thermodynamics of the enzymatic conversion of aqueous trans-cinnamic acid and ammonia to L-phenylalanine has been investigated using high pressure liquid chromatography. The reaction was carried out in 0.1 M Tris/HCl buffer containing ammonium chloride over the pH range 7.0 to 7.7, at ionic strengths from 1.0 to 2.1 mol kg^{-1} in the temperature range of 12 to 43 ^{o}C. Analysis of the HPLC data using an estimated heat capacity change of 50 kJ mol^{-1} K^{-1} and an ion size parameter of 1.6 mol$^{-1/2}$ kg$^{-1/2}$ leads to an equilibrium constant of 0.86 ± 0.22 at 25 ^{o}C for the process

$$\text{Trans-cinnamic}^{-}\ \text{acid} + NH_4^{+} = \text{L-Phenylalanine}^{\pm}$$

We were unable to bring about a sufficiently rapid reaction to permit a direct calorimetric measurement of the enthalpy of this reaction. The use of these thermodynamic parameters in an equilibrium model allows for the prediction of values of the apparent equilibrium constant as a function of pH, temperature and composition. These data are useful for optimizing the yield of phenylalanine. The available thermochemical data for this generic type of reaction (ammonia elimination and the formation of a double bond) can be rationalized in terms of a scheme which views the entropy changes for related processes to be comparable and then attributes differences in Gibbs energy changes to the enthalpy changes which can be influenced by resonance stabilization of the double bond which is formed. This study complements an earlier one on the conversion of fumaric acid and ammonia to aspartic acid.

4. Microcalorimetric Measurement of Enzyme Activity

In addition to thermodynamic studies, the microcalorimetric instrumentation can be used for the determination of enzyme activity. If the substrate is present in large excess relative to enzyme, the reaction will be slow and accompanied by a steady rate of heat production per unit time given by

$$dq/dt = (dn/dt)/\Delta H$$

where ΔH is the molar enthalpy of reaction and (dn/dt) is the number of moles of substrate converted per unit time. The quantity (dn/dt) is a measure of the enzyme activity and can be determined from the measured power (dq/dt) if the enthalpy of reaction is known. This technique may prove valuable for the measurement of the activity of creatine kinase. Currently, the activity of this enzyme is measured spectrophotometrically with a precision of about 16%. The procedure requires the coupling of three enzyme catalyzed reactions to produce an increase of absorbance at 340 nm. A single step process can be used to measure this process in a microcalorimeter.

$$\text{Creatine Phosphate} + \text{ADP} = \text{Creatine} + \text{ATP}$$

Results obtained have confirmed the literature results for the enthalpy of this reaction. Also the measurement of enzyme activity in aqueous buffer solutions have yielded results having an imprecision less than 10%. Measurements of this activity in human serum will require steps to eliminate and/or correct for possible chemical interferences in the measurements.

5. The Hydrolysis of Glucose 6-Phosphate and Fructose 6-Phosphate and the Isomerization of Glucose 6-Phosphate to Fructose 6-Phosphate.

$$\begin{aligned} \mathrm{G6P}^{-2} &= \mathrm{G} + \mathrm{HPO_4}^{-2} \\ \mathrm{F6P}^{-2} &= \mathrm{F} + \mathrm{HPO_4}^{-2} \\ \mathrm{G6P}^{-2} &= \mathrm{F6P}^{-2} \end{aligned}$$

Here glucose and fructose are abbreviated as, G and F, respectively. The aim of this research is to obtain enthalpy, heat capacity and Gibbs energy changes for these processes. The results will be examined in conjunction with the thermodynamic data obtained previously for the hydrolysis of ATP of glucose and fructose, and the phosphorylation of glucose and fructose by ATP.

To date, enthalpy measurements have been made on the first two processes as a function of pH, temperature and concentration of magnesium chloride and of Tris/HCl buffer. A preliminary set of measurements have been made on the third process. After completion of the measurements on the third reaction, the necessary corrections will be made to obtain the enthalpy changes and the formalism applied to the Krebs cycle will be used to obtain the best consistent set of thermodynamic parameters for the above reactions, phosphorylation of glucose and fructose by ATP, and hydrolysis of ATP.

6. Antigen-Antibody Interactions

A study of antigen-antibody reactions has been started, in cooperation with the Center for Analytical Chemistry, using monoclonal antibodies. This should aid in the molecular interpretation of the thermodynamic properties of the reaction. A sample of a monoclonal antibody, has been obtained. The antibody has a molecular weight of about 150,000 daltons and is specific for E-N-E dinitrophenyl-L-lysine (2,4 DNP). An affinity column is being used to purify the monoclonal antibody. We plan to measure the enthalpy of the antigen-antibody reaction using microcalorimetry and to measure the equilibrium binding using dialysis techniques. Differential scanning calorimetry will also be used to characterize both the bound and unbound antibody.

7. Plans for Next Year

Thermodynamic formation properties of the five and six membered monosaccharides will be determined using available literature, estimation methods and data from ours and others research. The study of the thermodynamics of the reactions of glucose and fructose with ATP and the isomerization of glucose 6-phosphate to fructose 6-phosphate will be completed. The thermodynamics of the reactions of a monoclonal antibody with its antigen will be completed. An examination will be made of the thermodynamics of the most important processes currently used industrial biotechnology. The available thermodynamic data will be given, best available values will be recommended and, where appropiate, experiments suggested. A thermodynamic investigation of the enzymatic conversion of penicillin G to 6-aminopenicillanic acid and phenylacetic acid will be initiated. Equilibrium measurements will be made using HPLC and, if kinetics allow, microcalorimetric studies will also be pursued.

B. Differential Scanning Calorimetry

(F. P. Schwarz and W. H. Kirchhoff)

Differential scanning calorimetry, provides thermodynamics information on biological systems which characterizes the interactions and conformational changes of biological molecules in solution. Studies of the effect of ligand concentration on the transition temperature and enthalpy of protein, such as human serum albumin, yield information on the binding energetics of the substrate to the enzyme. Comparison of the transition enthalpies and temperatures of synthetic oligonucleotides in solution yield information on the effect of the nucleotide sequence on the conformational stability of DNA species in solution.

1. Temperature and Enthalpy Standards for Differential Scanning Calorimetry

(F. P. Schwarz)

Differential scanning calorimetry standards for temperature and enthalpy are needed to validate comparisons of data from different laboratories. A differential scanning calorimetric standard should exhibit a well characterized transition in the temperature range from 0 to 100 °C, the normal operating temperature range for biological studies, with an accuracy in the transition enthalpy of ± 0.10 mcal and a temperature accuracy of ± 0.10 °C. It is also desirable to use a biological solution as a standard since many of the differential scanning calorimeters contain fixed cells which are filled through small capillary tubes. Ribonuclease A is a candidate. Ribonuclease A is an enzyme consisting of 124 amino acid residues (G.M.W. = 13,700). In buffer solutions, ribonuclease a exhibits an unfolding transition with a transition temperature and enthalpy depending on the pH of the solution. It is readily available in relatively high purity and is highly stable. Furthermore, its concentration can be readily determined by several simple spectroscopic methods.

Solutions of ribonuclease A in a HCL-glycine buffer were prepared, dialyzed, analyzed, and thermally scanned on a differential scanning calorimeter to evaluate the suitability of ribonuclease A as an enthalpy and temperature standard. The calorimetric results from solutions prepared from four different samples of ribonuclease A were determined with a computer-controlled, heat flow differential scanning calorimeter. The solutions ranged in concentration from 0.7 to 1.7 mM and a glycine buffer concentration of 0.1 and 0.2 M. A straight baseline was interpolated under the transition peak to obtain the enthalpy of transition. The transition enthalpies exhibited a linear dependence on the transition temperature, ranging from 66.0 ± 0.4 kcal/mole at 37.4 ± 0.1 °C (pH = 1.9), to 110.0 ± 0.5 kcal/mole at 64.0 ± 0.1 °C (pH = 4.2), with a standard deviation of 2.47 kcal/mole. The enthalpy determinations are in good agreement with values reported in the literature. The results are independent of the source of the ribonuclease A and the concentration of the buffer. The solutions are stable when stored in a refrigerator and can be analyzed by measuring the UV absorption at 278 nm at a pH of 7.0. An error analysis revealed that the major source of error was in determining the temperature limits in the integration of the enthalpy transition peak. It is anticipated that a computer algorithm based on the two state model, being developed by W.H. Kirchhoff, to fit the entire thermal scan, will further reduce the standard deviation in the linear fit of the enthalpy to the temperature.

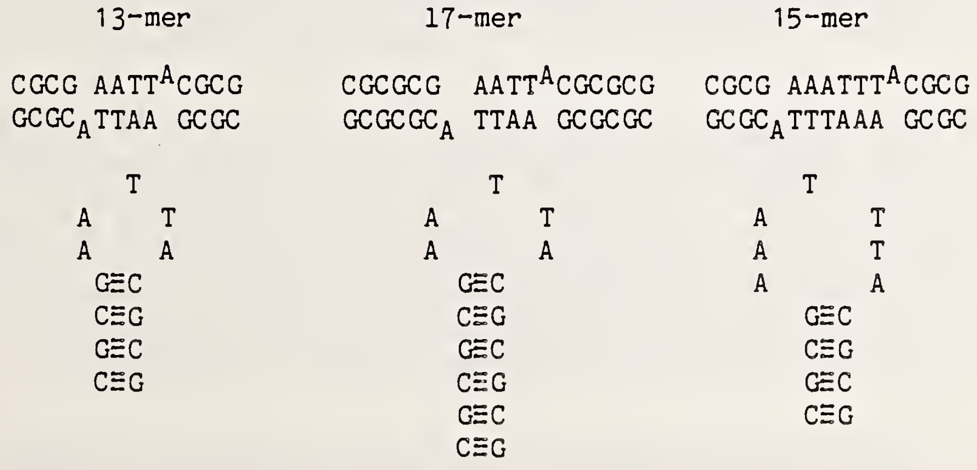
In summary, from the standpoint of ease of preparation, ease of characterization of the transition properties of ribonuclease A, and stability, ribonuclease A is an acceptable standard for the calibration of differential scanning calorimeters. The value of a ribonuclease A standard for measurement accuracy of the transition enthalpy and transition temperature is expected to be improved by the algorithms being developed.

2. Studies of the Thermal Stability of Synthetic, Quasipalindromic DNA Sequences in Solution.

(M. Miller, F.P. Schwarz, E. Appella (NIH), and W. H. Kirchoff)

Oligonucleotides consisting of prepared palindromic sequences have served as model systems for studying the effects of environmental variable (e.g. pH, temperature, electrolytic strength, etc.) on the stability of various forms of DNA - duplex (Z or B double-helix structures), cruciforms and hairpin loops. The palindromic sequences, which have the property of being self-complementary enabling the oligonucleotides to form exactly matching double-helices or exactly matching ends for stabilizing loop structures, have been extensively studied by crystallography, differential scanning calorimetry, UV spectroscopy and NMR. From these studies, the stabilities of all possible nearest-neighbor configurations have been computed and from this limited data base, the stability of any double-helix form of DNA may be estimated from its base-pair sequence.

We have begun to study a series of quasipalindromic sequences in order to determine the effects of mismatches on the stability and structure of DNA. In addition, spectroscopic and calorimetric measurements on systems with small enthalpies of reaction provide very broad transition envelopes which can further test mathematical models for the description of phase transitions in small systems. This work complements structural work being conducted in the Biomolecular Structure Group of the division. The species studied, along with their duplex and hairpin forms are shown below.



One of the variables in the study of these species is the total concentration of DNA strands. At high concentrations, the duplex form is favored. At low concentrations, the hairpin form is favored. The high concentration forms are most easily measured with a differential scanning calorimeter, the low concentration forms with a uv spectrometer. Both techniques were used and transitions between the species were analyzed. The van't Hoff enthalpies of transition were most accurately determined from the UV data. The 15-mer was found to form the most stable duplex form at low temperature and was selected for crystallographic studies. The thermodynamic data have been interpreted in terms of the relative strengths of G≡C vs A=T base pairs. Circular dichroism measurements indicate the presence of the Z form of the duplex and observed transitions have been tentatively ascribed to Z-B transitions.

3. The Effect of Ligand Concentration on the Thermal Stability of Human Serum Albumin

(F.P. Schwarz and A. Shrake)

Serum albumin is the most abundant protein in blood plasma, and information on its thermal stability can be used to improve commercial preparations of blood plasma. A detailed differential scanning calorimetry study has been completed on the dependence of the thermal stabilization of human serum albumin on the concentration of alkanoate anion ligands in solution. The increase in the thermal stabilization of serum albumin is monitored by the increase in its denaturation temperature and in its denaturation enthalpy in the presence of increasing ligand concentration. Two trends in the thermal stabilization were observed:
(1) The optimum denaturation temperature increased from 66.1 °C in the absense of ligand to 76.1 °C in the presence of formate and then to 79.0 °C in the presence of acetate, propionate, and butanoate.
(2) The optimum denaturation temperature increased to 81.2 °C in the presence of pentanoate and monotonically thereafter with increasing carbon chain length to 88.8 °C for the decanoate anion. An increase in thermal stability with chain length is anticipated since the binding constants of the alkanoate ligand to the serum albumin increase with chain length. The departure of propionate and butanoate from this behavior have been explained by assuming two different types of binding sites for the ligand to the serum albumin: (1) A large number of sterically hindered binding sites which bind only small ligands (formate to butanoate) and (2) a small number of large binding sites which bind all the ligands from formate to decanoate.

For FY 87, a number of studies are being planned which should serve as prototypes for assessing the applicability of DSC to the measurement of protein-substrate binding energies. The studies currently under consideration include: the thermal stability of monoclonal antibodies and their complexes with antigens; the thermal stability of the avidine and its unusually strong complex with biotin (vitamin H), and the effects of structural alterations on the thermal stabililty of chymotrypsin and trypsin and their respective proenzymes, chymotrypsinogen and trypsinogen.

4. Calculational Methods for the Characterization of Phase Transitions in Biomolecules

(W. H. Kirchhoff)

Computer programs have been written for analyzing phase transitions in biomolecules as measured by calorimetry or spectroscopy. The purpose of the programs is to characterize the measurement process and to determine the limits within which simple thermodynamic theories can duplilcate temperature profile measurements. Since the same theories are applied to both spectroscopic and calorimetric profiles, we may be able to separate instrumental effects from effects due to the non-ideality of true phase transition behavior.

The basis for the description of the spectroscopic and calorimetric profiles is the explicit dependence of the concentration of species on temperature. Phase transitions can be considered to be chemical reactions between initial and final states and can be written most generally as:

$$A <=> nB$$

and the concentration of species in states A and B is expressed in terms of the equilibrium coefficient

$K = \frac{[B]^n}{[A]}$ and its temperature dependence $d[\ln K]/dT = -\Delta H/RT^2$.

The enthalpy change, ΔH, is expressed as a power series about the standard state temperature, T_o:

$$\Delta H = \Delta H^o + \Delta C_p{}^o(T-T_o) + \ldots$$

The expression for the differential scanning calorimetry heat capacity, dQ/dT, is

$$dQ/dT = -\Delta H(dN_A/dt) + N_A C_{pA} + N_B C_{pB} + \text{baseline parameters}$$

while the expression for the temperature dependence of the spectrum of a biomolecule undergoing a phase transition is given by:

$$I = I_A[A] + I_B[B] + \text{baseline paramenters}$$

were I_A and I_B are the absorption coefficients or scattering intensities for the two species (which themselves may be expressed as power series in temperature). Simple algebra provides explicit expressions for dQ/dT and for I as functions of temperature.

Computer programs have been written for fitting these expressions by the methods of non-linear least squares to the experimental data. From the spectroscopic data, T_o and ΔH^o can be obtained, though the data are generally not sensitive enough to determine $\Delta C_p{}^o$. In the cases tested thus far, which have included the main phase transition in lipid bilayers, DNA fragments, and ribonuclease, the data have been fit to within experimental error. As a corollary, additional information may be obtainable from spectal measurements only through improved sensitivity, precision and temperature control.

From the calorimetric data, T_o, ΔH^o, $\Delta C_p{}^o$, and N, the number of moles of material present in the cell, can be determined. This approach differs from traditional approaches to the analysis of calorimetric data in that the baseline is a varying function of composition, and hence temperature. A so-called calorimetric enthalpy is not calculated. Instead, the van't Hoff enthalpy, ΔH^o, and the number of moles, N, are deemed the fundamental quantities to be determined. Although the fit of the model to experimental data seems excellent on casual inspection (the observed and calculated profiles are indistinguishable in graphical depictions) the difference between the calculated and observed profiles shows distinct trends and the standard deviation of the fit is an order of magnitude greater than the scatter in the data. This systematic error may be due to diffusion and other dynamic effects which have not been included in the analysis, the inadequacy of a simple power series in describing the instrumental background or a breakdown in the purely two state nature of the transition in ribonuclease A. Work in the coming year will focus on distinguishing between instrumental effects and effects due to the limitations of the purely thermodynamics model. The programs will also be expanded to include values of n greater than 1, the only case for which the programs have thus far been tested.

The computer programs have been written in standard Fortran 77 for personal computers compatible with the IBM AT and XT computers. In developing the programs, some degree of portability had to be sacrificed for ease of use. The lack of portability is related directly to the graphical displays that accompany the analysis. At this time, no standard protocols for graphical displays for Fortran-based programs exist. The programs are currently being distributed on a limited basis to those individuals who are willing to share their experience with the programs and who can offer critical reviews of the thermodynamic models, the statistics of the data analysis, the robustness of the algorithms, and ease of use.

The function for the spectral profiles is known as the logistic function and is commonly encountered in chemistry and other fields. Consequently, the spectral fitting program has been written in a more general manner for wider dissemination. It has been successfully used to analyze sputter depth profiles through interfaces where a simple diffusion model gives rise to the logistic function. The program has been distributed to laboratories performing depth profile analyses and is gaining in popularity.

3. BIOMOLECULAR STRUCTURE

A. Wlodawer, G. Gilliland, R. Harrison, M. Miller,
H. Savage, I. Weber

The Biomolecular Structure Group has developed an active program in measurement and analysis of the structure of biological macromolecules. We are developing new methods of X-ray and neutron structure determination and are applying these and other, more conventional, methods to selected structures of proteins and nucleic acids. Our general aim is to advance the understanding of the structure-function relationship in macromolecules, in particular by modifying the structure using genetic technology, by binding of ligands and by studying families of closely related proteins with different properties. We are also interested in the interactions of macromolecules with solvent, and such studies can particularly benefit from the availability of neutron diffraction data.

The physical facility available to us includes a well-equipped general purpose laboratory for protein purification, crystal growth and mounting, including a walk-in cold room, as well as computer and graphics areas. Instrumentation include a flat-cone neutron diffractometer located on the NBS Reactor, a conventional X-ray generator with two Buerger precession cameras (useful for preliminary data collection, but not for intensity measurements), and a gas-flow crystal temperature controller with a range of -80 °C to +60 °C. In the reporting period, we had no facilities for quantitative x-ray measurements, owing to the slow delivery cycle of a Nicolet area detector. For these reasons our capability to collect data was limited to the time donated to us by Genex Corporation, in collaborative efforts with Dr. Gary Gilliland, who subsequently joined our group in August 1986. Our computing facility includes an IBM4381 shared with the Quantum Chemistry Group of the Molecular Spectroscopy Division, a dedicated Evans and Sutherland Graphics facility which was upgraded this year from PS330 (vector graphics) to PS340 (vector and raster screens). This modification enables us to create both dynamic line drawings as well as static space-filling pictures. We have implemented programs for hard copy output of the images generated using various graphics programs. A recent upgrade to our computational facility includes a MicroVAX II equipped with a large disk and a tape drive, which will be dedicated to processing area detector data.

A number of problems initiated previously were continued in the last year and several new ones were initiated. Those individual projects on which significant progress was achieved are summarized below.

A. Structural Studies of Mutations in Catabolite Gene Activator Protein (I.T. Weber)

Catabolite gene activator protein (CAP) regulates transcription in *E. coli* in response to the level of cyclic adenine monophosphate (cAMP) which is an allosteric activator of CAP. CAP recognizes and binds to specific sequences of DNA at several operons, causing the stimulation or repression of transcription of cAMP-dependent genes. The crystal structure of a dimmer of CAP with bound cAMP has been determined at 2.5Å resolution and refined to an R factor of 0.207.

Several laboratories are investigating mutations in the crp gene that produces CAP. Three CAP mutants, 91, 220 and 222, that function in the absence of cAMP have been subjected to crystallization trials in order to study the structural changes associated with these mutations in amino acid sequence. Both CAP 91 and 222 form crystals with cAMP. CAP 91 also crystallizes in the presence of adenosine, an alternate activator for this mutant.

X-ray intensity data have been obtained for the crystals of CAP91 with cAMP which are isomorphous with the crystals of wild type CAP. These data have been refined to 2.4A resolution and an R factor of 0.186. The CAP91 structures are very similar although the Ala to Thr mutation is clearly visible. There also is a movement of Cys178. There are no significant differences around cAMP-binding sites. Smaller differences have been located by a vector average of the differences in atomic coordinates. These differences are located far from the site of mutation, in the hinge region between the two domains in the CAP subunit and in an adjacent loop between two β strands. These differences suggest that the Ala 144 to Thr mutation in CAP91 produces structural changes that propagate through the hinge region towards the DNA-binding site.

The CAP91 structure is being investigated in the absence of cAMP and in the presence of the analog, adenosine. Other CAP mutants will be studied.

B. Predicted Structure for Two Domains of the Regulatory Subunit of cAMP-dependent Protein Kinase

(I.T. Weber)

The mammalian cAMP-dependent protein kinase is an important regulator of many biochemical reactions. In the inactive state the holoenzyme consists of a complex of two regulatory subunits and two catalytic subunits. This is activated by the binding of cAMP to the regulatory subunits which then dissociate from the catalytic subunit. The active catalytic subunit phosphorylates other proteins. The regulatory subunit (R) contains two domains that bind to cAMP and have amino acid sequences that are homologous with the sequence of catabolite gene activator protein (CAP) from the bacterium, E. coli.

The crystal structure of the cAMP-binding domain of CAP has been used to model the cAMP-binding domains of the regulatory subunits. The amino acid sequence for the R-subunits was fitted into the CAP structure using a computer graphics system. The predicted R structure was overall very similar to CAP. The model structure was evaluated by comparison with other experimental evidence including photolabeling with 8-azido cAMP, the binding of cAMP analogs, and fluorescence quenching. This gave good agreement and the predicted structure of the regulatory subunits can be used as a model for site directed mutagenesis.

C. Structural Studies of Anti-tumor Amidohydrolases

(I.T. Weber, A. Wlodawer and R.W. Harrison)

Three homologous bacterial amidohydrolases with anti-tumor properties have been crystallized: a glutaminase-asparaginase from Acinetobacter glutaminasificans (AGA), a glutaminase-asparaginase from Pseudomonas 7A

(PGA) and an asparaginase from Vibrio succinogenes (VA). These enzymes in solution are tetramers with subunit molecular weights of ca. 34,000 daltons. AGA crystallizes in space group I222 with one subunit per asymmetric unit. PGA crystallizes as a tetramer in space group $P2_12_12_1$ and VA crystallizes in the same space group with a dimer in the asymmetric unit.

Native data are available to 2.9Å resolution for AGA and MIR data on three derivatives (5.3 to 4.0Å) permitted the direct phasing of 2617 reflections. Phase improvement and extension to 2.9Å resolution for an additional 4784 reflections was achieved by two complementary techniques of density modification. These are the method of B.C. Wang which flattens the solvent region and improves protein connectivity, and the method devised by R.W. Harrison that maps the distribution of density values onto a Gaussian distribution with the same mean and standard deviation. By examining electron density maps produced by the two methods it proved possible to trace a polypeptide chain, although the connectivity is ambiguous in several places. Since the amino acid sequence has not yet been determined, the type of amino acid was estimated from the shape of the electron density, and these coordinates were refined to an R factor of 0.30. The AGA polypeptide chain folds into two domains. The first amino terminal domain, contains a five-stranded β sheet and four of helices. The second domain has four of helices and several β strands. This model for the AGA structure has been used to phase the PGA data.

Intensity data have been obtained to 2.5Å resolution for the PGA crystals using a Nicolet-Xentronix area detector at Genex Corporation. The starting point for phase determination has been rotation and translation function techniques using the AGA map. This solultion was confirmed by using the AGA polyalanine coordinates. The rotation function has also been solved for VA. A starting PGA model was produced by rotation and translation of an AGA tetramer and this was refined to improve the phases. The tetramer model phases are being used as a prior in the maximum entropy technique that is under development by R.W. Harrison and the new electron density map is being intepreted. An active site inhibitor has been soaked into the PGA crystals in order to locate the active site of the enzyme.

D. Comparison of Two High Resolution Structures of Bovine Pancreatic Trypsin Inhibitor

(A. Wlodawer, with J. Deisenhofer and R. Huber (Max Planck Institute, Munich))

While it has been known for a long time that the structure of a protein in a crystal is similar to that present in solution, the limits of discrepancy have not been rigorously established. The availability of two distinct crystal forms for bovine pancreatic trypsin inhibitor (BPTI) made it a system of choice for such studies.

The structure of deuterated crystals of form II of BPTI has been refined using X-ray and neutron diffraction data. These crystals belong to space group $P2_12_12$, a=74.1Å, b=23.4Å, c=28.9Å and the packing of the molecules is related to form I structure previously solved in Munich by rotation of about 45° around y. X-ray intensities were collected on form

II crystals by the Munich group using standard diffractometry, while neutron data extending to 1.8Å resolution were collected at NBS. Joint restrained refinement using both types of data was performed by J. Walter and A. Wlodawer, resulting in a final model characterized by R values of 0.200 (X-ray) and 0.197 (neutron).

The two available high resolution structures of bovine pancreatic trypsin inhibitor, refined in two distinct crystal forms, have now been compared. After superposition, the molecules show an overall root-mean-squares deviation of 0.40 Å for the atoms in the main chain, while the deviations for the side chain atoms are 1.53 Å. The latter number decreases to 0.61 Å when those side chains which adopted drastically different conformations are excluded from comparison. The discrepancy between atomic temperature factors in the two models was 6.7 $Å^2$, while their general trends are highly correlated. About half of the solvent molecules occupy similar positions in the two models, while the others are different. As expected, solvents with the lowest temperature factors are most likely to be common in the two crystal forms. While the two models are clearly similar, the differences are significantly larger than the errors inherent in the structure determination. This study established the limits of discrepancy of atomic coordinates of proteins which can be expected to result from differences in crystal packing.

E. High Resolution Refinement of Ribonuclease A
(A. Wlodawer, with G. Gilliland and B. Finzel (Genex Corporation), A. Svensson and L. Sjolin (Chalmers Polytechnic)).

The structure of ribonuclease A was reinvestigated using a new set of X-ray diffraction data extending to 1.26 Å, the limits of detectable diffraction. The X-ray diffraction data were obtained from two phosphate-free crystals which were isomorphous with previously reported monoclinic crystals containing phosphate, or perhaps sulfate. The data were collected using an area detector, the Xentronics-Nicolet image proportional counter at Genex, and included 129,694 observations of 25,732 unique reflections out of the total of 31,730 possible at 1.26 Å. The data scaled with a weighted least squares R-factor on intensity for symmetry-related observations of 0.05, with 23,398 of the measured unique reflections having significant intensity ($F>2\sigma(F)$).

One of the first significant observations with the new data was the detection of a large number of side chains with multiple conformations. The structure was highly refined (R = 0.15) and was modeled with 13 residues having discrete multiple conformations of side chains. These residues are widely distributed over the protein surface, but only one of them, Lys 61, is involved in crystal interactions. The discrete conformers have no unusual torsion angles and their interactions with the solvent and with the atoms of the protein are similar to those residues modeled with a single conformation. For three of the residues, Val 43, Asp 83, and Arg 85, two correlated conformations are found. The observed plasticity in the protein surface will be of significance in analyzing structure-function relationships and in performing protein engineering.

Other new observations resulting from this refinement, in particular the details of the structure of ordered solvent, are still being analyzed.

F. Structure of the Solvent in Crystalline BPTI

(R. Harrison and A. Wlodawer)

Neutron data for bovine pancreatic trypsin inhibitor (BPTI) have been collected for crystals soaked in both deuterated and hydrogenous solvents. Deuterated data extending to 1.8Å resolution have been available for some time, while hydrogenous data were collected recently. This data set was virtually complete to 1.8Å resolution, with 3416 reflections showing observed intensity.

Since deuterium and hydrogen have greatly different scattering lengths it should be possible to use the difference between the scattering from deuterated and hydrogenous crystals to determine the positions and occupancies of exchangeable and solvent hydrogens. With X-ray diffraction data, differences in the scattering due to a change in the crystal such as the addition of a substrate can be used directly via a difference Fourier synthesis to show the location and orientation of the changes in the molecule or the complex. Because the differences are much larger with deuterium-hydrogen exchange, such a simple treatment is not correct when applied to neutron diffraction data. The problem with a simple treatment is the choice of the phase of each term used in the difference Fourier synthesis. With small differences in the scattering there are only small differences in the phase of the reflection. However, the phases of the deuterated data and the hydrogenous data determined by independently refined models are quite different, and there is no *a priori* reason to choose one or the other.

We have attempted to resolve this problem by constructing an enhanced model of the scattering from the protein. The scattering is treated as coming from two non-overlapping regions. Scattering from the part of the molecule that should not be altered by solvent exchange is required to be the same in both the hydrogenous and deuterated models, and scattering from everywhere else is independently refined for each model. Requiring that the structure in the non-exchanged regions of the map be the same for two different sets of data results in an improved model for the protein. The solvent regions are required to be featureless when far (>4 A) away from the protein. In addition a correction to the F(000) term of the Fourier series is refined. These procedures should result in a significantly enhanced model for the solvent near the protein surface. The structure of this local solvent is critical to the stability and function of proteins. The structure of solvent in BPTI is now analyzed in these terms.

G. Crystallization of Synthetic Fragments of DNA
(M. Miller, A. Wlodawer, and E. Appella (NIH))

We have been crystallizing a series of DNA oligonucleotides predicted to form structures deviating from the classical double-helix. A 13-mer d(CGCGAATTACGCG) derived from the self-complementary dodecamer d(CGCGAATTCGCG) by inserting an extra adenosine in the 9th position from the 5'-end was synthesized as a model of a frame-shift mutation. This sequence was expected to form an improper duplex with the unpaired adenine residue either looped out or intercalated into the double helix. The crystals that were grown were disorderd (or unstable). Our solution studies (done in collaboration with F. Schwarz and W. Kirchhoff of the Biothermodynamic's Group, see separate report) showed that the duplex undergoes a transition to a single stranded hairpin loop in the temperature range 0 - 6 ^{o}C. Subsequently we found that a 15-mer d(CGCGAAATTTACGCG) forms a much more stable duplex. The inserted nucleotides are now separated by an AT sequence two base pairs longer. Crystals of this material have been grown by the vapor diffusion technique at 4 ^{o}C. The space group is I222 with a=36.9 Å, b=53.8 Å, and c=102.7 Å. We are modifying the conditions of crystal growth with the aim of preparing a sufficient number of them for data collection. We have been also continuing our efforts to find a DNA oligomer which would crystallize in the form of a single stranded hairpin loop, but so far with little success.

H. Application of Repulsive Regularities Found in Water Structures.
(H. Savage)

Water structures in crystal hydrate systems have been studied in order to categorize the repulsive interactions between different classes of atoms (Nature 322, 717,(1986)). These interactions are divided into four groups (RR1 - RR4).

RR1: O...O repulsion of the H-bonds (H-bonds may bend, if necessary, to within a certain limit).

RR2: O...O repulsion between non-bonded water oxygens (minimum contacts of 3.1-3.6Å depending on orientations).

RR3: H2...O1 repulsion between H2 and O1 of the configuration O1-H1...O2-H2 (minimum contacts of 3.0Å).

RR4: H...H repulsions (minimum contacts of 2.1Å).

(where H1, H2, etc, refer to atoms belonging to two distinct water molecules)

These repulsive restraints explain several of the basic features found in water structures. For example, they can be used to describe the different structures found in the ice phase diagram. The pressure-temperature phase space can be divided into 4 separate regions (Fig 3.1) with respect to which of the repulsive restraints RR2 and RR3 are fully strained:

Region 1: H2...01 remote contacts,

Region 2: 0....0 non-bonded contact for a single lattice of H-bonds

H2...01 remote contacts
Region 3: H2...01 remote contacts,

Region 4: 0....0 non-bonded contacts for two interdigitating lattices of H-bonds

H2...01 remote contacts

In region 1 the RR3 contacts are fully strained, but the non-bonded RR2 0...0 contacts are not (all >3.5A). Thus, a reduction in volume can only take place with respect to reducing the RR2 contacts. In region 2 both the RR2 and RR3 contacts are at their limit and further contraction at higher pressures has to take place by the formation of interpenetrating lattices of H-bonds (self-clathrates). Compression of the 'double' lattice follows along similar lines to that of the single H-bond lattice case; firstly the RR3 contacts are fully strained (region 3), and then both the RR2 and RR3 contacts are at their minimum limits (region 4).

In regions 1 and 3 the non-bonded RR2 interactions are not fully strained and it is possible that some disorder of the water oxygens may be present. This has been found in some recent ultra-high resolution neutron diffraction experiments carried out at the Institute Laue-Langevin on ices Ih (Kuhs and Lehmann, 1986) and VI (Kuhs and Finney, 1986). In ice Ih the position of the oxygen was found to be disordered by up to 0.04A, while in Ice VI variations of up ~0.15A are present.

I. Plans for Next Year

We are planning to commission the X-ray diffraction instrumentation within the next few months. The system will consist of a Nicolet area detector mounted on a Huber diffractometer, with controlling electronics locally adapted by T. Buckley. When fully operational, this facility will obviate the need for the use of X-ray data collection facilities.

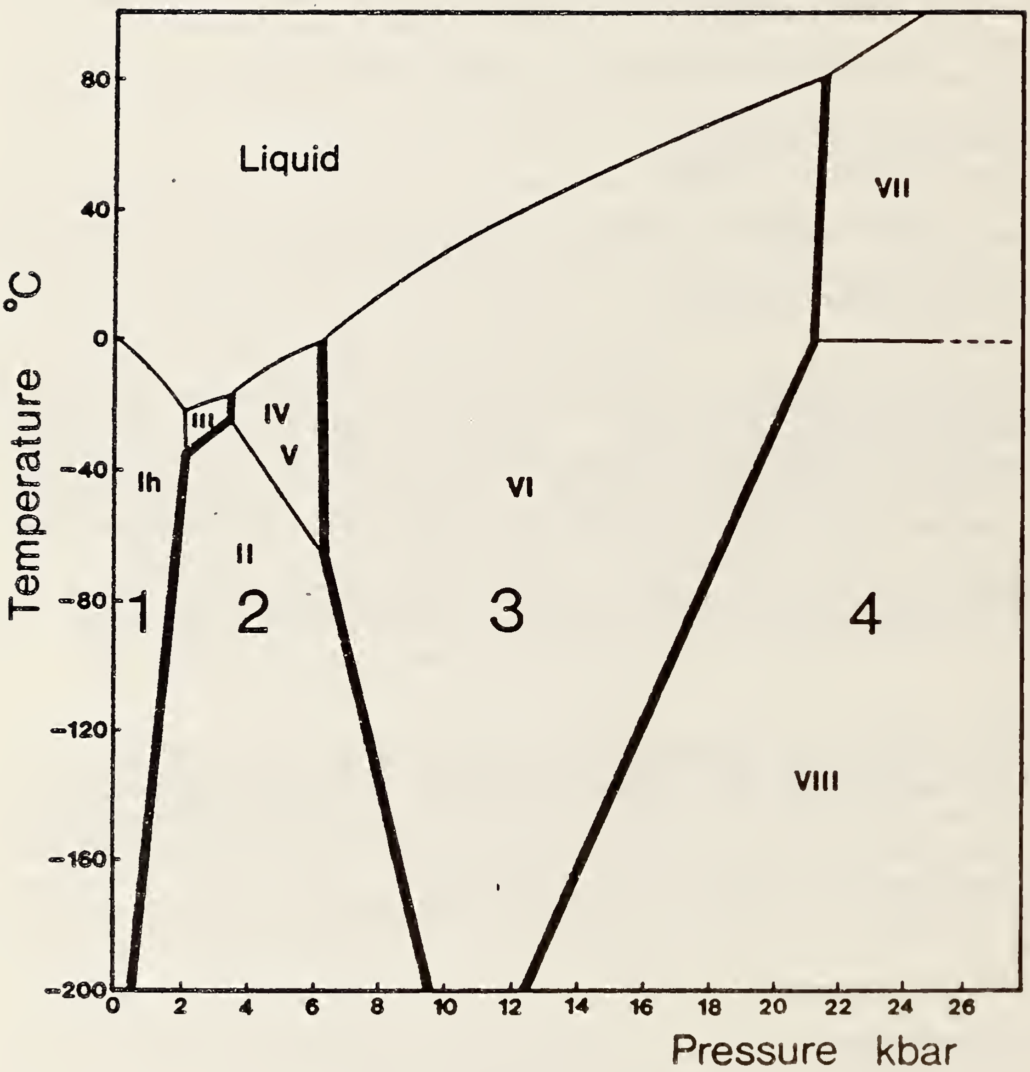


Fig. 3.1. Division of the pressure-temperature ice phase diagram into four regions with respect to the RR2 and RR3 repulsive limitations

Scientifically, we are planning a concerted effort directed to improving the ability to grow protein crystals in a predictable and reproducible manner. To that effect, we will implement a crystallization data base, originally developed by G. Gilliland at NIH, which lists all published conditions for growth of macromolecular crystals. We will develop software, in cooperation with the Chemical Thermodynamics Data Center's Group for manipulation and updating of this data base.

4. CHEMICAL THERMODYNAMIC MEASUREMENTS

E.S. Domalski, S.S. Bruce, K.L. Churney, T.J. Buckley, J. Colbert,
E. Diaz, D.A. Ditmars, D.R. Kirklin, A.E. Ledford

A. Large Sample Combustion Calorimetry

(E.S. Domalski, J.C. Colbert, K.L. Churney, J.E. Diaz, A.E. Ledford, S.S. Bruce, and T.J. Buckley)

This research is being performed in support of the Resource Conservation and Recovery Act and is funded by the U.S. Department of Energy. The purpose of this work is to provide measurement methods, standards, and baseline data for establishing calorific (heating) values and optimal combustion conditions for the control of pollutants for municipal solid waste (MSW) from various sources. Current emphasis is directed toward monitoring the fate of chlorine from input through MSW combustion. The presence of trace amounts of chlorinated organic compounds (i.e., dioxins) in the effluent and fly ash has hindered the construction and operation of MSW incinerators used for the generation of steam and electric power.

During FY 1984, samples of MSW were obtained from Brooklyn, NY, and Baltimore County, MD to generate data on the chlorine content of MSW. Quantitative information of this type is meager and is needed to evaluate the methods that have been proposed for reducing the emission of chlorinated dioxins and furans from incinerators. The main methods proposed are: (1) removal of the responsible components of the waste, (2) proper incinerator design, and (3) efficient operation of the incinerator. The results of the sampling study, which were evaluated in 1985, showed that all combustible components of MSW contained chlorine. Our study has shown that removal of plastics from MSW is not sufficient to reduce the chlorinated organic species formed during the combustion of MSW to negligible levels.

During FY 1985, studies were conducted dealing with laboratory and field data for the calorific value of MSW. The calorific value of the MSW that is needed in a performance or acceptance test is the heat liberated in the actual incineration process, however, the combustion of the organic fraction of MSW is incomplete in this process. The calorific value determined in laboratory tests is for conditions of complete combustion. Currently, no data are available for validating methods either for the measurement of incomplete combustion or the making appropriate calculations to correct for incomplete combustion. To obtain such data, the heat liberated for varying degrees of complete combustion was determined by burning microcrystalline cellulose and synthetic MSW in O_2/N_2 mixtures containing 100, 50, 35, and 21 mole % O_2 in the O_2 in the 2.5 kg capacity flow calorimeter. The synthetic MSW is microcrystalline cellulose which contains 20 mass % silica as the noncombustible component. The particle size of the silica and combustion conditions were such that the amount of char formed in the combustion of the synthetic MSW in air was about 5% of the mass of the ash, the approximate value for the amount of char formed in MSW incinerators. Gaseous hydrocarbons and CO were monitored as a measure of gaseous products of incomplete combustion. The combustion results are being examined to establish the methods for the determination of calorific corrrections for incomplete combustion.

Also during FY 1985, studies were carried out to develop procedures needed for the determination of the threshold conditions for the formation and for destruction of organic chlorine compounds during MSW combustion. The purpose of this study is to determine if we can reproducibly form and/or destroy these compounds and, if so, whether the combustion conditions in a large, laboratory-size combustor can be sufficiently well-characterized to allow application of the results to design or operation of real-world MSW incinerators.

An EPA modified method 5 (MM5) gas and particulate sample train for sampling the product gas and trapping both particulates and volatile organic chlorine compounds was constructed and installed as part of the combustion flow calorimeter. Procedures were developed by S. Chesler and R. Parris of the NBS Organic Analytical Research Division for separating the organic chlorine compounds trapped in the MM5 train into chemical classes of increasing clarity. The organic chlorine compounds were formed in the combustion of synthetic MSW doped with 1.5 mass % polyvinyl chloride (PVC) in 35 mass % O_2/65 mass % N_2. A qualitative analysis using gas chromatography with an electron capture detector was carried out on the separated organic chlorine product formed in the combustion of PVC doped synthetic MSW. Dioxin or furans were not found but could have been present below the detection of the instrumentation (several ppb), but substantial quantities chlorinated benzenes, chlorophenols, and chlorinated biphenyls (PCB's) were detected.

In FY 1986, significant accomplishments were made in the following areas:

1. Gram-size Test Samples to Characterize 2.5 kg Increments

An experimental test was conducted to verify the method used to calculate the heat exchange between the 2.5 kg capacity flow calorimeter and its environment. The test showed that the overall heat exchange corrections to the experimental data were negligible, less than 0.1%, despite significant departures from conventional gram-size combustion calorimeter operating conditions. The results were used to complete an evaluation of the bounds of systematic errors in the calorific values determined in the FY 1984 study involving gram-size test samples prepared from kilogram-size parent increments. The results of the error analysis are reported in a manuscript describing the 2.5 kg flow calorimeter and appears in the September 1986 issue of the NBS Journal of Research.

A summary of the results of the study concerning gram-size test samples from kilogram-size increments was prepared and published in the proceedings of the Twelfth National Waste Processing Conference sponsored by the American Society of Mechanical Engineers (ASME) held in Denver, CO, June 1986.

2. Chlorine Content of MSW

The results of the chlorine content of MSW study completed in FY 1985 are in press for a 1986 issue of Chemosphere devoted to papers presented at the 5th International Symposium on Chlorinated Dioxins and

Related Compounds held at the University of Bayreuth, West Germany, September, 1985 and also appear in the Proceedings of the Twelth National Waste Processing Conference sponsored by the American Society of Mechanical Engineers (ASME).

Four samples of MSW from Baltimore County, MD and Brooklyn, NY which were analyzed in the 1985 chlorine content study were sent to R. Wingender of Argonne National Laboratory for determination of the presence and amounts of chlorinated dioxins, furans, and related compounds (e. g. PCB's and chlorophenols). Input composition data of this type are not clearly established for MSW and are essential to establish how much dioxins or furans are formed during the incineration process.

3. Development of Corrections for Incomplete Combustion

The determinations of the calorific value and moisture content of the cellulose burned in the study to develop methods for correction for incomplete combustion were carried out. The determinations provide necessary auxiliary data to convert laboratory results so that they have a closer correspondence to real-world incinerator conditions. The combustion results obtained in the study for development of corrections for incomplete combustion were summarized and appear in a second manuscript published in Chemosphere (see following section).

4. Threshold Condition for Formation/Destruction of Organic Chlorine Compounds

The results of the FY 1985 combustion of synthetic MSW doped with PVC appear in a second manuscript in press for Chemnosphere, devoted to papers presented in the 5th International Symposium on chlorinated Dioxins and Related Compounds.

5. Modifications to Apparatus and Procedures

A number of hardware and software changes were made as a result of the shift in emphasis of the experiments from calorimetry to controlled combustion studies and chlorine monitoring. The changes were as follows:

- To better simulate combustion conditions in real-world incinerators, the combustor of the 2.5 kg capacity flow calorimeter was modified so that the CO produced in the combustion of synthetic MSW in air could be reduced to less than 1000 ppm. (In the FY 1985 study to develop corrections for incomplete combustion, the CO was in the 10,000-15,000 ppm range.) This was accomplished in a sequence of experiments in which various sources of heat loss from the combustion zone (i.e. region near the burning sample) were successively reduced, the most critical of which amounted to providing insulation between the combustor and combustor enclosure in the region below the reaction zone baffle. The option of burning synthetic MSW in dispersed rather than in pellet form was not explored in order to have a capability of studying the formation or destruction of dioxins under various conditions in the absence of fly ash.

- To minimize the time necessary to break down, reassemble, and leak check the gas supply and sampling lines in a calorimetric experiments, the combustor was permanently mounted on a frame outside the 2.5 kg capacity flow calorimeter. Auxiliary cooling sources were built for the outside of the combustor enclosure, for the heat exchange coil for the product gas, and for the collector for the water liberated in the combustion reaction to replace the cooling originally provided by the calorimeter water.

- Two oxygen detectors have been installed to improve the characterization of inlet and exit gas streams to the combustor. Backup CO and CO_2 detectors (NDIR) were installed in the product gas analysis train to provide redundancy and loss of data due to detector malfunction.

- To improve the collection of trace chlorinated organic species, the MM5 train was redesigned and is being rebuilt in cooperation with R. Wingender of Argonne National Laboratory, who will carry out the dioxin analysis in subsequent experiments. Changes are oriented towards improving the efficiency of recovery of organic chlorine compounds and reduction of possible contamination of the XAD-2 resin (used to trap gaseous organic chlorine compounds) prior to analysis by gas chromatography and mass spectrometry.

- To upgrade monitoring of the detectors for O_2, CO and Co_2, a new thirty channel scanner was installed. Since each combustion experiment now tends to be quite different in terms of the need for and time sequence for monitoring the various detectors, the original software for data acquisition for the fixed routine of a calorimetric experiment has become obsolete and has had to be replaced. We were fortunate to have a guest computer scientist from the Twente University of Technology, Netherlands, to help us in redesigning the data acquisition software. As a result of Mr. Rukkers three and a half month stay with us, we have a well designed data acquisition system which can be modified rapidly to fit the varying demands of any particular laboratory experiment. Other software for data analysis and plotting was developed by two summer students (S. Sung, R. Metz).

In the initial phase of the combustion experiments of this study, we are currently carrying out a set of chlorine mass balance experiments. The aim of these experiments is to determine the degree to which suitable clean up procedures will ensure that organic chlorine compounds detected in the combustion products of a given run are formed from chlorine containing compounds burned in the same rather than in previous runs.

During FY 1987 we plan to complete the remaining auxiliary measurements and analysis of the study for development of corrections for incomplete combustion. The initial phase of the study of threshold conditions for the formation/destruction of chlorinated organics will be completed with an attempt to determine the combined recovery efficiency of the combustor plus the MM5 sampling train for chlorinated organic compounds. In the second phase of the study, we plan to evaluate the use of calcium oxide binder in densified pellets of processed MSW as a possible method for reducing dioxin emissions from combustion of refuse. In the third phase of the study, we plan to resume our study of the combustion of synthetic MSW doped with inorganic as well as organic chlorine compounds.

Because the combustor of the 2.5 kg flow calorimeter cannot be economically altered to provide all the combustion conditions that must be studied in the threshold study, a new laboratory-size, two stage incinerator was purchased in FY 1986. It is our plan to instrument this unit and conduct trial experiments toward the latter part of FY 1987.

B. Calorimetric Update on SRM Coals 2682, 2683, 2684 and 2685

(J.C. Colbert)

The annual calorimetric update was performed on SRM Coals 2682, 2683, 2684 and 2685 to determine if there has been any change in the calorific value of these coals due to sample degradation as a result of aging or normal oxidation. Sixteen unopened bottles of coals were received from OSRM, four of each of the latter SRM's. One measurement was made for residual moisture and one for calorific value. The original certified value for sulfur was used in making the calculations since this constituent remains constant with time. All of the measurements were made in random order with one duplicate measurement for SRM 2684. The sampling procedure and run protocol was designed by R.C. Paule, NML Statistician.

Good agreement (<50 Btu/lb) was obtained between calorific values obtained for SRM 2683, 2684, and 2685 and their 1985 certified values, however, the average calorific value for SRM 2682 was 300 BTU/lb higher than the average result for 1985.

As a further check on the results, an additional set of four unopened coals were measured with only one sample giving a high calorific value. These eight coal samples were sent to an outside testing laboratory by the OSRM. The results of our lab and the outside lab agree to within 7 Btu/lb. The final statistical evaluation of the data led the OSRM to remove the calorific value certification from SRM 2682. This is due to a larger variability in the sample than anticipated, resulting in a larger variability in the calorific value than was predicted. It appears that the bottled material maybe degrading at an uneven rate, the cause of which is unknown at this time. Another parameter which should be examined is particle size variability in SRM 2682, within and between bottles, since particle size variability can influence the dispersion of results.

C. Bomb Calorimetric Measurements for Biotechnology

(J.C. Colbert and E.S. Domalski)

The enthalpy of combustion of the crystalline monsaccharides D-ribose and 2-deoxy-D-ribose (2-deoxy-D-erythro-pentose) have been determined by combustion bomb calorimetry. The standard molar enthalpies of combustion ($\Delta_c H$) and formation ($\Delta_f H$) at 298.15 K for crystalline D-ribose are: -2349.47 ± 0.95 kJ/mol and -1047.23 ± 1.66 kJ/mol, respectively. Similarly, for 2-deoxy-D-ribose, $\Delta_c H$ = -2527.39 ± 0.98 kJ/mol and $\Delta_f H$ = -869.31 ± 1.68 kJ/ mol. Proton NMR and C-13 NMR studies were conducted by B. Coxon of the Center for Analytical Chemistry, to determine the anomeric composition of the crystalline sugars. The crystalline D-ribose sample consisted of 64.4 mass % beta-pyranose, 35.4 mass % alpha-pyranose, and 0.2 mass % beta-furanose anomers. The sample of 2-deoxy-D-ribose was made up of 98.8 mass % beta-pyranose, 0.5 mass % alpha-pyranose, and 0.7 mass % beta-furanose anomers.

Combustion bomb calorimetric studies are in progress on crystalline hexaglycine. Elemental analyses on this compound for carbon, hydrogen, and nitrogen from two independent testing laboratories indicates that it is the hemihydrate. An examination of the literature combined with some preliminary calculations on diglycine, triglycine, and tetraglycine shows that the energy of the peptide bond in these compounds is constant. If one extends this energy constancy to hexaglycine, then the energy or enthalpy of hydration can be estimated as a result of conducting the combustion calorimetric measurements. This value for the enthalpy of hydration should provide some useful insight into the magnitude of hydration forces between an oligopeptide and water under conditions of initial bonding interaction.

Previous bomb calorimetric measurements in this laboratory on crystalline adenine, guanine, purine adenosine, guanosine dihydrate, D-ribose, and 2-deoxy-D-ribose provide the basis for establishing several energetic cycles for the formation of nucleosides as well as indicating research paths in which to pursue combustion bomb calorimetric measurements on key compounds. Three key compounds which are immediate candidates are: deoxyadenosine, deoxyguanosine, and nebularine. Energetic differences between ribose/deoxyribose, adenine/adenosine, guanine/guanosine, and purine/nebularine moieties in nucleoside formation could be established more precisely than are presently available and could be regarded as standard reference value points for thermodynamic assessments involving reaction processes of nucleosides.

D. Estimation Methods and Combustion Calorimetry an Organic Phosphorus Compounds

(D.R. Kirklin and E.S. Domalski)

Precise enthalpies of formation are not available for important industrial and biochemical compounds that contain phosphorus. Experimental determination of these properties for some of the compounds is not feasible because of their toxicity or limited availability. The objective of this research is to develop correlation and estimation schemes which are needed to predict enthalpies of formation at 298 K for compounds that have no reported experimental values. Also, combustion calorimetric determination of enthalpies of combustion will be conducted on key organic phosphorus compounds.

Precise and accurate enthalpies of formation are necessary to develop an adequate correlation and estimation scheme. However, there is a lack of precise and accurate thermodynamics literature data on organic phosphorus compounds. The existing thermodynamic data for organic phosphorus compounds, which are based upon bomb calorimetric data, are often inaccurate due to several problems associated with the combustion calorimetry of organic phosphorus compounds. Until the present time, there is only one set of data in the literature which has adequately addressed all of these problems. These data were obtained by Harrop and Head (J. Chem. Thermodynam. 9, 1067 (1977).) on crystalline triphenylphosphine oxide.

There are four major problems associated with the combustion calorimetry of organic phosphorus compounds. The first problem is the selection of an unreactive crucible material. Platinum crucibles, which work well with most organic compounds, are unsuitable because platinum reacts with organic phosphorus compounds at high temperatures. The second problem is that organic phosphorus combustion samples usually do not burn completely in a bomb combustion experiment. Phosphorus compounds are used commercially as flame retardants for various fabrics because of their resistance to burning. When phosphorus compounds burn in oxygen they produce oxides of phosphorus which dissolve in the water in the bomb to form various kinds of phosphoric acids. These phosphoric acids have appreciable energies of dilution and are produced as various concentrations in different parts of the bomb. Therefore, the attainment of a homogeneous solution of uniform concentration of these phosphoric acids constitutes the third problem area. The fourth problem is that the bomb solution must be analyzed to determine, qualitatively and quantitatively, the speciation of phosphorus acids formed as rapidly after the calorimetric measurement as possible because of slow oxidation of all phosphoric acids present to H_3PO_4.

The solution to the above mentioned problems are straightforward, but most laboratories are not equipped to handle them. Gold crucibles are found to be unreactive with organic phosphorus compounds but have a relatively low melting point. A sufficiently massive gold crucible performs well in most experiments. The problem of incomplete combustion can be overcome by determining the amount of carbon dioxide produced or by measuring the amount of carbon residue formed. The problem of obtaining a homogeneous solution of the phosphoric acids can only be solved by using a rotating bomb calorimeter. Most laboratories use static bomb calorimeters and therefore cannot obtain a homogeneous bomb at the end of the reaction period. The qualitative and quantitative analysis of bomb solutions can be only done by various forms of chromatography. Harrop and Head used paper chromatography, however, this method is very slow and not very quantitative. Ion chromatography seems to be ideally suited to solve this problem because it is quantitative and offers reasonable precision.

The NBS bomb calorimetry laboratory has a rotating bomb calorimeter that utilizes sample sizes on the order of 100-200 milligrams. The laboratory has equipment for measuring the amount of carbon dioxide produced during each combustion experiment. A DIONEX 2000i Ion Chromatograph was borrowed from the DIONEX Corporation to check the feasibility of analyzing the bomb solution composition for the various forms of phosphoric acids.

A set of measurements on triphenylphosphine oxide was made in the NBS rotating bomb calorimeter. Negligible amounts of carbon residue were produced. The carbon dioxide analyses verified these results. A DIONEX 2000i Ion Chromatograph was utilized to analyze the homogeneous bomb solution for the various oxyacids of phosphorus. Orthophosphoric acid, H_3PO_4, pyrophosphoric acid, $H_4P_2O_7$, and tripolyphosphoric acid, $H_5P_3O_{10}$, were observed to be produced in the following percentages, respectively: 76.3, 20.0, and 3.7. The analysis means that 59.9 % of the total phosphorus was quantitatively converted to orthophosphoric acid while 31.4 % and 8.7 % of the total phosphorus was converted to pyrophosphoric acid and tripolyphosphoric acid, respectively. These values were used to determine the amount of energy that would be needed to hydrolyze the condensed phosphoric acids to orthophosphoric acid.

A correction of −11.08 J/g for the hydrolysis of condensed phosphates to orthophosphate was added to our experimental energy of combustion, −35, 778.15 ± 5.06 J/g, for triphenylphosphine oxide to calculate the correct energy of combustion, −35,789.2 ± 5.06 J/g. This value agrees very well with the previous reported value of −35,789.6 ± 6.0 J/g by Harrop and Head. (J. Chem. Thermodynam. 9, 1067 (1977)). These authors have reported the only precise combustion data for an organic phosphorus compound which was based on a comprehensive analysis of the products of combustion, which included the quantitative determination of condensed phosphoric acids present in the bomb solution from a rotating bomb calorimeter. Bedford and Mortimer (J. Chem. Soc. 1622 (1960)) reported an energy of combustion of −35,943 ± 45 J/g based upon measurement using a static bomb calorimeter.

Experimental measurements were also made on triphenylphosphine. The methods and procedures established during the triphenyl phospohine oxide were utilized. The sample was vacuum dried for 12 h and found to contain 0.0077 % moisture. The sample was investigated with no further purification. The mean of seven measurements yielded a value of −39,200.73 ± 3.85 J/g for the internal energy of combustion without a correction for the hydrolysis of condensed phosphates to orthophosphate. Assuming that the condensed phosphates were produced in the same proportions as for the triphenylphosphine oxide would require an additional correction of −11.08 J/g. This would make the actual value determined to be −39,211.81 J/g. However, the actual correction for the hydrolsis of condensed phosphates must be determined on a set of combustions of triphenyl phosphine and will be performed during fiscal year 1987 when the combustion calorimetry laboratory receives a DIONEX Ion Chromatograph. The internal energy of combustion reported by Bedford and Mortimer is −39,245.8 ± 36.7 J/g based upon measurements using a static bomb calorimeter.

Future plans include bomb calorimetric measurements on other key organic phosphorus compounds. These measurements will provide the data necessary to determine estimation parameters for other organic phosphorus compounds. Proposed compounds are triphenyl phosphate, tri-n-octyl phosphine oxide and tricyanophosphine.

E. Drop Calorimetry of Non-Reacting Systems Below 2800 K

(D.A. Ditmars)

This activity is a continuation of a calorimetric research program whose goals are:

- to obtain accurate thermodynamics data on non reacting refractory materials in either the solid or liquid state up to 2800 K.

- to measure the specific heat at temperatures above 273 K of well-characterized materials of the highest attainable purity for which existing C_p data are insufficient or in conflict and which are: (a) critical to energy and space related technology, or (b) especially suite as a model on which to test refined lattice-dynamic calculations of thermodynamic properties.

- to produce and support high-temperature calorimetric standard reference materials (SMR's) for heat capacity and for differential thermal analysis (DTA) calorimetric measurements.

The number of facilities, nationally, which can sustain programs of high-temperature calorimetric research is seriously diminishing at a time of increasing needs for just the data produced through this type of investigation. There is a constant demand for thermodynamic data on new materials capable of functioning acceptably in the harsh environments associated with space propulsion systems or upon re-entry, new energy technologies and defense-generated needs for materials to enable space systems to withstand overt aggression. Also, the existing thermodynamic data on some elements is often not accurate enough to allow a meaningful test of theories which have recently been formulated to calculate thermodynamic functions directly.

The Chemical Thermodynamics Division has available two operative precision drop calorimeters for the ranges 273-1200 K (isothermal, phase-change calorimeter) and 1200-2800 K (adiabataic receiving calorimeter). These are being used in research intended to provide calorimetric measurements at the highest accuracy on materials related to the high temperature applications mentioned above. Every effort is made to coordinate this research with that of another NBS facility (very-high-temperature pulse calorimeter) in order to provide the capacity for continuous coverage of high-temperature thermodynamics studies up to 5000 K or above on especially important systems. We have in addition an operative high-temperature discrete-heating adiabatic calorimeter (300-800 K) and we maintain in reserve a low-temperature (4-300 K) adiabatic calorimeter for possible future research needs.

In order that NBS thermal data and that of other high-temperature investigations can be fairly intercompared and assessed for accuracy, we maintain a continuing effort to update or extend the range of coverage of high-temperature standard reference materials. In recognition of the growing need for accurate DTA temperature and enthalpy standards, we attempt to identify systems whose thermal properties can be measured by both conventional calorimetric and DTA techniques.

We have concentrated our experimental and data-analysis activity in FY 1986 among the alkaline earths Ca, Sr, and Ba and have continued our work on pure Cu. Of the alkaline earths, calcium is of particular economic and biological importance, yet the literature thermodynamic functions for calcium are certain to be seriously in error due to sample impurity effects. The situation of the thermodynamic functions for strontium is similarly unclear for no original published heat-capacity data exists for this element above room temperature. This is unfortunate, as knowledge of the thermodynamic properties of strontium compounds figures prominently in assessing the course and effects of potential nuclear power accidents.

In the conduct of thermodynamic research on these alkaline earth metals, one must confront the effects of low, but virtually irreducible, oxide and hydride impurity levels which nevertheless exert a substantial influence on the phase relationships among the allotropes of Ca and Sr and on Ba. Thus, a large fraction on ones total effort must be devoted obtaining pure samples, maintaining their integrity, and obtaining credible analysis for the oxygen and hydrogen present.

Our prior (FY 84) heat-capacity data on calcium, measured partly at NBS ($T>300$ K) and partly at the U.S. Geological Survey in Reston, VA (in the cryogenic range) employed two calcium samples of differing oxygen and hydrogen impurities. Of these data, only those in the high-temperature fcc region ($715>T>300$ K) were obtained using the sample of lower purity. Comparison at NBS with enthalpy data obtained in the fcc region for the high-purity sample led to the conclusion that the earlier NBS high-temperature data were subject to serious and uncorrectable systematic error arising from the method of encapsulation. Therefore, in FY 86 we repeated the entire fcc series of measurements on the higher-purity sample. In addition, a number of enthalpy measurements were made at closely and carefully-spaced temperatures throughout the fcc-bcc transition region. This new fcc data for calcium was analyzed in FY 86 and shown to merge, uncorrected, with the cryogenic data mentioned above. The enthalpy data for calcium in the fcc-bcc transition region indicated not a sharply temperature-resolved transition, but one occurring gradually over a 5 or 6-degree interval. This, we have interpreted using a model in which a trace contaminant (in this case CaH_2) enters into ideal solution with each of two allotropes of calcium. The results (Fig 4.1) indicate a lower temperature for the fcc-bcc transition temperature (710 K) than current values proposed in the literature (716 to 720 K).

Analysis of the strontium sample we had obtained from Prof. Westrum of the University of Michigan measured in FY 86 showed an unacceptably high level of hydrogen contamination. Therefore, we obtained in FY 86 a new, specially-prepared, diffusion-distilled strontium sample from the Metallurgy Department of Iowa State University. At the same time, we obtained a similar sample of barium.

Considerable effort was expended in FY 86 on the encapsulation of these materials and preparation of them for purification of hydrogen as well as for oxygen and hydrogen analyses. To bring this about, we developed a cooperative arrangement with the Metallurgy Division of the Naval Research Laboratory (Wash. D.C.) for the use of their electron-beam materials-processing facility.

In FY 87 we plan to extend the heat capacity measurements on calcium through the melting point into the liquid range. Also, purification and analysis of the strontium and barium samples will be carried out and measurement of their heat capacity in the solid range begun. Heat capacity measurements on the purified barium sample in the cryogenic range will concurrently be performed. In FY 86 we collaborated with a guest worker from Brock University (C. Plint, Ontario) to complete measurements on the heat capacity of highly-pure, polycrystalline copper (NBS Special Research Material 5 : a low-temperature heat capacity standard) up to 1173 K. We plan to extend these measurements in FY 87 to the melting point and to begin the analysis of our data and comparison to the extensive literature data available on copper. These copper data will have potential value in extension of the temperature range of the copper heat-capacity standard and in establishing more accurate heat capacity data against which to test new theoretical model in the calculation from first principles of the thermodynamic properties of fcc metals.

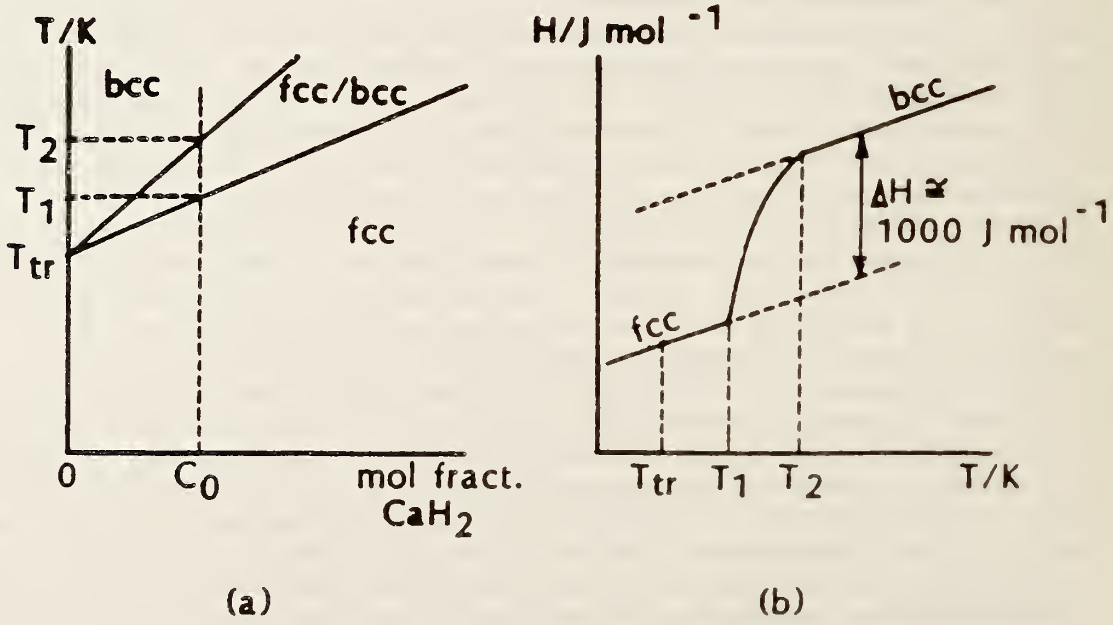


Fig.4.1(a): Idealized Ca-CaH_2 phase diagram including 2-phase region near peritectoid. Overall CaH_2 concentration (C_0)= 0.24 mol % ; (b): Schematic measured enthalpy function for Ca containing 0.24 mol % CaH_2 in solution. T_1= 714 K, T_2= 720 K, T_{tr}≅ 710 K.

5. CHEMICAL THERMODYNAMIC DATA ACTIVITIES

M.W. Chase, D.M. Bickham, D. Garvin, C.R. Jackson, T.L. Jobe, Jr.
W.L. King, D.B. Neumann, V.B. Parker, D. Smith-Magowan, R.H. Wood,
(Consultant), D.D Wagman (Guest Worker), E.D. Hearing, R.H. Nuttall,
R.H. Schumm, N. Young, and S.D. Wasik (Contractors)

The goal of this work is to provide reliable values of thermochemical and thermophysical properties of chemicals, both inorganic and organic. The values are intended to be useful throughout science and industry. Because of the widely differing needs of users, emphasis is placed in this work on generic information and methods of wide applicability. Two data centers carry on this function: the Chemical Thermodynamics Data Center (CTDC) and the Electrolyte Data Center (ELDC). Both are partly supported by the NBS Office of Standard Reference Data (OSRD).

The data group now consists of five thermochemists, a computer systems manager, two computer programmers, a chemical information specialist, a clerk, a consultant and a guest worker. In addition, four thermochemists do special tasks under contract.

The work of the two data centers is inter-linked. Together they cover the evaluation of thermochemical properties of chemical reactions, thermal functions of chemical species and thermophysical properties of solutions. These activities are being extended by extramural collaborations: participation in the CODATA Thermodynamic Tables project to build an international set of recommended values, and, cooperative work with the University of Delaware on methods for correlating thermophysical properties of solutions.

A major expansion of the data centers occured during the year. The JANAF Thermochemical Tables project was moved to NBS from the Dow Chemical Co., Midland, MI. Dr. M.W. Chase, leader of the JANAF project, became a member of the data center staff, and, at the end of the year, head of the Chemical Thermodynamics Data Centers Group.

The data centers are supported by a vigorous computer group which manages the mini- and microcomputer facility used by five CCP data activities.

The outputs from the centers are published in the Journal of Physical and Chemical Reference Data, the Journal of Research of NBS, CODATA Special Publications, Handbooks of DIPPR, and proceedings of various meetings. The annual index to the thermochemical literature on inorganic compounds that is prepared at NBS is published in the Bulletin of Chemical Thermodynamics.

Most of our prime activities are described in the following paragraphs. Topics in progress which will not be discussed further are:

- Installation of the computer program GAMPHI (calulates activity coefficients) on a microcomputer

- Final selection and documentation of the CODATA key values for chemical thermodynamics

- Preparation of recommendations for the solubility of eleven types of organic compounds in water

- Converted network calculation programs (CATCH) to be operational on the NOS CYBER (from the NBS UNIVAC); these programs are necessary for the evaluation of the calcium and key values results for CODATA and the rubidium network

A. Chemical Thermodynamics Data

1. Thermochemistry of Compounds of Iron
(V.B. Parker)

The evaluation of the thermochemical properties of iron compounds is being undertaken as part of a larger project, sponsored by CODATA, that will include thermal functions and the analysis of several binary systems. The thermochemical analysis is well underway. A reaction catalog (listing of pertinent measurements, each expressed as a chemical reaction, together with the values of the properties measured) has been assembled. It contains the evaluated thermochemical data on the reactions of the "key" iron compounds.

A "key" compound is a species whose thermochemical properties are of strategic importance because many other compounds are dependent upon its thermochemical properties. The properties of this compound may, in turn, be dependent upon those of other compounds (from various reaction paths). This group of compounds and its interconnections comprises the "key network".

The thermochemistry of iron compounds is complex. An example of this complexity is shown in Figure 5.1, which indicates the enthalpy relationships among the key compounds. A similar diagram, not shown, indicates the Gibbs energy relationships and measured entropies. Considering the importance of iron and its compounds, the disarray of the data for the basic thermochemical relationships is disturbing. Calculations of the same property via different paths in the network yield discordant values. This is demonstrated in the following brief analysis of the thermochemical properties of $Fe^{+2}(aq)$ and $Fe^{+3}(aq)$ in their standard states at 298.15 K. The cited reactions are from the network shown in Figure 5.1, the values are from individual studies or combinations of them. The enthalpy data are given first for the two ions and then the Gibbs energy data. The tentative selected values made to date conclude the presentation. The state designation "ao" means standard state. All thermochemical values are in kJ/mol.

Enthalpy of Formation: For the determination of the enthalpy of formation of $Fe^{+3}(ao)$ the measurements on the following reactions are used.

(1) $Fe(cr) + 1.5H_2O_2(ao) + 3H^+(ao) = Fe^{+3}(ao) + 3H_2O(l)$

(2) $FeCl_3(cr) = Fe^{+3}(ao) + 3Cl^-(ao)$

(3) $Fe(cr) + 1.5Cl_2(g) = FeCl_3(cr)$

(4) $Fe(cr) + 3HCl(\text{in } 12.73\ H_2O) + 0.5H_2O_2(l) = FeCl_3(cr) + H_2(g)$
$+ H_2O(l)$

Values obtained are:

From Reaction	$\Delta_fH^o(Fe^{+3},aq)$	$\Delta_fH^o(FeCl_3,cr)$
(1)	-46.6±0.8	
(2) and (3)	-53.8±0.9	
(2) and (4)	-57.0±1.0	
(3)		-396.02±0.14
(4)		-399.24±0.35

The agreement of the results in each column is not as good as anticipated, based on the claimed reliability of the individual studies.

Similarly a more extensive set of measurements may be used for the determination of the enthalpy of formation of $Fe^{+2}(ao)$. A similar conclusion is obtained. The resulting values show too much scatter; much larger than would have been expected based on interpretation of the individual studies.

In a third independent path, the difference between the enthalpies of formation of ferric and ferrous ion can be determined from:

(5) $Fe^{+2}(ao) + 0.5H_2O_2(ao) + H^+(ao) = Fe^{+3}(ao) + H_2O(l)$

(6) $Fe^{+2}(ao) + H^+(ao) = Fe^{+3}(ao) + 0.5H_2(g)$.

Again, from a collection of six results, the scatter in this enthalpy of formation difference is too great, casting suspicion on the results.

Gibbs energies of formations: The Gibbs energies of each of these species can be determined (independently) from cell measurements (7), equilibria and solubilities (8-10).

(7) $Fe(cr) + 2H^+(ao) = Fe^{+2}(ao) + H_2(g)$

(8) $Fe^{+2}(ao) + 2Tl(cr) = Fe(cr) + 2Tl^+(ao)$

(9) $(1/3)\ Fe_3O_4(cr) + 2H^+(ao) + (1/3)\ H_2(g) = Fe^{+2}(ao)$
$+ (4/3)\ H_2O(l)$

(10) $FeSO_4{:}7H_2O(cr) = Fe^{+2}(ao) + SO_4^{-2}(ao) + 7H_2O(l)$

The Gibb's energy of the ferrous ion $\Delta_fG^o(Fe^{+2},ao)$ is determined to be:

from (7)	from reaction shown
-80.14±0.20	-78.7±1.5 (8)
-90.11±0.80	-90.0±5.0 (9)
-78.8±0.5	-90.6±1.2 (10)
-84.91±0.20	

These numbers should exhibit much greater agreement. On the basis of the EMF data alone, a value $\Delta_f G^o(Fe^{+2},ao)$ of-80.14± 0.20 would be selected, using a study in which great care was taken to avoid electrode contamination by $H_2(g)$(from its preparation) and $O_2(g)$. The more negative values from (9) and (10), however, cast suspicion on this choice.

The Gibbs energy of formation of ferric ion, -11.4±1.5 kJ/mol can be obtained from:

(11) $FeOOH(cr, alpha) + H_2O(l) = Fe^{+3}(ao) + 3\ OH^-(ao)$

where $\Delta_f G^o(FeOOH, cr)$ is dependent upon $\Delta_f H^o(Fe_3O_4,cr)$ and

$S^o(FeOOH, cr, alpha)$.

Independently, the half cell

(12) $Fe^{+2}(ao) + H^+(ao) = Fe^{+3}(ao) + 0.5H_2(g)$

for which agreement among the various investigations is excellent,

yields $\Delta(\Delta_f G^o(Fe^{+3}(ao)-\Delta_f G^o(Fe^{+2},ao)) = 74.27\pm0.20$.

Selected values. Tentative selections have been made, based on the data given above:

	$\Delta_f H^o$	$\Delta(\Delta_f H^o)$	$\Delta(\Delta_f G^o)$
$Fe^{+2}(ao)$	-91.5±1.0		
$Fe^{+3}(ao)-Fe^{+2}(ao)$		42.5±1.5	74.27±0.20

so that:

$Fe^{+3}(ao)$	-49.0±2.0
$FeCl_2(cr)$	-342.8±1.1
$FeCl_3(cr)$	-396.0±2.0
$FeSO_4:7H_2O(cr)$	-3013.7±0.3

It is hoped that further analysis of the data, and the inclusion of more data, based on current measurements, will help establish the selections above and clarify the situation, particularly that for $\Delta_f G^o(Fe^{+2},ao)$. The following experimental data would be useful.

Activity coefficients for aqueous $FeSO_4$ solutions. Those used now for $\Delta^{sol}G^o(FeSO_4:7H_2O,cr)$ are estimated from $NiSO_4$, but it is not known how good this analogy is.

IRON KEY NETWORK – ENTHALPY

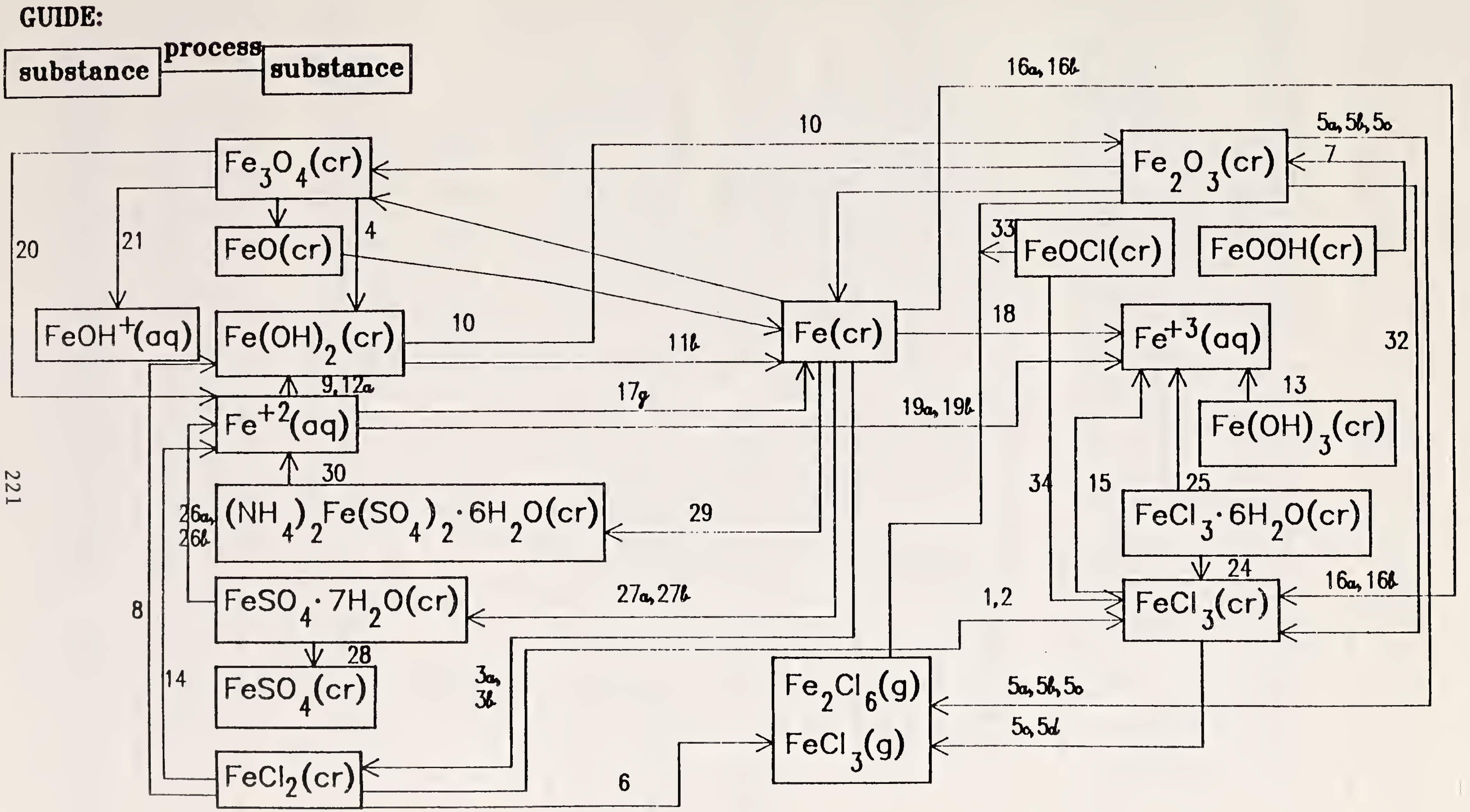


Fig. 5.1. Iron Key Network--Enthalpy. Measured processes are shown by arrows connecting the substances. (The numbers on the arrows refer to a larger reaction catalog than that discussed here, and are not the same as those used in the text).

- The $\Delta_f G^o(Fe^{+2},ao)$ value, now −80.14 ± 0.20 from EMF data should be verified.

- $\Delta_{sol} H_{sol} H(FeCl_3,cr)$ is needed as a function of concentration in water and aqueous HCl. The present data are not of high enough quality to permit confident extrapolation to the standard state.

- $\Delta_f H^o(FeCl_2,cr)$, $\Delta_f H^o(FeCl_3,cr)$, and $\Delta_r H^o$ for $FeCl_2(cr) + 0.5\ Cl_2(g) = FeCl^2(cr)$ should be redetermined. The $FeCl_2/FeCl$ couple is important outside the iron system as auxiliary data in redox reactions. The "NBS Tables" and others use $\Delta_r H_o = -57.5$, but there are conflicts in data in the uranium halide thermochemical network which might be a result of using this value.

2. JANAF Thermochemical Tables

(M.W. Chase)

This project was transferred in February 1986 from The Dow Chemical Company, Midland, MI to the Center for Chemical Physics at the National Bureau of Standards. Since that time, most of the effort has been directed at the establishment of JANAF resources within the Chemical Thermodynamics Data Centers. This includes the calculational programs, the literature and data files, and the backup information for the existing tabulations. In parallel with this, the third Edition of the JANAF Thermochemical Tables has been completed, at Dow Chemical, and sent to the American Institute of Physics for publication later this year in Journal of Physical Chemical Reference Data.

In our data evaluation activities reviews and thermochemical tables are being prepared for three classes of species: the alkaline earth metals, their monohydroxides and their dihydroxides. For the 3rd Edition of the JANAF Thermochemical Tables, the calcium thermal functions were estimated to be intermediate between those for magnesium and strontium; the strontium thermal functions being based on unpublished enthalpy data of Stephens and Roth. However, there now is additional information available from the recent heat capacity study of calcium by Robie (USGS) and the enthalpy studies of calcium and strontium by Ditmars. The low temperature study by Robie is in qualitative agreement with the recent JANAF analysis. However, the experimental results yield a considerably different Cp curve in the region below ~20 K, raising the entropy of calcium at 298.15 K by ~ 1.5 J/(mol K) above our recommendations. When the analysis of new information is completed, the thermodynamic functions of the metals will be much more firmly based. We will then be in a better position to judge the reliability of the existing enthalpy data for barium.

The alkaline earth monohydroxides have been studied experimentally during the last few years. A thorough spectroscopic study has been carried out for the magnesium, calcium, strontium, and barium species by Harris et al. and Bernath et al. These studies have yielded structures and two of the three vibrational frequencies ν_1, and ν_2. In all cases, ν_3, the O-H stretch is assumed to be ~3650 cm-1 in comparison with the alkali metal hydroxides. Now the thermal functions, in particular the entropy, are well-established, in comparison with the previously available entirely-estimated values. This results in the entropy at 298.15 K being shifted by 2.5 J/(mol K). However, for the case of beryllium, we still must rely on theoretical calculations for the structure and the vibrational frequencies.

Our review of the alkaline earth dihydroxide species is nearing completion. The full analysis of these species is limited by the lack of low temperature heat capacity data for $Sr(OH)_2$ and $Ba(OH)_2$ and high temperature enthalpy data for $Be(OH)_2$. The low temperature data for $Be(OH)_2$ has been measured in USSR, is available through VINITI (Russian Depository of Technical Data), and will enhance the quality of the beryllium dihydroxide thermal functions. The gas phase dihydroxide species are estimated based on comparisons with the gaseous difluorides, dichlorides and the monohydroxides. With more reliable data avalilable on these latter species, the resulting gaseous dihydroxide thermal functions (still estimated) should be much improved.

In addition, information has been collected for the analysis of the alkaline earth oxides, sulfides, sulfates, carbonates, and the halides. For each of these classes of species, annotated bibliographies exist and are being updated continuously. Data summaries are in preparation for these classes of species.

3. Thermochemical Properties of Compounds of Rubidium

(V.B. Parker, W.H. Evans, R.L. Nuttall)

The thermochemistry of rubidium compounds has been summarized in a paper accepted for J. Phys. Chem. Reference Data. This paper presents a catalog of the 420 measurements on 250 substances used in the preparation of the rubidium table in the "NBS Tables of Chemical Thermochemical Properties". It represents a comprehensive survey of thermochemical measurements on rubidium compounds. Included are enthalpies of reaction, Gibbs energies of reaction, based on equilibria and cell potentials, and entropies. For each process a comparison is made between the observed value and that calculated from the "NBS Tables". A feature novel to thermodynamic tables is that estimated reliabilities are given for the recommended values for each measured process.

4. Thermodynamic Properties of Compounds of Calcium

(D. Garvin, V.B. Parker)

The first volume of a new series of tables of evaluated thermodynamic properties of chemicals is being published this year. It is the "CODATA Thermodynamic Tables. Selections for Some Compounds of Calcium and Related Mixtures. (A Prototype Set of Tables.)", D. Garvin, V.B. Parker and H.J. White, Jr., editors. This is the report of the CODATA Task Group on Chemical Thermodynamic Tables and covers six years of work by an international team of data evaluators. NBS has taken the lead, providing evaluated thermochemical data, a definitive analysis of the $CaCl_2$-H_2O system, some thermal functions, extensive "catalogs of data", technical editing and preparation of the final book. Its contents are summarized below.

Recommended values are presented for chemical thermodynamic properties of selected compounds of calcium and their mixtures. These have been prepared in accord with and as a test of a plan developed by the CODATA Task Group on

Substance	Molar mass	$\Delta_f H^\circ(0\ K)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$H^\circ - H^\circ(0)$	S	
	$g.mol^{-1}$	....	$kJ.mol^{-1}$	....		-- $J.(mol.K)^{-1}$ --	
Mg(cr)	24.3050	0	0	0	4.998	32.671	24.869
CODATA Key Value [84COD].					±0.030	±0.100	±0.100
Mg(l)	24.3050		4.790	14.044	9.788 a	1.633	34.309
Extrapolated from high temperature.			±1.000	±1.200	±1.000	±2.000	±3.000
Mg(g)	24.3050	145.901	147.10	112.521	6.197	148.649	20.786
CODATA Key Value [84COD].		±0.800	±0.80	±0.800	±0.002	±0.005	±0.001
MgO(cr)	40.3044	-597.422	-601.60	-569.311	5.160	26.950	37.237
CODATA Key Value [84COD].		±0.300	±0.30	±0.30	±0.020	±0.150	±0.200
MgF_2(cr)	62.3018	-1120.297	-1124.2	-1071.051	9.920	57.200	61.587
CODATA Key Value [84COD].		±1.200	±1.2	±1.300	±0.060	±0.500	±0.2
Ca(cr)	40.0800	0	0	0	5.736	41.588	25.929
CODATA Key Value [84COD]. Alpha					±0.040	±0.400	±0.300
Ca(cr2)	40.0800		1.056	0.614	0.792 a	43.070	25.951
Beta, extrapolated from high temperature.			±0.300	±0.800	±0.300	±0.700	±1.200
Ca(l)	40.0800		7.788	6.619	13.524 a	45.510	35.000
Extrapolated from high temperature.			±1.000	±1.200	±1.000	±2.000	±3.000
Ca(g)	40.0800	177.339	177.80	144.020	6.197	154.887	20.786
CODATA Key Value [84COD].		±0.800	±0.80	±0.810	±0.002	±0.004	±0.001
Ca^+(g)	40.0795	767.152	773.81	732.057	6.197	160.650	20.786
		±0.830	±0.83	±0.84	±0.002	±0.002	±0.001
Ca^{+2}(g)	40.0789	1913.645	1926.50	1880.210	6.197	154.887	20.786
		±0.920	±0.92	±0.930	±0.002	±0.005	±0.001
Ca^{+2}(ao)	40.0789		-543.0	-552.807		-56.2	-281.38
CODATA Key Value [84COD].			±1.0	±1.100		±1.0	±5.0
Ca_2(g)	80.1600	341.982	341.7	289.819	11.190	257.185	36.577
		±1.800	±1.7	±1.800	±0.100	±1.500	±0.500
CaO(cr)	56.0794	-631.594	-634.92	-603.297	6.750	38.100	42.049
CODATA Key Value [84COD].		±0.900	±0.90	±0.920	±0.060	±0.40	±0.400
CaO(g)	56.0794	24.623	23.5	0.974	8.953	219.718	32.455
		±8.000	±8.0	±8.000	±0.001	±0.020	±0.010

Fig. 5.2. Selected values for $\Delta_f H^o$, $\Delta_f Go$, $H^o - H^o(0\ K)$, S^o, $C_p{}^o$ at 298 $\Delta_f H^o(0\ K)$ at 0.1 MPa. First page of a 5 page table of thermochemica the CODATA Thermodynamic Tables.

Chemical Thermodynamic Tables. All values in the present table are mutually consistent and are consistent with the CODATA Key Values for Thermodynamics. The values are recommended for general use.

The evaluated data are for common compounds of calcium (element, oxide, hydroxide, peroxide, fluoride, chloride, sulfate, nitrate and carbonate, their hydrates and their ions in aqueous solution) and for three systems: Ca-Mg, $CaCl_2$-KCl and $CaCl_2$-H_2O.

Forty one tables of thermal functions (heat capacity, entropy, enthalpy and Gibbs energy functions) are given for those compounds of magnesium, calcium and potassium for which the properties have been evaluated in this work. Twenty four tables of thermal functions are given for auxiliary substances. Each table spans the temperature range 0 to 4000 K, to the extent that data are available. Formation properties at 298.15 K (enthalpy and Gibbs energy of formation) are given for 68 compounds of calcium, magnesium and potassium plus the relevant values of 54 auxiliary substances. A sample page from the formation property table is given in Figure 5.2.

For each of three binary systems recommendations are given for mixing properties (enthalpies and Gibbs energies), partial molar or excess properties of the components (activities, enthalpies, heat capacities) and phase transformation data. All selections of data are accompanied by uncertainties, and are documented. Detailed lists of the measurements used in the evaluations are given for the thermochemical, alloy and aqueous solution sections.

The preparation of this compendium involved work at five geographically separated institutions, assembly of machine readable data bases, transfer of data by magnetic tape and interactively, and extensive development of computer programs for both thermodynamic calculations and document preparation and printing.

5. Needs for Thermochemical Data
(D. Garvin, V.B. Parker)

In the course of work on the CODATA Key Values for Thermodynamics and the CODATA tables on calcium compounds, deficiencies in the presently available thermodynamic data have become apparent. Very brief summaries of these are given here. Publication of this material is planned, in order to alert the thermodynamic and spectroscopic communities to these needs.

(a) K_2(g): Dissociation Energy. The 1930's spectroscopic data (used in a Birge-Sponer extrapolation), the vapor pressure data and recent theoretical calculations do not agree (range 4 kJ). Current spectroscopic techniques are adequate for the solution of this problem.

(b) Ca(cr): Thermal Properties. Ditmars (NBS) and Robie (U.S.G.S) have measured the heat capacity of Ca up through the alpha-beta transition. On the basis of preliminary results, their work leads to a value for S(298.15 K) that is 1.5 J/(mol.K) greater than the CODATA Key Value, to different heat capacities for the alpha and beta forms, a lower T_{fus}, 710 K versus 716 K, and a revised $\Delta_{tr}H\Delta_{tr}H$. (Only the liquid remains to be done). These data, if accepted, will change selections for all species whose properties depend on high temperature data, such as Ca(g), a CODATA Key Substance, CaH_2(cr), and possibly $Ca(OH)_2$(cr) and $CaCO_3$(cr). Gibbs energies of calcium compounds will also change. However, these changes, <0.5 kJ/mol of Ca, usually are less than the uncertainties in the values themselves.

(c) $CaCl_2.nH_2O$(cr), n= 1,2,4,6: Heat Capacity. These hydrates are the stable forms of the salt in equilibrium with aqueous solutions, −50 to +175 °C. For none of them are there low temperature C_p data from which entropies can be calculated. Instead, the entropies are calculated from enthalpy and Gibbs energy of solution data, and the resulting values of S do not show the smooth variation that might be expected. Recent measurements by Meisingset and Gronvold treat the hexa-, tetra- and di-hydrates above 288 K and can be combined with low temperature data to provide the thermal functions needed for a modern optimization of the $CaCl_2$-H_2O system. Such data will also be useful in the development of estimation methods.

(d) CaF_2(cr): Solubility and Thermal Properties. Existing measurements give pK_{sp} values varying from 11.6 to 8 at 298.15 K. The likely value is 10.6, although the most recent extensive study gives 11.6. Solubility should be studied between 298 and 500 K (to allow for geochemical applications), from both under- and over-saturation as a function of ionic strength, acid concentration, particle size, time to reach equilibrium, source and preparation of the samples. Choice of method will be important.

In addition this substance has a lambda-type transition in the heat capacity at 1424 K. There are enthalpy measurements, but these are insufficient to define the transition. Heat capacity measurements are needed.

(e) $Ca(OH)_2$(cr): Enthalpy of Formation. The "best" data lead to $\Delta_f H$ values that do not mesh well with those for $CaCO_3$ and CaO. Nor do the Gibbs energy data (solubility and high temperature decomposition). Enthalpy of solution and solubility studies should be repeated.

(f) Ca^{+2}(aq,std. state): Entropy and Enthalpy of Formation. This Key Substance has surprisingly poorly defined properties: S to ±1.0 J/mol K, $\Delta_f H$ to ±1.0 kJ/mol. Its properties are based on those of $Ca(OH)_2$, $CaSO_4$, $CaCO_3$ and $Ca(NO_3)_2$ and their aqueous solutions. The spread in values from system to system is larger than within each system. Any type of experimentation that would improve the properties of Ca^{+2}(aq) would be useful.

(g) CaO(cr) and MgO(cr): Enthalpy of Fusion. Both of these substances melt above 3000 K. Measurements of T_{fus} have proved to be very difficult, the melting point of CaO may still be in dispute. The enthalpies of fusion are derived from phase boundary information: $d(\ln a_i)/dT = \Delta_{fus}H_i/R$. Older values are 77 kJ/mol for MgO (from the MgO-ZrO_2 system) and 52 kJ/mol for CaO (CaO-ZrO_2 system), in both cases assuming ideal solutions. A recent optimization of the MgO-CaO system [Chand and Howald, 1982] selected values of about 58 kJ/mol for both, allowing for non-ideality in the liquid and solid phases. Unfortunately, phase boundaries in the CaO-MgO system are very poorly delineated and are based in part on studies that lead to incorrect melting points. A comparative study of other binary systems should be made.

(h) $CaMg_2$: Thermochemical and Thermophysical Data. The analysis of this system in the CODATA Thermodynamic tables showed that the data are in very poor shape. Enthalpy data above 298 K show large scatter, a new study is needed. This may indicate that the limited low temperature heat capacities need to be remeasured. Enthalpies of fusion measurements disagree, and are not consistent with mixing data and enthalpies of formation. Almost any attack would help.

B. Electrolyte Data

1. Electrolyte Data: The Calcium Chloride-Water System

(D. Smith-Magowan)

Evaluation of data on the physical and chemical properties of aqueous electrolytes is done by the Electrolyte Data Center with two fundamental objectives: (1) to provide reference data for use in scientific and technical applications and (2) to present data and analyses which will highlight challenges for future experimetal or theoretical investigations. The results of a study of the $CaCl_2$-H_2O system provide an example of the realization of these two goals.

A correlation of experimental data on the heat capacity of $CaCl_2$ solutions as a function of temperature and composition has been combined with separate NBS correlations of excess Gibbs energy and excess enthalpy as functions of composition at room temperature to create a "skeleton table" of values for all three properties throughout the temperature range 273.15-373.15 K and composition range 0-11 molal. The heat capacity correlation was made using a model-independent spline fit on the T-x surface. The other two correlations used the Pitzer formulation (although this was not essential). The apparent molar heat capacities are shown in Figure 5.3. The maximum with respect to temperature in the apparent molar heat capacity is found in other salts and is analogous to the trends observed for excess volume. This behavior has not yet been interpreted in terms of the structure of the solutions.

The resulting values for the excess properties C_p^{ex}, H^{ex} and G^{ex} are considered to be the most accurate representation of the experimental data available and cover the broadest range of composition of any study presented to date. The procedure includes the systematic treatment of data on aqueous systems at elevated temperatures, where the pressure is greater than one atmosphere. The effect of pressure has routinely been neglected in most previous treatments of the data for this system. Comparison with previous correlations where the effect of pressure has been neglected reveals a tangible systematic error in those studies.

Heat capacity data are lacking or of low quality in several temperature-composition regions. Below 298.15 K, the evaluation is based on scattered, imprecise data at intermediate compositions. More accurate measurements at all concentrations are desirable, but measurements below 1 molal and above 8 molal are imperative if the correlations are to be improved. This is an important temperature region as the structure of water and of solutions is changing rapidly with temperature. Data at high concentrations (7 molal to saturation) are needed at all temperatures. Experimental values are not available, even at 298.15 K and estimates had to be made in our work, based

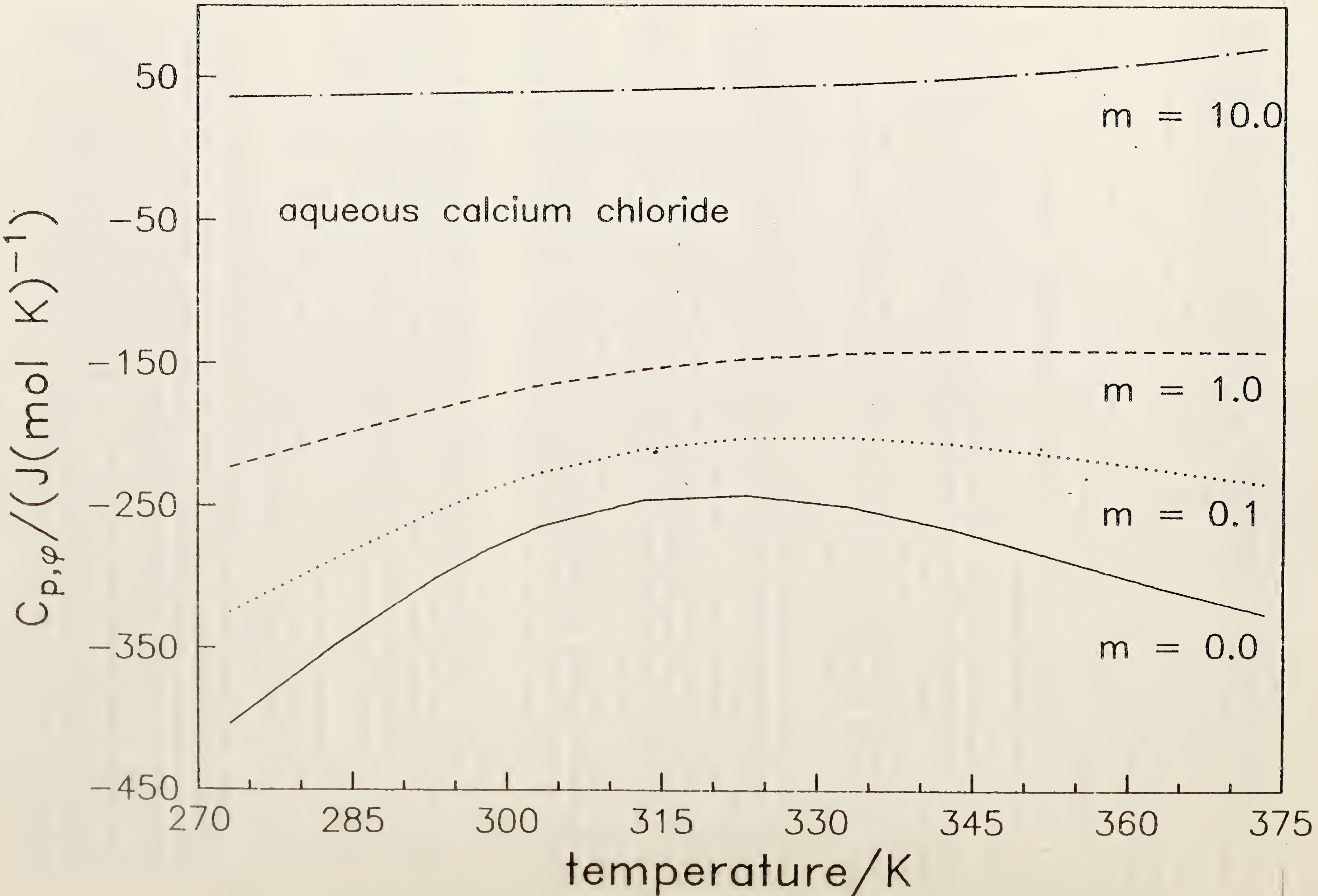


Fig. 5.3. Apparent molar heat capacity for calcium chloride-water mixtures, 273-373 K.

on a small set of measurements at 323 and 348 K. The high concentration region is important because, more often than not, the industrial applications involve concentrated solutions.

Enthalpy of dilution data are available only at or near 298.15 K. There is only one published study that covers any large range of concentrations at other temperatures (273 and 323 K). Above 298 K there are no data that reach the saturation line. Most useful would be a study at 373 K, from 0 molal to saturation, and a study at 323 K from 0 to 4 m, to validate the existing study. For both C_p and $\Delta_{dil}H$, data from 373 K to the critical line will be welcomed.

This study has also raised a significant problem for the theoretical interpretation of thermodynamic properties of electrolytes concerning the permittivity (dielectric constant) of $H_2O(l)$. It was necessary to choose a consistent formulation for the Debye-Huckel limiting law slopes A_ϕ (activities), A_H(enthalpies) and A_J (heat capacities). Later on A_V (volumes) will be required. The limiting law slopes for all properties can be calculated for any temperature or pressure provided that the density, the permittivity and their derivatives with respect to temperature and pressure are known. The Haar-Gallagher-Kell equation of state for water (NBS-NRC Steam Tables) is nearly a universal standard for the PVT properties of water. There are available, however, several formulations for the dielectric constant of water all of which represent the experimental measurements equally well, at least superficially. Our first selection was the dielectric constant correlation of Uematsu and Franck, because of the wide range of temperature and pressure at which it is applicable, the extensive data base considered, and its status as a standard.

A reviewer of the work pointed out that the formulation of Bradley and Pitzer should be used as it more accurately reproduced the measured permittivity values and derivatives at temperatures below 298.15 K. (Differences in the calculated D-H limiting law values are inconsequential for the Gibbs energy or enthalpy, but are quite dramatic, 30%, for heat capacity.) The reviewer's comment appears to be correct, and, because of our concern for fitting the lower temperature data, we have adopted his suggestion for the present.

An ensuing examination of the available experimental permittivity data, however, indicated they are not accurate enough for our purposes especially below 298.15 K. There are several detailed studies that show similar trends with temperature, but the studies disagree in absolute value. Thus it is difficult to establish the second derivative. The data are compared in Figure 5.4. The trend with temperature (below 298.15 K) in the Bradley-Pitzer formulation is steeper than in the Uemetsu-Franck treatment, and is closer to the trends in the principal studies. It is clear, however, that this important property of an important substance needs to be redetermined.

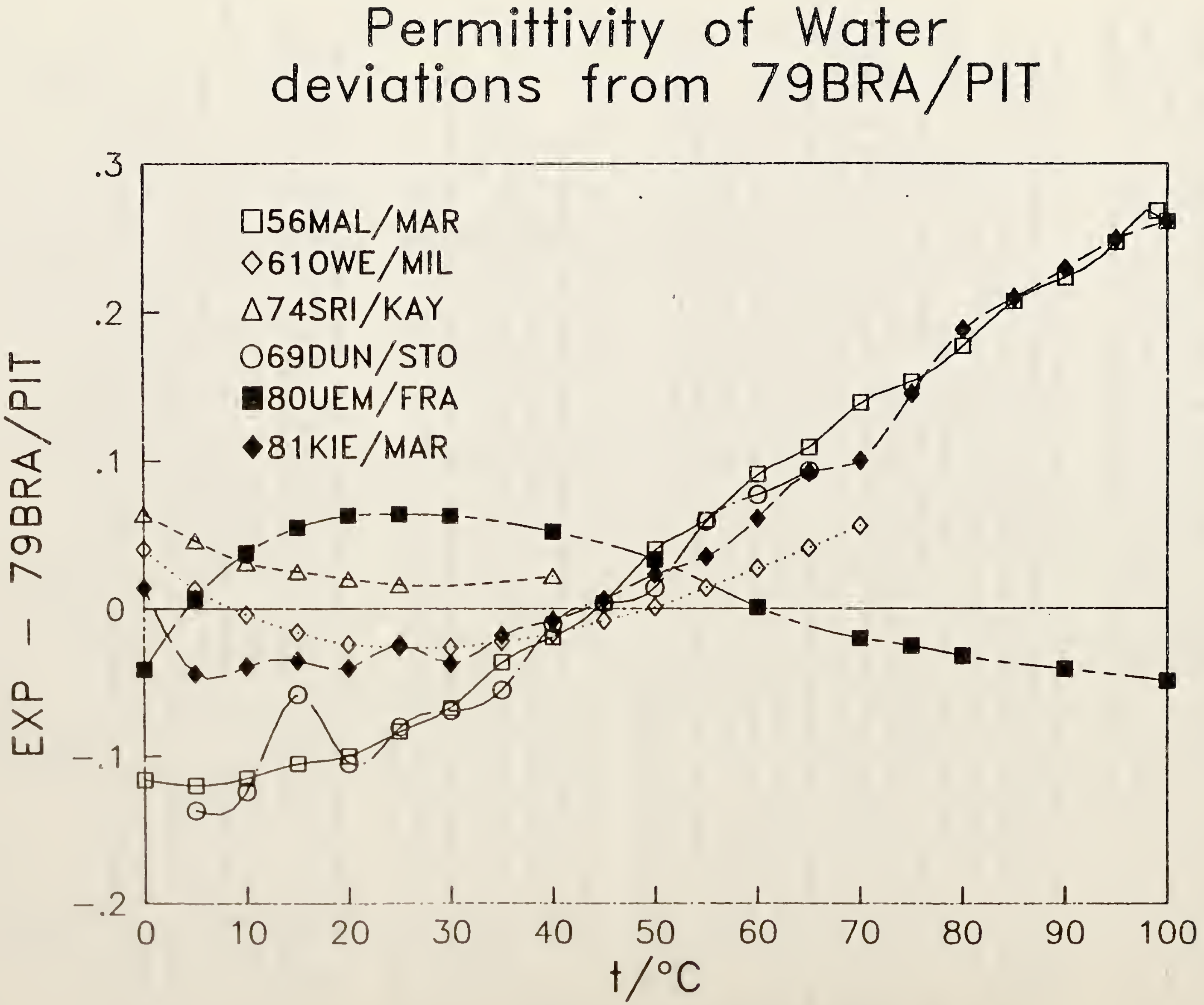


Fig 5.4 The two correlations represented by solid points are compared to the 79 BRA/PIT correlation. Four experimental data sets represented by open points are compared to the BRA/PIT correlation.

2. Krebs Cycle Thermodynamics
(D. Smith-Magowan)

The thermochemical analysis of the reactions comprising the Krebs cycle has continued during the year. The value of the network method for obtaining thermochemical properties for metabolic substrates has been shown in several aspects of the work thus far.

Inconsistencies in the results for several reactions suggested, after some thought, that the value of the reduction potential for the Nicotinamide Adenine Dinucleotide/Nicotinamide Adenine Dinucleotide (NAD/NADH) couple (0.311 ± 0.006 V from potentiometric measurements), which is widely adopted and was input to the network, must be in error. This is indeed the case as our subsequent investigation revealed. It was discovered that an error in the formation data for the reduction of acetaldehyde to ethanol obtained from the compilation by Stull, Westrum and Sinke leads to an error in the interpretation of equilibrium measurements for alcohol dehydrogenases from which this potential has been deduced. Recent equilibrium measurements for the acealdehyde/ethanol system have been used to obtain a more reliable value for the NAD/NADH potential (0.3165 ± 0.001 V) that is more consistent with the other reactions of the Krebs cycle.

For many of the substances involved in the Krebs cycle it is virtually impossible to obtain an estimate of the Gibbs energy of formation in solution by the more traditional approach of combining enthalpy of reaction and heat capacity determinations (to get entropies) for the pure substance with measurements of the solubilities (to get $\Delta_{sol}G$), because the necessary data are lacking. Lactic acid, for example undergoes polymerization in aqueous solution, making it impossible to measure its solubility accurately. Using the power of the network analysis, which includes reactions linking lactate with pyruvate, oxaloacetate, and acetate, a value for Gibbs energy of formation (-519.77 kJ/mol) has been obtained that is accurate to ±0.4 kJ/mol. Similar situations can be quoted for other substances.

The Krebs cycle is common to almost all aerobic respiration pathways, which implies, at least in principle, that the network can be extended to encompass metabolic substances of unlimited complexity. If this is indeed possible, it could be the most reliable way to quantify and relate the subtle effects of changes in structure, in solution, of the complex substances that biotechnology seeks to exploit.

3. Electrolyte Solution Properties Data Base
(D. Smith-Magowan)

A computer database of thermodynamic properties for electrolytes is being developed for the Design Institute for Physical Property Research (DIPPR). DIPPR is sponsored by AIChE and is a consortium of about 50 major chemical companies that support various research projects depending upon their individual interests. The database will consist of a collection of the activity, enthalpy, heat capacity and volume properties for electrolyte solutions supplemented by computational utilities to aid the engineering application of these properties. These utilities will provide the ability to calculate values of properties for simple binary solutions using several different models for extrapolation, prediction, or comparison; the calculation of properties for ternary or more complex mixtures; and methods for integrating these properties to obtain consistent sets of properties for a range of temperature, pressure and composition.

4. Temperature-Density-Composition Correlations of Excess Properties
(D. Smith-Magowan)

The correlation of thermodynamic properties of electroytes as a function of temperature, pressure and composition is underway using an algorithm that simultaneously treats temperature, density and composition as independent variables. The experimental data for calcium chloride are being used as a test case so that comparison with the CODATA skeleton table can provide an indication of the quality of the performance of this algorithm. The choice of density as an independent variable instead of pressure is made because of the PVT behavior of water at elevated temperatures. As the critical point is approached, the compressibility of water increases greatly and the excess thermodynamic properties of binary electrolytes appear to show corresponding trends. For example, the apparent molar heat capacity (at constant pressure) of aqueous NaCl seems to diverge to a value of negative infinity as the temperature of the critical point (674 K) of water is approached. A polynomial in temperature to fit such behavior requires terms of very high order. The heat capacity at constant density (or volume) on the other hand, is not divergent and can be fitted with a less complicated expression.

C. Thermodynamic Properties of Organic Compounds
(E.S. Domalski, E.D. Hearing, J.F. Liebman, D. Garvin)

1. Prediction of Properties

An estimation method developed by S.W. Benson and coworkers for calculating thermodynamic properties for gas phase organic compounds from structural group parameters has been extended to the liquid and solid phases for hydrocarbons. The work is in the process of being reviewed for publication in the Journal of Physical and Chemical Reference Data.

The group parameters for hydrocarbons in gas, liquid and solid phases at 298.15 K have been tested in 1267 comparisons with experimental data. For 527 comparisons with enthalpy of formation data, the average difference is ± 2.8 kJ/mol. The average differences for 396 comparisons for heat capacity and 344 comparisons for entropy in all three phases are ±2.6 and 3.1 J/(mol.K), respectively. The publication will include examples of the method of calculation, total symmetry numbers and methyl corrections for hydrocarbons plus a bibliography on the development of estimation methods since 1932.

This estimation procedure is now being extended to C-H-O compounds in the gas, liquid and solid phases at 298.15 K, and it is planned to apply it to C-H-N and C-H-N-O compounds.

2. Thermochemistry of Organic Compounds of Interest in Biotechnology.

A preliminary machine-readable data base has been compiled for evaluated data on the chemical thermodynamic properties of a thousand organic compounds at 298.15 K. Four general classes of compounds are covered, all of interest to researchers in biotechnology, namely: (1) amino acids, peptides and related compounds, (2) heterocyclic nitrogen compounds, (3) heterocyclic oxygen compounds, and (4) heterocyclic sulfur compounds. The properties covered are enthalpy of combustion, enthalpy of formation, heat capacity, entropy, Gibbs energy of formation and the logarithm of the equilibrium constant of the formation reaction. The data base is now being annotated. Publications are planned for each section.

3. Enthalpies of Combustion of Components of Natural Gas.

Recommended values have been prepared and published for the enthalpies of combustion of the C_1 -C_6 alkanes, C_2 - C_3 alkenes, acetylene, benzene and C_3 - C_6 cyclolkanes. In addition to the thermochemical data, corrections are given for non-ideal behavior of the gases. This work has been incorporated in a handbook on properties of natural gas for use in the liquified natural gas industry (prepared for the International Group of Importers of Liquified Natural Gas, GIIGNL), included in the Gas Producer Association standards, recommended to ASTM, discussed withan ISO Task Group, and reported on at an industry conference on "Gas Quality". In the course of this work it has been noted that thermochemical data for the hexanes are conflicting. Predicted enthalpies of combustion (and formation) of 2,2-dimethyl and 2,3-dimethyl alkanes tend to be outliers in estimation schemes. That is true for the hexanes 2,2-dimethylbutane and 2,3-dimethyl butane. Their enthalpies of combustion also are the least well defined of those for the lower molecular weight hydrocarbons. Calorimetric, isomerization equilibrium and correlation results spread by 2.5 kJ/mol. Combustion calorimetry on these two hexanes (now known only from relative measurements) could lead to a solution of the general problem of how to treat such isomers.

D. Automating Data Center Procedures

(D.B. Neumann, D.M. Bickham)

Automation efforts in the Chemical Thermodynamics Data Centers are oriented toward providing for the following needs: (a) data analysis, (b) on-line access to data and bibliography, (c) transfer of data to other media or other data bases, (d) re-formatting data for publication, and (e) graphical presentation of data.

This year, three generic solutions to data center problems have been developed. The problems are: search for and retrieval of chemical data, bibliographic data management, and, printing and publication of results. The solutions are applicable to the work of all the CCP Data Centers.

1. Search and retrieval systems.

A general keyed access search-retrieval system called SETKY-GETKY has been written and implemented on the HP-1000. It is suitable for indexed material containing either text or tabular material.

SETKY-GETKY provides rapid access to free formatted textual or tabular material stored in large data files on the mini-computer. As a "keyed access" system it permits the user to create editable files with the usual system editor. Index commands, or "keys", are placed into the file by the user.

SETKY is then invoked. It reads the original file and creates a file of keys that will be searched. The key file contains only the keys and the physical disc positions of the text in the original file to which the keys refer.

In its on-line mode the user invokes GETKY with a key or an approximate key. The GETKY program rapidly searches for the key in the key file. Using the physical disc position retrieved from the key file, GETKY retrieves, by direct access in the original file, the indexed item of text and displays it. If the key cannot be found, Getky returns the 20 keys alphabetically nearest to it and prompts the user to select one.

There are several aspects of the system that has made it unique and highly useful for Data Center work:

Text related to a key may be obtained from within programs, i.e. the GETKY functions are callable from user programs. This has been used to build retrieval systems for the JANAF Thermochemical Tables and the CTDC abstract files.

The original text files can be used for text processing as well as for on-line or programmatic retrieval. This has been accomplished by choosing the syntax of the index commands in the original files to be compatible with the TEXED system currently used for text formatting of reports and papers. This feature has been used in building a system for printing the CODATA Thermodynamic Tables.

The original file remains accessible, may be corrected or expanded by its owner. (This is much easier than when a Data Base Management System is used.)

The number of index items per entry is unlimited.

SETKY-GETKY is written in FORTRAN 77.

It is expected that these programs will be transferable to other systems such as the NBS Cyber or micro-computers such as the IBM-PC/XT, or AT. It may prove advantageous to use it as the search system for data distributed on floppy discs.

A users guide for SETKY-GETKY is being published in the proceedings of the 1986 International Users Group for Hewlett-Packard minicomputers. The applications of the system to date are (1) in printing a large section of the CODATA Task Group on Chemical Thermodynamic Tables, (2) a combined users manual and on-line help system for the HP-1000 was created, (3) a retrieval system for the JANAF Tables, (4) the NBS Telephone Book on-line, and (5) a retrieval system for abstracts of thermochemical data.

The motivation to create the SETKY-GETKY system was to automate CTDC's large data base of literature extracts, some 50,000 in number. In FY86 a section of this data base was re-formatted for this application. Using this section as a test we expect to remove remaining problems from the retrieval system and put the entire data base on line in early FY1987. At that point retrieval by substance formula, property, name, Wisswesser line notation, and registry number will be possible.

2. Common Bibliographic System.

A bibliographic system for CTDC and the other Data Centers, DB-BIB, was placed on-line and is being tested. Initial test applications are with a small Ion-Energetics bibliography and a bibliography of sputtering data (Surface Chemistry Division). The goal of this effort is to load, as an on-line searchable data base, all 60,000 -70,000 CTDC bibliographic citations. This is necessary to permit the more efficient preparation and publication of reaction catalogs such as that for rubidium thermochemistry, which is now in press.

3. Printing and Text Formatting Utilities. A program utility, (called PTTL), for printing using the OSRD laser printer was written by CTDC. This system is now in use by the Atomic Spectra Data Center, the Kinetics Data Center, and is used heavily by CTDC. Its function is to provide for sub- and super-scripts, Greek and math symbols, italics, bold, various line spacing needs, as well as a general and consistent input technique for Data Center staff. OSRD staff have made a number of improvements to this utility.

A utility for formatting reports containing text as well as tabular material, called TEXDA, was implemented by CTDC on the OSRD and CTDC mini-computers. It is an expansion of TEXED distributed by the International HP Users Group. A User's Guide covering both these utilities is in preparation by OSRD.

4. CTDC Abstracts Data Base.

Twenty six hundred current articles on thermodynamics were abstracted during the ten months Nov 1985 through Aug 1986. The process for doing this has been refined to make use of the Chemical Abstracts Data Base. Articles of interest are selected by inspection of CA or of high-yield journals. This is done by a contractor and by CTDC staff. The abstracts of the articles are retrieved from CA and then a decision is made by CTDC staff about the usefulness of each article and how it is to be abstracted. Copies of the articles to be retained are obtained, if possible, and microfilmed. Each article is indexed for its thermodynamic data content (in terms of substance and property studied), either from the article or its abstract, depending upon the subject and on the availability of the original. This material becomes part of the computerized CTDC Abstracts Data Base.

This data base is the ready reference used in the Center when evaluations of data are made. In addition, it is used to answer questions from the public.

All of the Abstracts Data Base since 1970 is machine-readable. During the year new programs have been written for processing the input. The programs have been tested extensively and are being used in a production mode. They have also been used to prepare indexes for the Bulletin of Chemical Thermodynamics. CTDC has processed the material for the inorganic index (prepared here), the organic index (prepared at Texam A&M Univ.), and the organic mixture index (prepared at Univ. Paris) into a form that can be handled by the index formatting programs of the Bulletin. The programs used here have also been supplied to the editor of the Bulletin who plans to do the entire processing task next year.

6. PUBLICATIONS

(a) Publications of Past Year

Churney, K.L., E.S. Domalski, A.E. Ledford, Jr., J.C. Colbert, S.S. Bruce, T.J. Buckley, and M.L. Reilly, "Assessing the Credibility of the Calorific Value of Municipal Solid Waste", Proceedings of the 1986 National Waste Processing Conference, ASME, New York, 1986.

Ditmars, D.A., Plint, C.A. and Shukla, R.C., "Aluminum (I): Measurement of the Relative Enthalpy from 273 to 929 K; Derivation of Thermodynamic Functions for Al(s) from 0 K to Its Melting Point", Int. J. Thermophysics 6, 495 (1985).

Domalski, E.S., Churney, K.L., Ledford, A.E., Bruce, S.S., Buckley, T.J., Parris, R., and Chesler, S.N., "Monitoring the Fate of Chlorine from MSW Sampling through Combustion", Proceedings of the EPRI Seminar on Municipal Solid Waste as a Utility Fuel, EPRI, Palo Alto, CA, (1986), 14pp.

Domalski, E.S., Churney, K.L., Ledford, A.E.,Jr. and Reilly, M.L., "MSW Calorimetry", Mechanical Engineering 108, 32 (August, 1986).

Domalski, E.S., A.E. Ledford, Jr., S.S. Bruce, and K.L. Churney, "The Chlorine Content of Municipal Solid Waste from Baltimore County, Maryland, and Brooklyn, New York", Proceedings of the 1986 National Waste Processing Conference, ASME, New York, NY, 1986.

Domalski, E.S., "NBS Research Program in Municipal Solid Waste Combustion", Proceedings of the Biofuels and Municipal Waste Technology Division, U.S. Department of Energy, 1986, 28 pp.

Evans, W.H., Grimes, J.J., Jobe, T.L., Young, N.W., Foreman, R., Thompson, R.C. and Seymour, C.L., "Substance - Property Index Section III. Inorganic Substances", Bull. Chem. Thermodynamics, 26, pp 219-286 (1983).

Evans, W.H., Grimes, J.J., Jobe, T.L., Young, N.W., Foreman, R., Thomspon, R.C., and Seymour, C.L. "Substance - Property Index Section III. Inorganic Substances", Bull. Chem. Thermodynamics, 26, pp 473-542 (1983).

Gajewski, E., Goldberg, R.N. and Steckler, D.K. "Thermodynamics of the Conversion of Fumarate to L(-)Malate", Biophys. Chem., 22, 187 (1985).

Garvin, D., Domalski, E.S., Wilhoit, R.C., Somayajulu, G.R., and Marsh, K.N., "Physical Properties of Pure Components of Natural Gas", in 'Gas Quality', van Rossom, G.J., editor, Elsevier Science Publ., Amsterdam, 1986, p.59.

Garvin, D. and Parker, V.B., "CODATA Chemical Thermodynamic Data Bases for Science and Technology", in 'Scientific Program and Abstracts, Tenth International CODATA Conference', CODATA Bull, 61 48 (1986).

Garvin, D., and White, H.J., Jr., "Comprehensive, Consistent Thermodynamic Tables", in 'Thermodynamic Databases', CODATA Bull 58, 1, (1986).

Goldberg, R.N., Gajewski, E., Steckler, D.K., and Tewari, Y.B., "Thermodynamics of the Conversion of Aqueous 1-Aspartic Acid to Fumaric Acid and Ammonia", Biophys. Chem. 24, 13 (1986).

Goldberg, R.N. and Parker, V.B., "Thermodynamics of Solution of SO_2(g) in Water and of Aqueous Sulfur Dioxide Solutions", J. Res. NBS, 90, 341 (1985).

Johnson, W.H. and Prosen, E.J., "Determination of Enthalpies of Combustion and Formation of Substituted Triazines in an Adiabatic Bomb Calorimeter", J. Res. NBS, 90, 295 (1985).

Karpas, Z., Stevens W.J. Buckley, T.J. and Metz, R., "The Proton Affinity and Gas Phase Ion Chemistry of Methyl Isocyanate, Methyl Isothiocyanate and Methyl Theocyante", J. Phys. Chem., 89, 5274 (1985).

Kirchhoff, W.H., Chambers, G.P., Fine, J., "An Analytical Expression for Describing Auger Profile Shapes of Interfaces.", J. Vac. Sci. Tech. A4, 1666 (1986).

Kirchhoff, W.H., "A National Program of Measurement Services and Standards for Biotechnology at the National Bureau of Standards, Planning Report 22 (Revised)", February, 1986.

Kirchoff, W.H. "Who Needs Standards," Chemtech 16, 280 (1986).

Kirklin, D.R. and Domalski, E.S., "Estimation Methods and Combustion Calorimetry on Organic Phosphorus Compounds", Proceedings of the 1985 Scientific Conference on Chemical Defense Research U.S Army, Research Directorate, CRD&EC Aberdeen Proving Ground, 1986.

Miller, M.M., Wasik, S.P., Guang, G.L. Shiu, W.Y. and MacKay, D., "Relations Between Octanol-Water Partition Coefficients, Aqueous Solubility and Biocentration Factors", Enviromental Science and Technology, 19, 522 (1985)

Neumann, D.B. "Data Base Management Systems, Part I. A Quick Overview", Non Bibliography Data Banks in Science and Technology, S. Schwarz, D.G. Watson , O. Alvfeldt, eds. ICSU Press, 1985, p. 139.

Neumann, D.B., "Data Base Management Systems, Part II, An Application to Scientific Technical Data and its Associated Bibliographic Data", Non-Bibiographic Data in Science and Technology, S. Schwarz, D.G. Watson, O. Alvfeldt, Eds., ICSU Press, 1985, p. 153.

Owens, J.W., Wasik, S.P. and DeVoe, H., "Aqueous Solubilities and Enthalpies of Solution of n-Alkylbenzenes", J. Chem. Eng. Data, 31, 47 (1986)

Savage, H., "Repulsive Regularities of Water in Ices and Crystalline Hydrates", Nature 322, 717 (1986).

Schwarz, F.P. "Biological Standard Reference Materials for Calibration of Differential Scanning Calorimeters: Di-alklyl-Phosphatidylcholine in Water Solutions," Thermochim. Acta 106, 347 (1986).

Shukla, R.C., Plint, C.A. and Ditmars, D.A., "Aluminum(II): Derivation of C_vo from C_p and Comparison to C_vo Calculated from Anharmonic Models", Int. J. Thermophysics, 6, 517 (1985).

Steckler, D.K., Goldberg, R.N., Tewari, Y.B., Buckley, T.J. "High Precision Microcalorimetry: Apparatus, Procedures, and Biochemical Applications", J. Res. NBS 91, 113 (1986).

Steckler, D.K., Goldberg, R.N., Buckley, T.S. "Computer Software for Acquisition and Treatment of Calorimetric Data", NBS Tech Note 1224, U.S. Government Printing Office, Washington, D.C. (1986).

Tewari, Y.B. and Goldberg, R.N., "An Investigation of the Equilibria Between Aqueous Ribose, Ribulose, and Arabinose", Biophys. Chem. 22, 197 (1985).

Tewari, Y.B., Steckler, D.S. and Goldberg, R.N., "Thermodynamics of the Conversion of Aqueous Xylose to Xylulose", Biophys. Chem. 22, 18 (1985).

Weber, I.T. and Steitz, T.A., "The Crystallization of rec A protein from proteus mirabilis, J. Mol. Bio. 188, 109 (1986).

Wlodawer, A., "A Facility for Data Collection and Processing at the National Bureau of Standards Reactor", in Methods in Enzymology, H.W. Wyckoff, C.H.W. Hirs, and S.N. Timasheff, eds., Academic Press: New York, 114, 551 (1988).

Wlodawer, A., Borkakoti, N., Moss, D.S. and Hawkin, B., "Comparison of Two Independently Refined Models of Ribonuclease A", Acta Cryst., B42, 379 (1986).

(b) Publications in Progress

Bickham, D.M., Neumann. D.B., "Setky-Getky User's Manual", NBS-IR, (in press).

Bickham, D.M., Neumann D.B., "Setky-Getky. A Keyed Access System for the HP-1000." Proc. INTEREX North Am. Conf., (in press).

Bickham, D.M., "User Manual for the Chemical Thermodynamics Data Center Hp-1000 mini-computer", NBS-IR (1986), (in press).

Chase, M.W., Davies, C.A, Downey, J.R., Frurip, D.J., McDonald, R.A., and Syvervd, A.N., 'JANAF Thermochemical Tables, Third Edition, Phys. Chem. Ref. Data, 14, Supplement No. 1, 1985, (in press).

Churney, K.L., Ledford, A.E., Jr., Reilly, M.L., and Domalski, E.S., "A Multi-Kilogram Capacity Calorimeter for Heterogeneous Materials", J Res NBS (in press).

Colbert, J.C. Domalski, E.S., and Coxon, B., "Enthalpies of Combustion of D-Ribose and 2-Deoxy-D-ribose, J. Chem. Thermodynamics, (in press).

Ditmars, D.A., "Drop Calorimetry above 300 K", McGraw-Hill/CINDAS Data Series on Material Porperties, Chap 13, Compendium of Thermophysical Property Measurement Methods, Vol. I, Plenum Publishing Corporation, 1986, (in press).

Domalski, E.S., Churney, K.L. Ledford, A.E., Jr., Bruce, S.S., "Monitoring the Fate of Chlorine from MSW Sampling Through Combustion, Part I: Analysis of the Waste Stream for Chlorine", Chemosphere (in press).

Domalski, E.S., Churney, K.L., Ledford, A.E, Jr., Bruce, S.S., Buckley, T.J., Parris, R.M., and Chesler, S.N., "Monitoring the Fate of Chlorine from MSW Sampling through Combustion, Part II: Combustion Studies", Chemosphere (in press)

Domalski, E.S., and Hearing, E.D., "Estimation of Thermodynamic Properties of Hydrocarbons at 298.15K", J. Phys. & Chem. Ref. Data, (submitted).

Domalski, E.S., Jobe, T.L., Jr., and Milne, T.A., "Thermodynamic Data for Biomass Conversion and Waste Incineration", (submitted).

Garvin, D., Parker, V.B., and White, H.J., Jr., editors 'CODATA Thermodynamic Tables: Selections for Some Compounds of Calcium and Related Mixtures. (A Prototype Set of Tables)', CODATA Special Report, 1986, 370 pp., (in press).

Garvin, D., Schumm, R.H., Parker, V.B., and Nuttall, R.L., "Thermochemical Properties at 0 and 298.15K", in 'CODATA Thermodynamic Tables: Selections for Some Compounds of Calcium and Related Mixtures. (A Prototype Set of Tables).' CODATA Special Report, 1986, section 6.2, pg. 100-196, and section 7.1, pg 216-318, (in press).

Gurvich, L.V., Yungman, V.S., Chase, M.W., and Bergman, G.A., "Thermodynamic Properties of Individual Substances", in 'CODATA Thermodynamic Tables. Selections for Some Compounds of Calcium and Related Mixtures. (A Prototype Set of Tables).' CODATA Special Report, 1986, section 6.1, pg. 42-179, (in press).

Gajewski, E., Steckler, D.K., Goldberg, R.N., "Thermodynamimcs of the Hydrolysis of Adenosine 5' - Triphosphate to Adenosine 5'- Diphosphate," J. Biol. Chem., (in press).

Harrison, R., "Sayres Equation is a Chernov Bound to Maximum Entropy", Acta Crystallographica, (in press).

Miller, M., Apella, E., Schwarz, F.P., Kirchhoff, W., Sussman, J., "Possible Conformations in Solution for Synthetic Quasipalindromic DNA Sequences.", (submitted).

Parker, V. B., Evans, W.H., Nuttall, R.L., "The Thermochemical Measurements on Rubidium Compounds: A Comparison of Measured Values with those Predicted from the NBS Tables of Chemical Thermodynamic Properties", J. Phys. Chem. Ref. Data, (in press).

Raghavan, N.V. and Wlodawer, A., "Neutron Crystallography of Proteins," Methods in Experimental Physics, (in press).

Roy, S., Weinstein, S., Borah, S., Nickol, L., Appella, E., Sussman, J.L., Miller, M, Shindo, H. Cohen, J.S., "The Mechanism of Olignonucleotide Loop Formation Solution", Biochem., (in press).

Savage, H. and Wlodawer, A., "Determination of Water Structure Around Biomolecules Using X-ray and Neutron Diffraction Methods", Methods in Enzymology (Biomembranes), (in press).

Savage, H. "Water Structure in Vitamin B-12 Coenzyme Crystals II, Biophysical Journal", (in press).

Savage, H. "Water Structure in Crystalline Solids: Ices to Proteins Water Reviews", (in press).

Smith-Magowan, D., Garvin D., Parker, V.B., Nuttall, R.L., and Staples, B.R., "The Aqueous System $CaC1_2$ H_2O", in 'CODATA Thermodynamic Tables. Selections for Some Compounds of Calcium and Related Mixtures. (A Prototypoe Set of Tables).' CODATA Special Report, 1986, section 6.5, pg. 216-243, section 7.3, pg. 326-342, (in press).

Smith-Magowan, D., editor, "Bibliographies of Industrial Interest: Thermodynamic Measurements on the Systems CO_2-H_2O, CuCl-H_2O, NH_3-H_2O, $ZnCl_2$-H_2O, H_3PO_4-H_2O." NBS Special Publication (in press).

Svensson, A., Sjolin, L. Gilliland, G.L., Finzel, B.C., Wlodawer, A., "Multiple Conformations of Amino Acid Residues in Ribonuclease A", (submitted).

Tewari, Y.B., and Goldberg, R.N., "Thermodynamics of Carbohydrate Isomerization Reactions: The Conversion of Aqueous Allose to Psicose", Biophys. Chem., (in press).

Tewari, Y.B., and Goldberg, R.N. "An Equilibrium Study of the Conversion of L-Phenylalanine to Trans-Cinnamic Acid and Ammonia.", J. Phys Chem., (in press).

Weber, I.T., "The Structure of Catabolite Gene Activator Protein Crystallized with Cyclic Amp" in Methods of Enzymology (Hormone Action) Cyclic Nucleotide Action and Degradation, J.D. Corbin and R.A. Johnson, eds, (in press).

Weber, I.T., Steitz, T.A., Bubis, B. Taylor, S.S., "Predicted Structures of the c AMP Bindine Domains of the Type I and II Regulatory Subunits of a c AMP-dependent Protein Kinase, (submitted).

Wlodawer, A., Deisenhofer, J., Huber, R., "Comparison of Two Highly Refined Structures of Bovine Pancreatic Trypsin Inhibitor", J. Mol. Biol., (in press).

Wlodawer, A. and Sjolin, L. "Experience with the Use of a Neutron Data Collection Facility Equipped with an Area Detector.", Les Editions de Physique, (in press).

Zielinski, W.L., Miller, M.M., Ulma, G. and Wasik, S.P., "GLC Separation of Polychlorinated Biphenyl Isomers Between a Nematic Liquid Phase and a Non-Polar Base", Analytical Chem., (in press).

7. Talks

Abramowitz, S., "Thermodynamic Properties of High Temperature Materials", Air Space Technology Center, Albuquerque, NM, November 19, 1985.

Abramowitz, S., "Biochemical Research in Support of NBS' Biotechnology Program", Center for Chemical Engineering, Boulder, CO, September 15, 1986.

Abramowitz, S., "NBS' Biotechnology Program", Thermochemical Brigham Young University, Provo, UT, 84602, September 24, 1986.

Bickham, D.M., "SETKY-GETKY, A Keyed Access System for the HP-1000", INTEREX North Am. Conf., Detroit, MI, September 28-October 3, 1986.

Buckley, T.J., "Formation and Reactions of Hydrocarbon Ions Under Ionospheric Conditions." The 1985 AFOSR Scientific Conference on Laser-Material Interaction in Obscuration Research, Albuquerque, NM, November 19, 1985.

Buckley, T.J., "Design of a Real Time Data Acquisition for Combustion Calorimetry", 41st Annual Calorimetry Conference, Somerset, NJ, August 18, 1986.

Chase, M.W., "JANAF Thermochemical Tables", AFOSR/AFRPL Rocket Propulsion Research Meeting, Edwards Air Force Base, CA, September 9-11, 1986.

Churney, K.L., "Assessing the Calorific Value of Municipal Solid Waste", Twelfth National Waste Processing Conference, Denver, CO, June 4, 1986.

Churney, K.L., "Design and Performance Tests of a Multi-kilogram Capacity Flow Calorimeter", 41st Annual Calorimetry Conference, Somerset, NJ, August 18, 1986.

Domalski, E.S., "The Chlorine Content of Municipal Solid Waste", Derwood Lions Club, Derwood MD, May 20, 1986.

Ditmars, D.A., "Heat Capacity of Solid Calcium; a Tour de Force of Equilibrium Macrocalorimetry", Chemical Thermodynamics Seminar, NBS, Gaithersburg, MD, September, 30, 1986.

Domalski, E.S., "The Chlorine Content of Municipal Solid Waste from Baltimore County, MD, and Brooklyn, NY", Twelfth National Waste Processing Conference, Denver, CO, June 4, 1986.

Domalski, E.S., "Monitoring the Fate of Chlorine from MSW Sampling through Combustion", DOE/EPRI Seminar on Municipal Solid Waste as a Utility Fuel, Madison, WI, November 22, 1985.

Domalski, E.S., "A Status Report of Research Activities on the Combustion Calorimetry of MSW", Solar Energy Research Institute (SERI), June, 4, 1986.

Domalski, E.S., "Monitoring the Fate of Chlorine from MSW Sampling through Combustion", Acid Gas and Dioxin Control for Waste-to-Energy Facilities Conference, Hyatt Regency, Crystal City, VA, November 26, 1985.

Gajewski, E., "The Enthalpy of Hydrolysis of Adenosine 5' - Triphosphate", 76th Annual Meeting of the American Society of Biological Chemists, Washington, DC, June 12, 1986.

Gajewski, E., "Thermodynamics of the Conversion of L-Aspartate to Fumarate and Ammonia", 5th International Symposium on HPLC of Proteins, Peptides, and Polynucleotides", Toronto, Ontario, November 6, 1985.

Garvin, D., "Physical Properties of Pure Components of Natural Gas", 1st International Congress on Gas Quality--Specification and Measurement of Physical and Chemical Properties of Natural Gas, Groningen, the Netherlands, April 22-25, 1986.

Goldberg, R.N., "A Computerized Database of Activity and Osmotic Coefficients", Nuclear Regulatory Commission, Silver Spring, MD, December 1985.

Goldberg, R.N., "A Computerized Database of Activity and Osmotic Coefficients", Office of Standards Reference Data Advisory Panel, December, 1985.

Goldberg, R.N., "Thermodynamics of Enzyme-Catalyzed Reactions", Chemical Thermodynamics Division, NBS, Gaithersburg, MD, March, 1986.

Goldberg, R.N., "Thermodynamics of Enzyme-Catalyzed Reactions", Laboratory of Metabolism, NIH, Rockville, MD, May, 1986.

Goldberg, R.N., "Thermodynamics of Enzyme-Catalyzed Reactions", Laboratory of Metabolism, NIH, Rockville, MD, May, 1986.

Goldberg, R.N.,"Current Research in Chemical Thermodynamics", ICI, Runcorn, Cheshire, United Kingdom, July 7, 1986.

Goldberg, R.N., "Thermodynamics of Enzyme-Catalyzed Reactions", University of Newcastle-upon-Tyne, United Kingdom, July 9, 1986.

Goldberg, R.N., "GAMPHI-A Database of Activity and Osmotic Coefficients", University of Newcastle-upon-Tyne, United Kingdom, July 10, 1986.

Goldberg, R.N., "Thermodynamics of Enzyme-Catalyzed Reactions", University of Glasgow, United Kingdom, July 11, 1986.

Goldberg, R.N., "Thermodynamics of the Conversion of L-Aspartate to Fumarate and Ammonia", 9th IUPAC Thermodynamics conference, Lisbon, Portugal, July 18, 1986.

Goldberg, R.N., "The Enthalpy of Hydrolysis of Adenosine 5'-Triphosphate", 9th IUPAC Thermodynamics Conference, Lisbon, Portugal, July 18, 1986.

Goldberg, R.N., "The Enthalpy of Hydrolysis of Adenosine 5'-Triphosphate", 41st Calorimetry Conference, Somerset, NJ, August 21, 1986.

Goldberg, R.N., "Thermodynamics of the Conversion L-Plenylalanine to Trans-Cinnamic Acid and Ammonia", ACS Middle Atlantic Regional Meeting, Baltimore, MD, September 2, 1986.

Goldberg, R.N., "Thermodynamics of the Hydrolysis of Adenosine 5'-Triphosphate", ACS Middle Atlantic Regional Meeting, Baltimore, MD, September 2, 1986.

Harrison, R., "A Common Sense Guide to Maximum Entropy", Mid-Atlantic Protein Cystallography Workshop, NBS, May 15-17, 1986.

Kirchhoff, W.H., "An Analysis Program for the Characterization of Interface Profile Shapes", 8th Symposium on Applied Surface Analysis, University of Dayton, Dayton, OH, June 4, 1986.

Kirchhoff, W.H., "A Computer Program for Describing the Denaturation of Biopolymers, as Measured by Differential Scanning Calorimetry, in Terms of a Two State Model", 41st Calorimetry Conference, Somerset, NJ, August 22, 1986.

Kirklin, D.R., "Estimation Methods and Combustion Calorimetry on Organic Phosphorus Compounds", 1985 Scientific Conference on Chemical Defense Research, Aberdeen Proving Ground, MD, November 22, 1985.

Kirklin, D.R., "Enthalpies of Formation of Organic Phosphorus Compounds", 41st Annual Calorimetry Conference, Somerset, NJ, August 21, 1986.

Miller, M., "Oligomers of DNA", Mid-Atlantic Protein Crystallography Workshop, NBS, May 15-17, 1986.

Newmann, D.B., "The Chemical Thermodynamics Data Center Bibliographic Data Base System", Chemical Thermodynamics Division Seminar, April, 1986.

Newmann, D.B., "The Application of the IMAGE/1000 Database Management System to Scientific Data", Baltimore-Washington HP-1000 Users Group, Baltimore, MD, November 15, 1985.

Parker, V.B., "CODATA Chemical Thermodynamic Data Bases for Science and Technology", Tenth International CODATA Conference, July 15, 1986, Ottawa, Canada.

Smith-Magowan, D., "A Database of Thermodynamic Properties of Aqueous Electrolyte Solutions with Computational Procedures for Industrial Applications", AIChE National Meeting, Chicago, IL, November 1985.

Smith-Magowan, D., "Effects of Temperature, Pressure and Composition on the Thermodynammic Properties of Electrolytes", International Association for Properties of Steam, Dusseldorf, W. Germany, Sept 22-26, 1986.

Tewari, Y.B., "Thermodynamic Investigations of Reactions Catalyzed by Glucose Isomerase", Indian Institute of Technology, New Delhi, India, October 29, 1985.

Tewari, Y.B., "Thermodynamic Investigations of Enzyme Catalyzed Reactions", Indian Institute of Technology, Bombay, India, November, 21, 1985.

Tewari, Y.B., "Thermodynamics of Carbohydrate Isomerization Reactions: Conversion of Aqueous Allose to Psicose", 41st Calorimetry Conference, Somerset, NJ, August 21, 1986.

Tewari, Y.B., "Thermodynamics of the Conversion of L-phenylalanine to Trans-Cinnamic Acid and Ammonia", 41st Calorimetry Conference, Somerset, NJ, August 21, 1986.

Tewari, Y.B., "Thermodynamics of Carbohydrate Isomerization Reactions: The Conversion of Aqueous Allose to Psicose", ACS Middle Atlantic Regional Meeting, Baltimore, MD, September 2, 1986.

Weber, I.T., "The Analysis of Protein Structure from Crystallographic Data". The Structure of Catabolite Gene Activator Protein and its Complex with DNA", Course on Protein Structure and Function, Les Diablerets, Switzerland, September 30 to October 3, 1985.

Weber, I.T., "Model for the Complex of Catabolite Gene Activator Protein and Its Site in Lac Operon", Series on the Relation between DNA Structures and their Interactions, NIH, Bethesda, MD, March 19, 1986.

Weber, I.T., "The Structure of a Mutant of Catabolite Gene Activator Protein.", Mid-Atlantic Protein Crystallography Workshop, NBS, Gaithersburg, MD, May 15-17, 1986.

Weber, I.T., "The Crystal Structure of a Mutant of Catabolite Gene Activator Protein.", Gordon Conference: Diffraction Methods in Molecular Biology, New Hampshire, June 30-July 4, 1986.

Wlodawer, A., "A Novel Method for the Determination of Solvent Structure in Protein Crystals", Max-Planck-Institut, Munich, West Germany, January 28, 1986.

Wlodawer, A., "High Resolution Studies of Proteins Using X-ray and Neutron Diffraction", University of Washington, Seattle, WA, June, 3, 1986.

Wlodawer, A., "Bound Solvent in Proteins: Improvement of Fourier Maps by Protein Averaging Combined with Flattening of the Solvent", Gordon Research Conference, Andover, NH, June 30, 1986.

Wlodawer, A., "Bound Solvent in Proteins - a Novel Technique for its Analysis", Tenth European Crystallographic Meeting, Wroclaw, Poland, August 5, 1986.

Wlodawer, A., "High Resolution Refinement of BPTI and Ribonulcease", Department of Crystallography, Birkbeck College, University of London, England, August 15, 1986.

Wlodawer, A., "X-ray and Neutron Diffraction Studies of Proteins and Nucleic Acids", NBS Staff Research Seminar, September 5, 1986.

8. Chemical Thermodynamics Division Seminars

Kamlet, M.J., Navel Surface Weapons Center, Silver Spring, MD, "A General Equation for Correlation and Prediction of Solute--Solvent Interaction in Chemical and Biological Systems", October 1, 1985.

* Bott, R., Genentech, Inc. South San Franciso, CA, "Protein Engineering, Modification of the Oxidative Stability of Subtilisin", October 18, 1985.

Ditmars, D.A., NBS, Gaithersburg, MD, "Heat Capacity of Solid Calcium: a Tour de Force of Macrocalorimetry", September 30, 1986.

* O'Leary, T.J., NIH, Bethesda, MD, "Spectroscopic and Calorimetric Studies of Biomembranes", October 24, 1985.

* Osman, R., Department of Physiology and Biophysics, New York, NY, "A New Mechanism of Action of Superoxide Dismutase", November 7, 1985.

* Rein, R., Department of Biophysics, Roswell Park Memorial Institute Buffalo, NY, "Multistep Modeling of Bioactive polypeptides in 3-Dimensions", November 14, 1985.

* Hyde, C., NIH, Bethesda, MD, "Three Dimensional Structure of Aspartate Aminotransferase and Substrate Complexes", December 18, 1985.

Thompson, P.T., Chemistry Department, Swarthmore College, Swarthmore, PA, "Progress Towards the Development of Simple Potential Functions for Solute-Solute Interactions in Non-electrolyte Aqueous Solution", January 13, 1986.

* Goldberg, R.N., NBS, Gaithersburg, MD, "Thermodynamics of Enzyme Catalyzed Reactions", February 21, 1986.

* Wlodawer, A., NBS, Gaithersburg, MD, "Structure of a 'Standard' Protein Bovine Pancreatic Trypsin Inhibitor at High Resolution", February 28, 1986.

Neumann, D., NBS, Gaithersburg, MD, "A Bibliographic Database for the HP-1000 Mini-Computer", March 5, 1986.

Roy, R., Drury College, Springfield, MO, "Thermodynamics of Mixtures of Strong Electrolytes: Applications of Pitzer's Equations", March 20, 1986.

* Gitomer, W., NIH, Bethesda, MD, "The Estimation of the Free Mitochondrial Ca^{2+} Concentration in Vivo", April 15, 1986.

* Zeyfus, M., Department of Biological Chemistry, Pennsylvania State University, University Park, PA, "Compact Domains of Proteins", April 17, 1986.

* Pember, S., Department of Chemistry, Pennsylvania State University, University Park, PA, "Mechanism and Structure of Chromobacterium Violaceum Phenyl Alanine Hydroxylase", April 22, 1986.

* Harman, J.G., NIH, Bethesda, MD, "Structure - Function Analysis of Cylic AMP Receptor Protein", May 12, 1986.

* McKenney, K., NIH, Bethesda, MD, "Protein Structure Function Studies Using Synthetic Oligonucleotides", May 14, 1986.

* Tweedy, N.B., Department of Chemistry, Pennsylvania State University, University Park, PA, "Effects of Point Mutations on Protein Folding", May 21, 1986.

* Biotechnology Seminars

9. TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Abramowitz, S.
Member, ASTM Commitee E-38 on Resource Recovery, Subcommittee E38.01 Energy

Bickham, D.
Member, Baltimore-Washington HP-1000 Users Group

Chase, M.
Vice-chairman, ASTM Committee E-27 on Hazard Potential of Chemicals

Consultant, CODATA Task Group on Chemical Thermodynamic Tables,

Corresponding member, Engineering Science Data Unit - Physical Data and Reaction Committee

Churney, K.L.
Member, ASTM Committee E-37 on Thermal Measurements

Member, ASTM Committee on Hazard Potential of Chemicals, Subcommittee E-27.02 on Thermal Stability

Member, ASTM Committee E-38 on Resource Recovery

Colbert, J.C.
Member, ASTM Committee E-38 on Resource Recovery, Subcommittee E38.01 Energy

Member, ASTM Committee D-05 on Coal and Coke

Ditmars, D.A.
Member, ASTM Committee E37.05 on Thermal Measurements/Thermophysical Properties working group I (Thermodynamics) Task Group 1.5 (Drop Calorimetry), 1.6 (Adiabatic Calorimetry)

Division Safety Officer

Member, Standards Committee, U.S. Calorimetry Conference

Domalski, E.S.
Member, ASTM Committee E-27 on Hazard Potential of Chemicals, Subcommittee E-27.07 Computational Methods

Member, ASME Research Committee for Industrial and Municipal Wastes

Member, ASTM Committee E-38 on Resource Recovery, Subcommittee 3-38.01 Energy

Garvin, D.

Secretary, CODATA Task Group on Chemical Thermodynamic Tables

Member, ASTM Committee E-38 on Resource Recovery

Member, ASTM Committee E-27 Hazard Potential of Chemicals

Kirchoff, W.H.

Immediate Past Chairman, ASTM Committee E-47 on Biological Effects and Environmental Fate

Member, ASTM Committee E-48 on Biotechnology

Titular member, IUPAC Commission I.1. on Physicochemical Symbols, Terminology and Units

Kirklin, D.R.

Member, ASTM Committee E-38 on Resource Recovery, Subcommittee E-38.01 on Energy, Subcommittee E-38.02 on Research

Director, U.S. Calorimetry Conference

Neumann, D.

Member, Hewlett-Packard HP-1000 International Users Group

Member, Baltimore-Washington HP-1000 Users Group

Parker, V. B.

Consultant, IAEA Committee on Chemical Thermodynamics of Actinide Elements and Compounds,

Member, Subcommittee IAEA.WG.01 Actinide Halide Thermodynamics.

Corresponding member, CODATA Task Group on Chemical Thermodynamic Tables

Member, Chemical Thermodynamimcs Advisory Committee on Aqueous Solutions Data Base, (Lawrence Berkeley Laboratories, Sidney Phillips)

Smith-Magowan, D.

Organizing Committee of the 'International Conference on Thermodynamics of Aqueous Solutions with Industrial Applications', Airlie House, May 1987.,

Member, International Association for the Properties of Steam

Wlodawer, A.

Treasurer, Neutron Special Interest Group of the American Crystallographic Association

Member, Apparatus and Standards Committee, American Crystallographic Association

10. PROFESSIONAL INTERACTIONS, CONSULTING AND ADVISORY SERVICES

Abramowitz, S.

Collaborated with I.W. Levin, National Institute of Arthritis and Metabolic Disease, NIH, on vibrational analysis of small molecules and some biological species.

Formulated cooperative research program on high temperature thermodynamics with AFOSR.

Interacted with the following agencies and organizations regarding the NBS program in Biotechnology: National Aeronautic and Space Administration (NASA), National Academy of Science (NAS), National Science Foundation (NSF), Office of Technology Assessment (OTA).

Chase, M.

Reviewed and planned for physical property data issued by Engineering Science Data Unit.

Participated in the development of ASTM Standard on "Calculation of Hazard Potential Figures of Merit for Thermally Unstable Materials" prepared by ASTM. Committee E-27 on Hazard Potential for Chemicals.

Supplied thermal functions to the Therdynamic Research Center, Texas A & M University, for inclusion in the TRC Hydrocarbon and Non-hydrocarbon Tables.

Collaborated with AIP on the design and publication of the JANAF Tables, 3rd edition.

Prepared tables of thermal functions for the CODATA Thermodynamic Tables and for CODATA Key Values for Thermodynamics, and participated in meetings of the CODATA Task Group on Chemical Thermodynamic Tables.

Interacted to obtain data needed for development of theoretical concepts used in the JANAF Tables with J.L. Haas, Jr, United States Geological Survey (USGS), T. Chart, & A. Dinsdale, NPL, U.K., M.H. Rand, AERE, Harwell, U.K., L. Brewer, U. CA, Berkley, P.F. Bernath, AZ State U., and D.O. Harris, U. CA, Santa Barbara, CA.

Reviewed an extensive series of articles on Isomer Group Thermodynamics (R.A. Alberty, MIT).

Churney, K.L.

Interacted with R. Wingender of the Analytical Chemistry Lab of Argonne National Laboratory, Argonne, IL on analysis of effluent fractions from combustion measurements for chlorinated dioxins and related compounds.

Colbert, J.C.

Interacted with ASTM Committee D-05 on Coal and Coke and its Subcommittee 21.02 on Methods of Analysis. Membership and active participation with subcommittee members on the evaluation of calorimetric procedures for determining the calorific value of coal and coke.

Cooperated in research with B. Coxon of the NBS Organic Analytical Research Division on bomb calorimetric and NMR studies of D-ribose and 2-deoxy-D-ribose.

Ditmars, D.

Cooperated with R.A. Robie of the U.S. Geological Survey, Reston, VA, on preparing a sample of pure calcium and measuring the heat capacity of the solid phases from 4K to the melting point, 1112K.

Interacted with Commission on Standardization of Thermophysical Preperty Measurements of the European Thermophysical Properties Union. This Commission is sponsoring and coordinating the assembly of a two-volume compendium of apparatuses and techniques for the measurement of thermophysical properties. One chapter has appeared in press on a survey of high temperature drop calorimetry. Another chapter on hardware design is in preparation.

Cooperated with C.A. Plint, Physics Department, Brock University, Ontario, Canada, on measurement of the high-temperature heat capacity of pure copper.

Cooperated with the investigator on U.S.-Yugoslav cooperative research project being carried out at NBS (Chemical Thermodynamics Division) and at Boris Kidric Institute, Belgrade (Institute for Thermal Engineering and Energy Research).

Provided advisory service to U.S. Naval Weapons Ordinance Center, Crane, Indiana on calorimetry hardware, techniques for studying low-level degrading reactions in solid propellants and explosives.

Domalski, E.S.

Cooperated with engineers involved in solid waste disposal, solid waste processing, and resource recovery from the ASTM Committee E-38 on Resource Recovery and The ASME Research Committee on Industrial and Municipal Wastes concerning combustion characteristics of waste materials.

Participated in the USUK collaboration for Waste Combustion. Areas of interest are : (1) chlorine content analysis of municipal solid waste, (2) calorific value data derived from U.S. and U.K. one kilogram-capacity calorimeters, and (3) combustion studies on threshold conditions for the formation/destruction of chlorinated species.

Interacted with the U.S. Department of the Army, Chemical Research and Development (CRDC), Aberdeen Proving Ground, Maryland to carry out combustion calorimetry and develop estimation methods for organic phosphorus compounds (CRDC) has continued in FY 1986.

Negotiated for the publication of a compilation entitled: "Thermodynamics Data for Biomass Conversion and Waste Incineration", prepared at NBS, compiled at the Solar Energy Research Institute, and funded by DoE, as an ASME document.

Interacted with engineers from Combustion Engineering (J. Orcutt and D. Borio) during a visit to the large sample flow calorimeter facility and through discussion of plans for future research on monitoring chlorine during MSW combustion.

Gajewski, E.

Interacted with Anne Plant, Center for Analytical Chemistry, purification of monoclonal antibodies.

Garvin, D.

Worked with CODATA on the preparation of thermodynamic data bases, jointly with groups at AERE, Harwell, U.K., (M.H. Rand), LIPCM-ENSEEC, Grenoble, France (I. Ansara), Univ. of Sussex, Brighton, UK, (J.B. Pedley), and TERMOCENTER Akad. Nauk, Moscow, USSR (L.V. Gurvich, V.A. Medvedev, V. Yungman), and US Geolog. Survey, Reston, VA, USA (J.L. Haas, Jr.).

Visited British Gas, London Research Station, London, U.K. (A.E. Humphreys) regarding calorimeter design.

Selected values for properties of components of natural gas: Thermodynamic Research Center, Texas A & M Univ., College Station, TX, (K.N. Marsh, R. Wilhoit).

Participated in completion of the handbook for calculation of properties of natural gas for the International Group of Importers of Liquified Natural Gas (GILGNL), NBS, Boulder, CO, (D. Mann).

Interacted with international standards (Chemical) community. Observer at IUPAC General Assembly, Lyons, France, Commission I.3 [Nomenclature], I.2 [Thermodynamics], I.4 [Chemical Kinetics], and II.3 [High Temperature Chemistry].

Attended DOE Contractor's Meeting for Department of Energy on clean up of coal combustion stack gases, assessment of industry needs.

Goldberg, R.N.

Met with Richard Veech, National Institutes of Health, general discussions on the thermodynamics of enzyme-catalyzed reactions.

Met with Richard Virdins, University of Newcastle-upon-Tyne, United Kingdom, to discuss possible work in the penicillinase reaction.

Met with Arthur Carrington, University of Newcastle-upon-Tyne, United Kingdom, to discuss pH Standards.

Discussed with Yung-Chi Wu, Center of Analytical Chemistry, the treatment of electrochemical data.

Kirchhoff, W.H.

Collaborated with I.W. Levin, et. al. Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes and Digestive and Kidney Diseases on thermodynamic properties of lipids.

Worked with J.D. Fine, Surface Science Division, on the statistical analysis of depth profile data.

Neumann, D.B.

Collaborated with Freeman, Oklahoma State Univ. on the publication of the Bulletin of Chemical Thermodynamics.

Interacted with A. Maczynski, Institute for Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland - Protocal for the international exchange of chemical thermodynamic data - IUPAC sponsored activity.

Participated in Task Group meetings at Ottawa, July 1986. CODATA Task Group on Chemical Thermodynamics Tables.

Provided computer programs to Office of Standard Reference Data to assist in the production of camera ready documents and tables, acted as consultant for the planning of automation activities at NBS and DOC.

Consulted with J.W. Gadzuk, Division 541, on graphics for publication.

Consulted with D.J. Orser, Division 739, on presentation of topology of phase diagrams.

Consulted with G. Klopman, Dept of Commerce, on oceanographic data (Netherlands) to the NBS computer.

Parker, V.B.

Consulted with E. Busenberg and N. Plummer, USGS, Reston, VA concerning the thermochemistry of $BaCO3(cr)$ and the selection of the "best values" for the enthalpy of formation at zero K; also concerning Ba^{+2} (aq. std. state) and values for the enthalpy of formation at 0 K and the entropy.

Consulted with John Haas, USGS Geological Survey, concerning the thermochemical behavior of iron oxides.

Discussed with V. Medvedev, Institute for High Temperatures and I. Khodakovsky, Vernadsky Institute for Geochemistry and Analytical Chemistry, Moscow, the evaluation of the thermochemistry of key iron compounds.

Held discussions on USA/USSR Science exchange: Exchange of data, calculational methods and interpretations of data between the Chemical Thermodynamics Data Center and a similar group at the Institute for High Temperatures, Moscow.

Collaborated with members of the CODATA Task Group on the preparation of Chemical Thermodynamic Tables: Preparation of thermodynamic data bases, jointly with groups at AERE, Harwell, U.K., (M.H. Rand), LIPCM-ENSEEG, Grenoble, France, (I. Ansara), and TERMOCENTER Akad. Nauk, Moscow, USSR, (L.V.Gurvich, V.A. Medvedev, V. Yungman), and USGS, Reston, VA, USA (J. Haas Jr.)

Held discussions, provided advice and guidance to Phillips, Lawrence Berkeley Lab. and M. Siegel, Sandia National Lab. on the need for and the construction of thermodynamic data bases for modelling in geothermodynamic equilibrium calculation in aqueous solutions.

Provided advice and guidance on handling uncertainties in thermodynamic data to NRC, DOE, and USGS at a panel meeting Dec. 17, 1985 at NRC Silver Spring, MD.

Collaborated with D.D Wagman, former NBS staff scientist, on chemical thermodynamic key values and thermodynamic tables.

Schwarz, F.P.

Collaborated with I.W. Levin, Laboratory of Chemical Physics, National Institute of Arthritis, Diabetes and Digestic and Kidney Diseases on the thermal properties of lipids.

Collaborated with A. Shrake, Office of Biologics, FDA on the thermal stability of serum albumen.

Smith-Magowan, D.

Collaborated with R.H. Wood, University of Delaware, on the development of methods for the correlation and theoretical interpretation of the thermodynamic properties of aqueous solutions at elevated temperatures and pressures.

Interacted with S.L. Miller, Univ. of California, San Diego, on the correlation of equilibria comprising the Krebs (tricarboxylic acid) cycle and associated metabolic pathways. Joint manuscript is in preparation.

Interacted with J.O.M. Levelt-Sengers, Thermophysics Div, NEL, NBS; on the interpretation the properties of aqueous electrolytes near their critical points.

Interacted with P.T. Thompson, Swarthmore College, on the calculation of virial coefficients of small organic compounds in aqueous solution.

Provided advice to Dewey, Reynolds Metals Co., Richmond, Va; on the vapor pressure and enthalpy of concentrated NaOH solutions at elevated temperatures.

Provided advice to J. Erwin, SWRI, San Antonio TX, on the electrical conductivity of aqueous mixtures of CO_2.

Provided advice to R.L. Truitt, Dallas TX, on the formulation of colloidal suspensions of magnetic materials.

Provided advice to W. Kelly, Nuclear Regulatory Commission, on the data for aqueous solutions used in codes to predict the stability of nuclear waste storage deposits.

Tewari, Y.B.

Held discussion with and interacted with Dr. William Gitomer of the Laboratory of Metobilism at NIH on the equilibrium measurement for the process: hydrolysis of glucose 6-phosphate.

Weber, I.T.

Held discussions and interacted with Dr. Sancar Adhya, NIH, on the crystallization and structural studies of E. coli gal repressor.

Held discussions and interacted with Professor Herman Ammon, Department of Chemistry, University of Maryland, on structural studies of glutaminase-asparaginases from several bacterial sources.

Collaborated with Dr. Gary Gilliland, Genex Corporation, Gaithersburg, MD, on data collection from crystals of catabolite gene activator protein.

Interacted with Dr. Keith McKenny, NIH, on the crystal structures of mutants of catabolite gene activator protein.

Interacted with Dr. Alan Peterkofsky, NIH, on the crystal structures of several mutants of catabolite gene activator protein.

Interacted with Professor Thomas Steitz, Department of Molecular Biophysics and Biochemistry, Yale University, New Haven CT, on crystallization of rec A protein and on refinement of the structure of catabolite gene activator protein.

Interacted with Professor Susan Taylor, Department of Chemistry, University of California, San Diego CA, on the prediction of the structure of the regulatory subunit of mammalian cAMP-dependant protein kinase.

Interacted with Dr. Susan Wickner, NIH, on the crystallization of 'O'-protein that is required for transcription in phage λ.

Wlodawer, A.

Collaborated with Professor Robert Huber, Max Planck Institute, Martinsried, West Germany, on the comparison of two crystal forms of bovine pancreatic trypsin inhibitor.

Collaborated with Professor Lennart Sjolin, Chalmers Polytechnic, Gothenburg, Sweden, on the structural investigations of ribonuclease and bovine pancreatic trypsin inhibitor.

Collaborated with Dr. Franz Schmid, University of Regensburg, West Germany, on crystallographic studies of porcine ribonuclease.

Collaborated with Dr. David Moss, University of London, England, on comparisons of independently refined structures of bovine ribonuclease.

Collaborated with Professor Herman Ammon, University of Maryland, on crystallographic studies of glutaminase-asparaginases from several bacterial sources.

Collaborated with Dr. Giuseppe Zaccai, Institute Laue-Langevin, Grenoble, France, and Dr. Martin Gellert, NIH, Bethesda, MD, on the low-angle neutron scattering studies of gyrase and gyrase-DNA complexes.

Collaborated with Dr. Ettore Appella, NIH, Bethesda, MD, on crystallization of DNA fragments.

Collaborated with Dr. Joyce Jentoft, Case Western University, OH, on crystallographic studies of the RNA-binding protein from the phage pp12.

Collaborated with Dr. Gary Gilliland, Genex Corporation, Gaithersburg, MD, on crystallographic studies of a sweet protein, monellin, and on high resolution refinement of ribonuclease.

Collaborated with Dr. Matthew Pincus, Brooklyn Polytechnic, on crystallography of covalent complexes between ribonuclease and nucleotides.

11. VISITING SCIENTISTS

The Thermodynamics Division has been host in the past year to the following scientists who have worked with NBS scientists on problems of mutual interest.

Liebman, J.F., University or Maryland-Baltimore County, Baltimore, MD, completed an evaluation of enthalpies of formation of amino acids, peptides, heterocyclic and related compounds. He is an expert on techniques in estimating thermodynamimc properties of organic compounds and on strain energies in organic compounds.

Miller, M., University of Warsaw, Poland, Dr. Miller is working on the crystallographic structure of proteins and DNA fragments.

Nachmann, J., Weizmann Institute of Science, Rehovot, Israel. Dr. Nachmann is a protein crystallographer conducting neutron and x-ray diffraction measurements of macromolecules of biological importance in the Biomolecular Structure Group of the Division

Nuttall, R., Former NBS employee, is an expert on solution thermodynamics and evaluation of thermochemical data. Dr. Nuttall participated in developing the data for electrolyte data bases and catalogs of measurements of thermochemical data.

Rukkers, K., graduate student in the Department of Applied Physics, Twente University of Technology, Enschede, Netherlands, spent three and a half months (Feb-May 1986) providing assistance to the large sample flow calorimetry group improving the data acquisition and data handling procedures.

Savage, H., National Institute of Health, Bethesda, MD. Dr. Savage is working on neutron diffraction of protein hormones and the structure of bound water in biological systems.

Schumm, R.H., Former NBS employee, is an expert on the evaluation of thermochemical data. Mr. Schumm evaluated data on sulfur compounds relevant to flue gas desulfurization.

Shrake, A., Food and Drug Administration, Washington, D.C. Dr. Shrake is an expert in the area of thermodynamics of phase transitions in proteins and protein ligand complexes of biological interest.

Thompson, P.T., Swathmore College, Swathmore, PA. Dr. Thompson is an expert on the interaction of organic species with water in terms of hydrophobicity. He performed both experimental and theoretical research during his sabbatical at NBS during calendar year 1985.

Wagman, D.D., Former NBS employee, is an expert on the evaluation of thermodynamic data. Mr. Wagman has prepared the CODATA key values for thermodynamics.

Wasik, S.P., Former NBS employee, is an expert on the evaluations of solubility data for organic species in aqueous and mixed media. Dr. Wasik evaluated data on the thermodynamic properties of alkanes in aqueous media.

Weber, I., University of Maryland, College Park, MD. Dr. Weber is working on the molecular structure of complex biomolecules using both x-ray and neutron diffraction.

Wood, R.H., Chemistry Department, University of Delaware, Newark, DE, worked with the staff on solution thermodynamics, theory and experiment; electrolyte theory of weak electrolytes, speciation calculations, molecular interactions in solution; and the solubilities of non-electrolytes in aqueous solution as a function of concentration and temperature.

MOLECULAR SPECTROSCOPY DIVISION

A. Weber, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1986

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 spectroscopy in order to:

Advance spectroscopic measurement methods and techniques

Develop models, theoretical concepts and quantum theoretical methods for predicting molecular properties and interactions

Obtain reliable reference spectroscopic data for NBS, 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 NBS Divisions, other government agencies, industry and the research community.

Within the framework of these general goals the Division also follows three specific thrusts which are 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 develop a data base to understand conformation, thermodynamics, and reactivity of such systems. The objectives of our thrust in biotechnology are to develop and implement methods for the study of metal interactions in proteins and nucleic acids using primarily quantum mechanical techniques, while the major effort of the third thrust is directed to the study of vibrational energy transfer.

This summary contains a report of the activities of each of the three groups within the Division during the past year and demonstrates how they are meeting the above objectives.

B. Organization

To carry out its work the Molecular Spectroscopy Division is organized into three working groups: High Resolution Spectroscopy (HRS), Laser Photochemistry (LPC), 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 fourteen guest scientists and four post doctoral fellows engaged in Division projects. In addition, two members of the Surface Science Division participated in the work of the LPC 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 NBS, the Center for Chemical Physics (CCP), 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, unknown problems. This approach is justified by the past and present applications of experimental and theoretical spectroscopy by our Division. These applications also provide much of the direction and motivation for our efforts. Remote sensing for industrial and atmospheric monitoring, laser chemistry, and combustion diagnostics are a few of the many important high technology areas that depend on modern spectroscopic techniques.

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 atmosphere, 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 and AFGL. 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 during the past year and will continue to do so in the future. 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 buttressed by the analytical and computational theoretical expertise available in the Division.

The Division is the home of the NBS Molecular Spectra Data Center. This Center, supported by the Office of Scientific Reference Data and staffed by members of the HR group provides evaluated data on molecular rotational spectra in the microwave region and develops evaluated infrared spectra to be used as standards in calibrating diode lasers and infrared laser spectrometers. This work is based on the needs of the user community. Thus the work on infrared standards is a response to requests from the instrumentation industry, industrial research laboratories, applied technological user groups, and government agencies and laboratories. Improvements in the stability of diode lasers have emphasized the need for accurate calibration standards. The absorption frequencies of N_2O that involve the lower energy levels are now being tied to the cesium frequency standard. This work has been made possible through the joining of the unique facilities of the Time and Frequency Division of NBS/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. A recent activity is the critical evaluation and tabulation of the vibrational and electronic energy levels of transient molecules. Section 2.A of the HR group report describes the various activities of the Data Center.

The LPC 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 vibrational energy transfer. This research was extensively discussed in the Annual Report for FY85 and the research outlined and proposed there has been pursued successfully during the past year in the determination of the rates of energy transfer from vibrationally excited chemical bonds in liquids, solids, and on molecules bound to surfaces.

In the second 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 creation of an experimental facility to perform state-resolved studies of thermally and laser desorbed molecular processes at well characterized surfaces. Details about this year's accomplishments are presented in Section 3.B.

The capability to perform time resolved spectroscopic measurements at the picosecond level has been turned to good advantage in the study of vibrational predissociation of van der Waals molecules. The experiments are performed in the time domain and thereby yield a direct measure of the lifetimes of the predissociating states. This work is described in Section 3.C of the LPC group report.

The field of Quantum Chemistry continues to experience new developments which 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. The ability of the QC group to attack large scale computational problems using ab-initio rather than semi-empirical methods is significantly enhanced by the dedicated IBM 4381 superminicomputer located in the Molecular Structure and Modeling Facility of the Molecular Spectroscopy Division.

A major effort of the QC group described in Section 4.A is in the field of theoretical calculations on biomolecules. The goal of this program is the theoretical calculation of the energetics, spectroscopy, and reaction behavior of biomolecules with emphasis on the role of metal interactions in biomolecules. Ab initio methods are used to the exclusion of semi-empirical methods to insure predictability. The program is developed on three levels. At the first and fundamental level is the development of an ab initio electronic structure, reaction field method and code which will allow quantum mechanical calculations on systems of the order of 1000 atoms. Molecular and statistical mechanics is used to provide conformation for quantum models and to determine the environment for a reaction field approach. At the second level accurate ab initio calculations of small prototype systems provide data on a wide range of properties which also contributes to the large theoretical data base required in the reaction field code. At the third and applied level, model calculations that relate to specific problems of current interest are undertaken. The reaction field code development is the major thrust of this program.

During the last few years the three groups have been engaged in the study of the properties of van der Waals and hydrogen bonded complexes. This activity is continued using the experimental and theoretical expertise represented in each group and the individual group reports give detailed description of the work done. Only free complexes (i.e., gas phase) are investigated in order to obtain clearly interpretable data on molecules which are unperturbed by molecular interactions that exist in the condensed phase. Thus the HR group reports on its studies of the resolved microwave rotation and infrared rotation-vibration spectra while the LPC focusses its attention on the dynamics of vibrational pre-dissociation. In many cases the interpretation of the experimental results is aided by the analytical and computational theoretical studies performed in the HR and QC groups. The work done by the three groups on weakly bound complexes constitutes therefore a Division wide effort in which the groups are participating in a mutually supportive and beneficial manner. The study of weak molecular interactions as exemplified by the van der Waals and hydrogen bonded molecules is a field of considerable present and future interest and our Division is expected to fully participate in these investigations during the coming years (cf. the Pimentel Report "Opportunities in Chemistry," National Academy Press, Washington, D.C., 1985, and the more recent Brinkman report on "Physics Through the 1990s," National Academy Press, 1986).

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 non-NBS visiting scientists. Some of these use the facilities of the Division and are appointed Guest Scientists at NBS. Section 10 of this reports 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 and private industry which in turn support some of the work done in the Division. The various agencies of the Department of Defense (ONR, ARO, AFGL, AFOSR), NASA, DOE, as well as the National Foundation for Cancer Research 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 (Section 5, 6), Division seminars (Section 7), outside professional activities by the staff (Section 8), professional interactions and consultations by the Division staff (Section 9), and guest scientists (Section 10).

2. HIGH RESOLUTION SPECTROSCOPY GROUP

N. Craig, G. T. Fraser, C. W. Gillies, J. T. Hougen, M. E. Jacox,
W. J. Lafferty, F. J. Lovas, A. G. Maki, W. B. Olson, A. S. Pine,
G. Rotter, R. D. Suenram, G. A. Thompson, A. Weber, and J. Zozom

The work of this group spans a variety of spectroscopic topics many of which are a part of programmatic efforts. Accordingly the activity reports are grouped into five separate sections: Calibration and Data Center Activities, Spectroscopy for Environmental Studies, Spectroscopy of Hydrogen-bonded and van der Waals 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.

A. 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 in other laboratories are also proceeded. 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. N_2O Frequency Measurements Extending Calibration Data into the 2800 cm^{-1} Region

(A. G. Maki, J. S. Wells, and A. Hinz)

In a continuation of our collaborative work with Joe Wells (NBS, Boulder) we have this year measured the frequency of several important hot band transitions in the 1257 to 1335 cm^{-1} region. These data were used to provide a finer comb of calibration features in this region, but their most important contribution has been to tie more energy levels of N_2O to the cesium frequency standard. From these accurate energy level determinations, it is possible to obtain accurate transition frequencies outside the area of direct measurement. In particular, these new frequency measurements allow us to extend our calibration tables to the 2800 cm^{-1} region, which was the primary goal of this year's work.

This work has also given us the opportunity to compare our frequency measurements with frequencies derived from wavelength measurements coming from various other laboratories. It appears that the recent work reported by Toth (JPL) using the Brault interferometer at Kitt Peak gives wavenumber values that are consistently close to those we measure. Toth's accuracy seems to be largely due to the calibration procedure he has been using based on frequency measurements of several bands.

Some of the hot band measurements that were made this past year will assume greater importance next year if we are able to measure some of the other transitions that are on our agenda. These measurements will provide frequency values for new energy levels and this will lead to new calibration bands in the 2300 to 3000 cm^{-1} region. This work is supported by NASA.

2. OCS Heterodyne Measurements for Calibration from 1866 to 1920 cm^{-1}
(A. G. Maki, J. Wells, and A. Hinz)

Another advance in the development of OCS absorption lines as convenient frequency standards was made by the heterodyne measurement of a number of transition frequencies in the 1866 to 1915 cm^{-1} region. These measurements have allowed us to prepare an improved calibration table for this region and also provide a good measure of the energy levels for the 12°0 state from which other transition frequencies can be calculated. This work is supported by NASA.

3. Recommended Rest Frequency List
(F. J. Lovas and G. Rotter)

The first revision of the paper originally entitled "Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions - 1984 Revision" was published in the January 1986 issue of J. Phys. Chem. Ref. Data. While the manuscript was in the publication process, we continued to update the spectral entries through 1985 so the title was modified to "- 1985 Revision" to reflect the content more accurately.

The next revision of this paper is planned for 1988, so the literature search of radio astronomy papers and data evaluation of new microwave studies of these species will continue. Last year preprints were widely distributed and very favorable responses were received. Since the manuscript was published in January, several requests for magnetic tape copies have been received and very recently Professor K. R. Lang of Tufts University requested permission to reproduce the frequency list in a forthcoming book Astrophysical Formulae.

4. Microwave Spectral Tables
(F. J. Lovas, G. Rotter, and R. S. Suenram)

The general search for all papers dealing with microwave spectral data continues. Reprints or photocopies of all pertinent reports are obtained and filed according to empirical formula. These files are the source of data for spectral evaluation reported in the various publication series which the data center produces.

Work continues on the Part III of the Microwave Spectral Table series. This involves the spectra of simple hydrocarbon species C_xH_y. During the current year we have been carrying out evaluations on species exhibiting internal rotation from methyl groups. This project is slated for completion in September 1986 and appears to be on schedule. This is part of the long range plan to develop a microwave spectral atlas, so care is taken to keep all the coding compatible with previous compilations in this series.

We continue to up-date our computer files on diatomic and triatomic species. Since the publication of Part I. Diatomic Molecules, 21 new species have been added and the spectra for 34 species have been augmented. Similarly for Part II. Triatomic Molecules, spectra for 15 new species have been added and the data on 30 other species have been updated.

5. Update of Landolt-Börnstein Structural Tables of Free Polyatomic Molecules

(J. H. Callomon, E. Hirota, K. Kuchitsu, and W. J. Lafferty)

A project to update the Landolt-Börnstein compilation, "Structure Data of Free Polyatomic Molecules," has just been completed. This effort includes all structural data of gas phase molecules reported in the literature since the last volume was published in 1976 up to the end of 1985. It includes structures obtained by microwave, infrared, Raman, and visible spectroscopy as well as electron diffraction techniques. About 1500 new or improved structures are included in this work which has been a collaboration between workers in England, Japan, and the United States. The new volume is expected to be in press in early 1987.

6. Vibrational and Electronic Energy Levels of Transient Molecules

(M. E. Jacox)

All of the data previously compiled on the ground-state vibrational energy levels of polyatomic transient molecules have been transferred to a new IBM PC-AT computer system. This system not only is much more efficient, but also will facilitate possible future development of a version of the tables amenable to digital search. The tables of ground-state vibrational energy levels have been kept current; new or revised tables have resulted for approximately 75 molecules per year.

Matrix effects on the electronic spectra of diatomic molecules have been surveyed in a paper entitled, "Comparison of the Electronic Energy Levels of Diatomic Molecules in the Gas Phase and in Inert Solid Matrices," to be published in a forthcoming issue of Journal of Molecular Structure honoring Professor George C. Pimentel. Electronic band origins and vibrational band spacings in excited electronic states have been compared for the approximately 230 electronic transitions of diatomic molecules which have been observed both in the gas phase and in rare-gas or nitrogen matrices. With few exceptions, valence transitions and the associated vibrational band spacings are shifted by less than about 1% in neon matrices. Somewhat larger shifts, often to longer wavelengths, result from isolation of the molecule in a heavier rare gas or a nitrogen matrix. The perturbation of Rydberg transitions by the matrix, the effects of charge-transfer interaction with the heavier rare-gas matrices, and the behavior of the potential curve of the matrix-isolated molecule in the vicinity of the dissociation continuum are discussed.

With partial support from the NBS Office of Standard Reference Data, experimental data are being critically evaluated and compiled for the electronic energy levels of transient molecules possessing from 3 to 6 atoms. Both gas-phase and inert matrix data will be included. A wide variety of observation techniques, including high resolution absorption spectroscopy, laser-excited fluorescence, multiphoton ionization, and photoelectron spectroscopy, are being surveyed. Energies of band origins, fundamental vibration frequencies, rotational constants (A, B, C), and radiative lifetimes are among the properties now being entered. When complete, the tables will include well over 150 molecules.

7. Future Plans

Further work in our frequency standards effort is to systematically develop the N_2O spectrum and energy levels for use as frequency calibration bench marks by heterodyne frequency measurements of the 10^00-02^00 transitions near 1060 cm^{-1} and the 10^00-01^10 transitions near 1635 cm^{-1}. When combined with other frequency measurements made earlier in this program, these new measurements will provide the first frequency data on the 02^00-00^00 transitions near 1168 cm^{-1} and thereby will provide improved data for the 10^00 and 01^00 levels of N_2O.

Evaluation of microwave spectra data will continue to focus on the two major projects in progress. The radio astronomy literature is continually searched for new observations to be included in the next revision of the Recommended Rest Frequency compilation. When the current work on the Microwave Spectral Tables - Part III on simple hydrocarbons is finished, we will begin evaluation of the next group, hydrocarbons containing oxygen.

The compilation of the electronic spectral data tables is nearing completion. It is planned to submit these tables to the Journal of Physical and Chemical Reference Data late in FY87.

Revisions and additions to the tables of ground-state vibrational energy levels will continue to be kept current. It is also planned to submit a supplement to these tables to the Journal of Physical and Chemical Reference Data late in FY87. This supplement will include a master index, in order to facilitate a complete search of the experimental literature on the vibrational and electronic spectra of polyatomic transient molecules.

B. 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. N_2- and Air-Broadening in the Fundamental Bands of HF and HCl (A. S. Pine)

N_2- and air-broadened lineshapes of HF and HCl transitions in the $v=1 \leftarrow 0$ bands have been measured at T=295 and 202 K with a high-resolution difference-frequency laser spectrometer. Pressure broadening and shifts and collisional narrowing parameters have been extracted by least squares fitting of several collisional profiles to the spectra. Figure 2.1 shows the observed lineshape of the R(0) line of HF as a function of N_2 pressure fit to Voigt and Galatry (soft collision model) profiles. 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. The pressure broadening parameters, Γ, were effectively linear with pressure for the Galatry collisional narrowing model as they should be, whereas the Voigt fits were highly nonlinear as shown by the ratios of Γ for the two models in Fig. 2.1. 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. Fig. 2.2 indicates this asymmetry for the P(9) line of HF at $P(N_2)$ ~ 54 Torr fit to the formally symmetric Voigt, soft and hard collisional narrowing profiles.

The ratio of air-to-N_2 broadening varies systematically with rotational levels and is always somewhat larger than that given by the relative quadrupolar contributions of O_2 and N_2. 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. These effects are summarized in Fig. 2.3 as a function of the rotational index m. This work is supported by NASA.

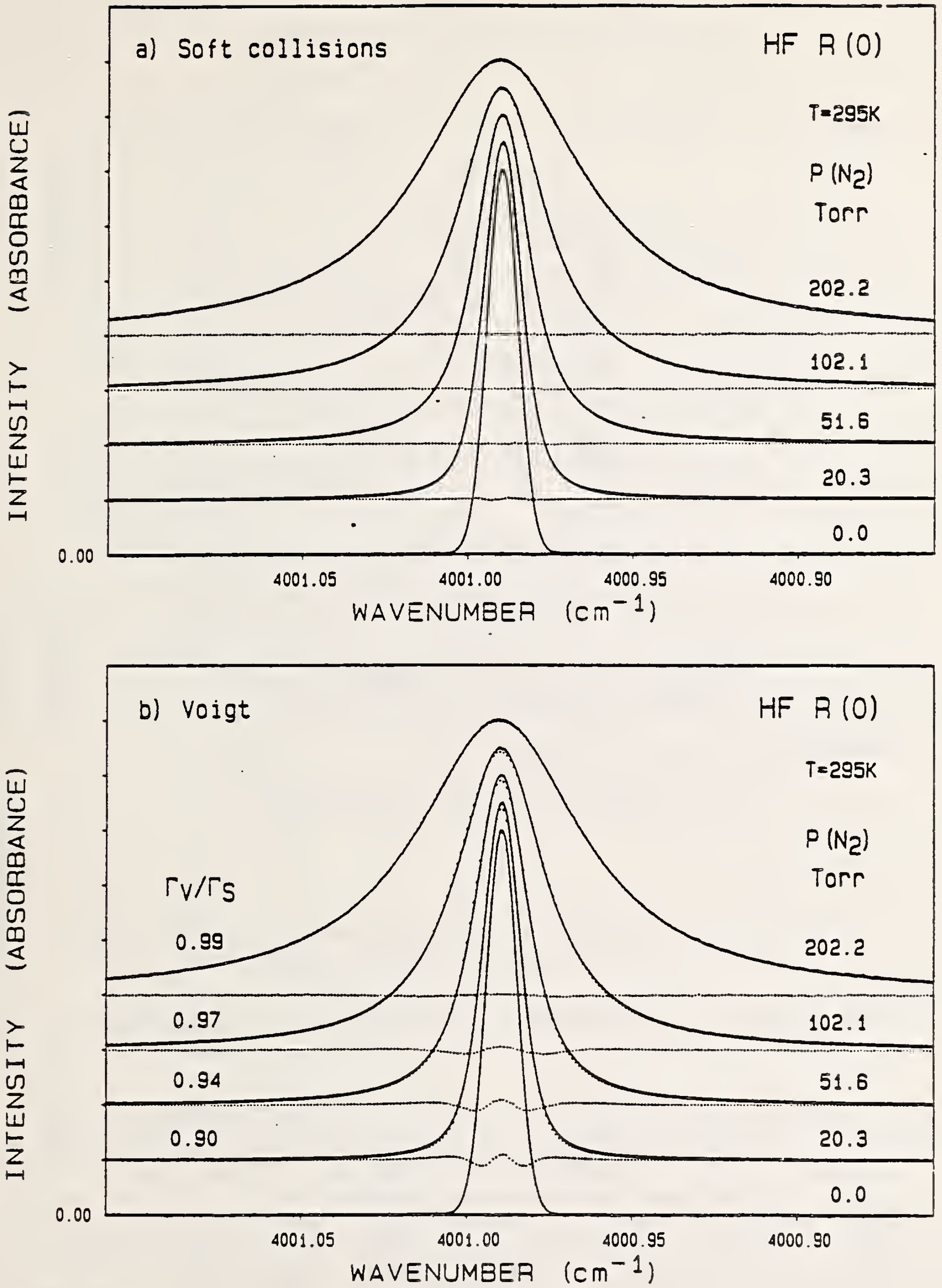


Fig. 2.1 Lineshape of HF as a function of N_2 pressure fit to Voigt and soft collision models.

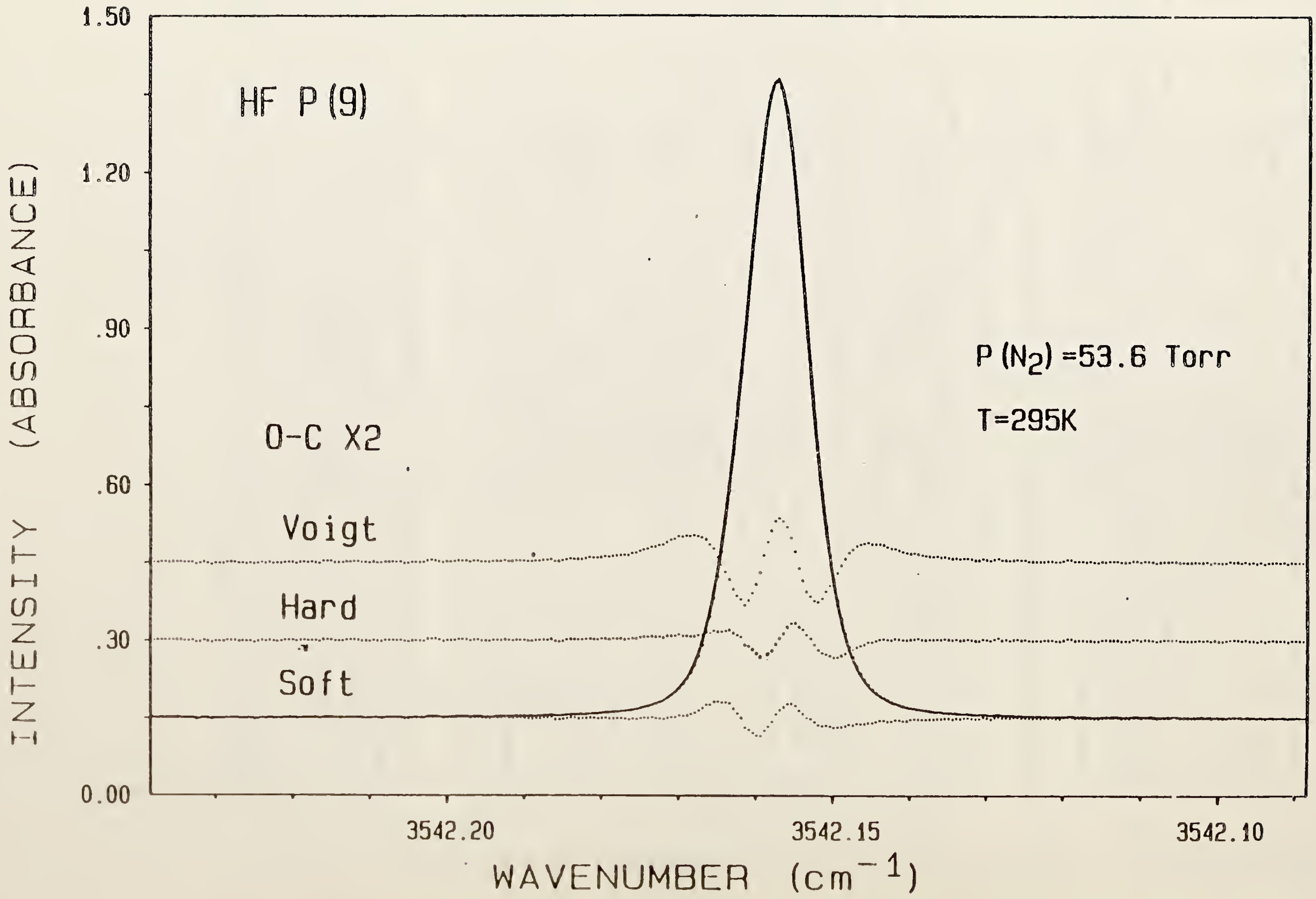


Fig. 2.2 The P(9) line of HF shown fit to the Voigt, hard, and soft collisional narrowing models.

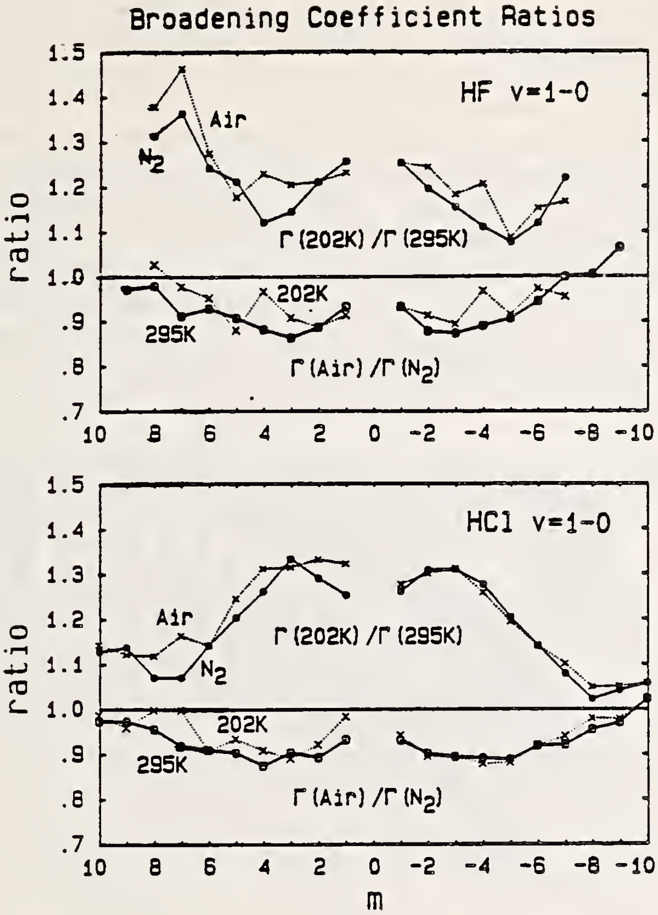


Fig. 2.3 Ratio of the air-to-N_2 broadening of HF and HCl as a function of temperature and rotational index, M.

2. Measurements of Collisional Interference in Nitrous Oxide

(A. S. Pine)

We have been making a number of collsional lineshape studies in support of a NASA program to monitor the upper atmosphere for trace contaminants using sensitive infrared techniques. One of the major uncertainties is how to interpret the observed profile of a dense unresolved spectrum, such as occur for the strong, characteristic Q-branch and band-head features used for monitoring various species. When spectral lines overlap due to collisional broadening, the resulting envelope may not be the simple addition of individual component lineshapes if the collisions actually transfer excitation between energy levels involved in the unresolved transitions. This nonadditivity is a collisional interference effect, akin to motional narrowing, variously known as line coupling, line mixing or rotational collapse, and is well known for densities approaching the condensed phase. However, in the range of pressures below 10^5Pa, pertinent to atmospheric and stratospheric conditions, the deviations from additivity are typically small and subtle and require exceptionally high resolution, good signal-to-noise ratio and wide linear dynamic range as well as precise scanning control in order to be reliably measured.

Collisional interference at subatmospheric pressures has been observed recently using high resolution coherent Raman gain techniques for the Q branches of N_2, CO and NO and in the infrared for Q branches of CO_2 using diode lasers and Fourier transform interferometers. In the present work we have performed measurements on N_2O with a precision tunable difference-frequency laser system. Preliminary transmission spectra of the Q branch of the $\nu_1 + \nu_2$ combination band of N_2O as a function of pressure are shown in Fig. 2.4 illustrating the high quality of the data.

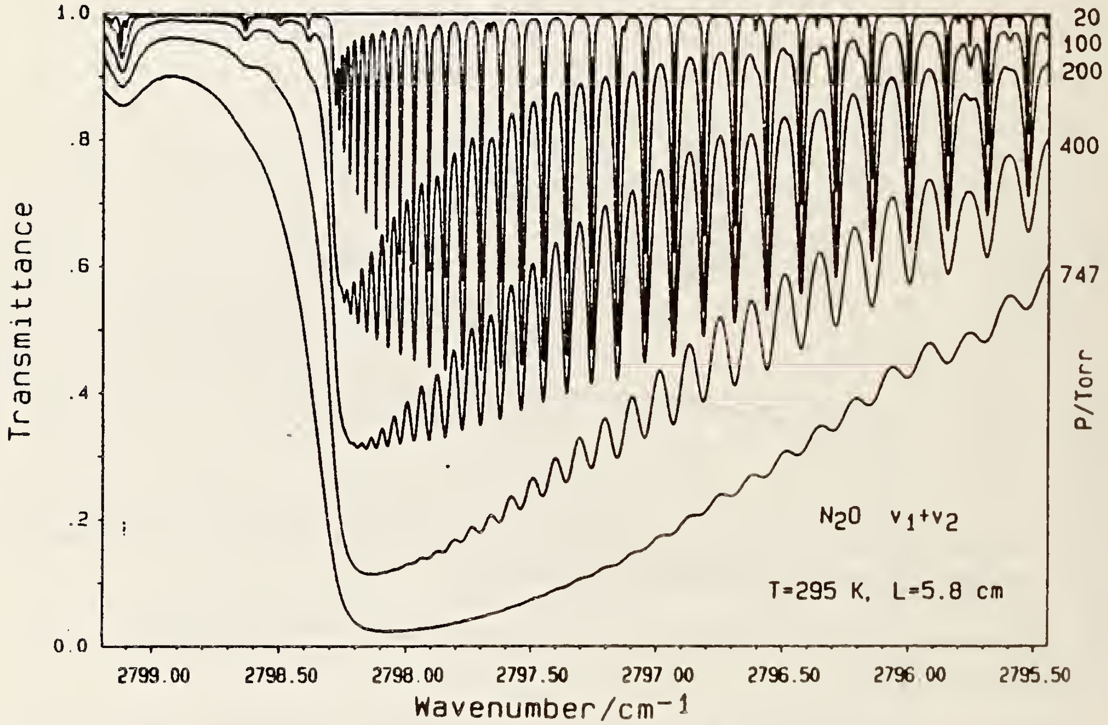


Fig. 2.4 Transmission spectra of the Q branch of the $\nu_1 + \nu_2$ combination band of N_2O as a function of pressure.

The wavenumber scale is linear and reproducible to $\leq 5 \times 10^{-5}$ cm^{-1} using digital scanning servo control; the signal-to-noise ratio and the linear dynamic range are $\geq$ 1000:1 using real-time division of the transmitted light by the incident light. The 0% transmission baseline is stable to within 0.1% and the 100% transmission baseline is reproducible to within 1%. This latter baseline uncertainty is the principal source of error in these measurements, particularly for the higher pressure traces where the troughs between the lines exhibit strong absorption and there is no clue as to the position of the baseline over an extended spectral range. The baseline is then determined from a sequential empty cell trace. However, trace-to-trace variations in the relative sample and reference beam channels arise predominantly due to drifts in the interference fringes of the two detectors windows and filters (the sample cell windows are mounted at Brewster's angle to minimize reflections) and to beam wander from pressure-induced displacements and from thermals drifts of the phasematching oven for the $LiNbO_3$ nonlinear optical mixing crystal. The phasematching fluctuations are peculiar to the difference-frequency laser, but the other problems are common to any high-resolution transmission measurements. We are now developing a digitally-tuned F-center laser system with enough power to do direct optoacoustic absorption (rather than transmission) spectroscopy in order to improve the baseline reproducibility for collisional interference and for wing measurement. This work is supported by NASA.

3. Heterodyne Frequency Measurements for Nitric Oxide (NO)
(A. G. Maki, J. S. Wells, and A. Hinz)

For certain measurement applications, especially those involving laser techniques, it is often important to know quite accurately the frequencies of the absorption lines of NO. By using heterodyne frequency counting techniques we have measured 28 transitions of NO from 1750 to 1930 cm^{-1}. With the help of other measurements in the literature, especially microwave and radio frequency measurements, we have determined an improved set of constants to describe the infrared spectrum of NO. With these constants, very accurate tables of energy levels and transition frequencies have been prepared for NO. This work is supported by NASA.

4. New Measurements and Analysis for Nitric Acid (HNO_3)
(A. G. Maki, A. Fayt, J. Wells, Wm. B. Olson, and A. Goldman)

Over the past several years we have been involved in the measurement and analysis of the spectrum of nitric acid with the goal of producing an atlas or compilation of transition frequencies and intensities. Such a compilation is very useful for the analysis of remote sensing data being accumulated in various programs run by NASA and other agencies. As an example, Dr. Linda Brown (JPL) has taken our latest line-list for the ν_2 band of HNO_3 (near 1723 cm^{-1}) and added it to the data bank she has accumulated to help her in the analysis of ATMOS data. She was very pleased with the accuracy and completeness of our data. Dr. A. Goldmann (University of Denver) has also been very anxious to use our data on nitric acid and from time to time requests an updated copy of our latest data.

This past year new diode measurements were completed on the high rotational transitions of the ν_5 band of HNO_3. These measurements, when combined with microwave and earlier infrared measurements from this laboratory, provided a more accurate set of ro-vibrational constants for the ν_2 band that enabled us to calculate an improved line-list. This improved line-list, consisting of about 12,000 entries, has been circulated to various interested parties and will be included in the next version of the AFGL-trace gases tape, which is the major data source for most atmospheric workers.

The analysis of the highly perturbed ν_5 and $2\nu_9$ bands has been sucessfully accomplished by using a new computer program which fits data for two asymmetric rotor bands that are coupled through Fermi resonance and certain other resonances. This analysis allows us to fit even the most highly perturbed transitions with an overall standard deviation of 0.0007 cm^{-1} which is the accuracy expected since a number of transitions used in the fit are known to be overlapped even though a diode laser with nearly Doppler limited resolution was used for the measurements. Fig. 2.5 shows a particularly clean portion of the P-branch region of ν_5 in which the transitions are identified. In this figure it is easy to see how the perturbation shifts the $K_a < 13$ transitions to high frequencies while it shifts the $K_a > 13$ transitions to low frequency.

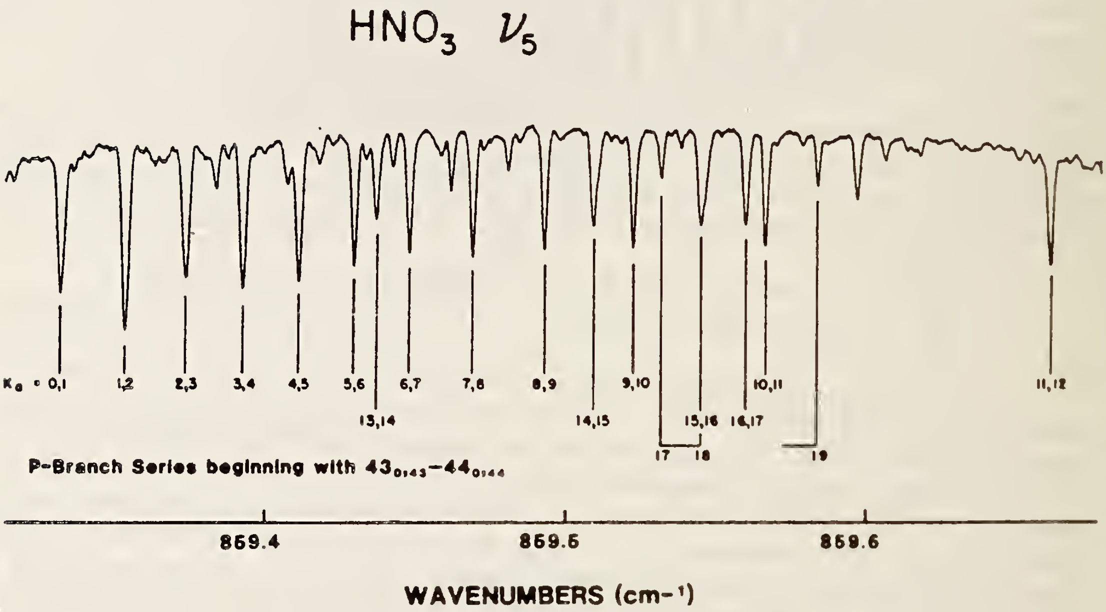


Fig. 2.5 Region of the P-branch in the ν_5 band of nitric acid.

Because of a high degree of correlation between some constants, this work will not be complete until a few more carefully chosen transitions are measured to try to reduce the correlation as much as possible. Then it will be necessary to test a new computer program which has been written to prepare an atlas of line positions and intensities for these two bands. We can anticipate that a complete line-list will be ready for the 850 - 930 cm^{-1} region of HNO_3 within the next year. An important part of this work will be the determination of the relative signs and magnitudes of the transition moments for ν_5 and $2\nu_9$. This work is supported by NASA.

5. Rotational Intensity Dependence Measured for ClO

(A. G. Maki, J. B. Burkholder, P. D. Hammer, C. J. Howard, G. Thompson, and C. Chackerian)

New frequency and relative intensity data on ClO have been determined using some diode laser measurements from this laboratory and some FTS measurements from the NOAA-Environmental Research Laboratory in Boulder, CO. Last year we described the reasons for this work, namely the need to verify the line positions and intensities in a search for the reason for discrepancies between infrared and microwave measurements of atmospheric ClO. After the work was begun here, it was learned that NOAA was making similar measurements and we joined forces.

One of the goals of this work was to measure the rotational dependence of the intensities of the fundamental infrared band of ClO. The rotational dependence is related to the ratio of the dipole moment of ClO to the vibrational transition moment. Since the transition moment seems to be small and the dipole moment is known to be fairly large, it was expected that the rotational dependence would be significant and could, in fact, be used to determine the transition moment. Our measurements did not require a knowledge of the concentration of ClO whereas all previous techniques had involved a measurement of the concentration of ClO in the absorption cell; a difficult and controversial measurement.

This work is now completed and a manuscript has been prepared but the results can be summarized as follows:

o The ClO line frequencies are now known with greater accuracy, especially for the P-branch lines. While the new line positions are different from the old by as much as 20 MHz, the difference is not enough to reconcile the problems with the field measurements.

o The rotational dependence of the line intensities is now known, but it only affects the derived concentration of ClO by 10 to 15% whereas the discrepancy is larger than that.

o From the rotational dependence, the transition moment has been derived and it agrees with the previous value of 11.8 cm^{-2} atm^{-1}, although the present results are not as accurate as we had hoped for.

o By several arguments, including a determination of the temperature from intensity measurements, it has been shown that the laboratory measurements involve ClO that is in thermodynamic equilibrium at room temperature.

o It has been shown that both the infrared and microwave field measurements involve ClO transitions that originate from the same vibronic state which is the lowest vibronic state.

The net results of this work is that we are unable to explain the problems with the field measurements, but the problems do not come from the laboratory data. This work is supported by NASA.

6. Analysis of the Spectrum of H_2O_2

(W. B. Olson, R. H. Hunt, A. G. Maki, and J. W. Brault)

Rotational constants of the 0G and 1G torsional states and the matrix element coupling these states have been determined by fitting to a model of two coupled asymmetric rotors. The fitted data were primarily combination differences. Those for the 0G torsional state were formed from published values of submillimeter wave transitions for low values of K_a, and those for high K_a (up to K_a = 10) were obtained from assigned transitions in the ν_5 OH stretching band. There are as yet no assigned submillimeter transitions involving the 1G torsional state, and all of the combination differences for this torsional state were obtained from the assigned transitions in the torsional hotband $\nu_5 + \nu_4(1U) - (1G)$.

Combination differences alone do not supply enough information to determine all the relevant parameters, i.e., they do not give direct information on the energy difference between the origins of the 0G and 1G torsional states. The rotational-torsional energies of the 0G state for K_a = 8 are only about 3 cm^{-1} above those for K_a = 6 in the 1G torsional state at low J, but because of the perturbation the levels of the two states are pushed apart, the separation increasing with increasing J to about 7 cm^{-1} at J = 25. Mixing of the wavefunctions of the 0G, K_a = 8 levels with those of 1G, K_a = 6 through the perturbation leads to perturbation enhanced transitions from 1G, K_a = 6 to the ν_5 state with K_a = 7. Although these could be considered normally allowed transitions of a difference band, no transitions can be observed at J values lower than 15. It is only at this and higher values of J (to 25) that the wavefunction mixing is sufficiently large so as to provide sufficient intensity that the transitions may be observed. Differences between the normal transitions from 0G, K_a = 8 to K_a = 7 in ν_5, and the perturbation enhanced transitions from 1G, K_a = 6 to the same upper state levels provides direct information on the separation of the lower torsional state origins.

We obtained valuable supplementary information by assignment of the weak spectrum of the sum band from the 0G state to $\nu_5 + \nu_4(1U)$. Direct differences between levels of the 0G and 1G torsional states were obtained by differences of transitions with the same J and K_a in the 0G and 1G torsional states to the same upper state level in the $\nu_5 + \nu_4(1U)$ vibrational-torsional state. Final constants are not yet available, but the fit is quite satisfactory at the present stage of refinement. The origin of the 1G torsional state is 254.550 cm^{-1}, about 0.35 cm^{-1} above the value obtained from the medium resolution far infrared spectrum. Our experimental value for the matrix element for the interaction of the 0G and 1G torsional states proves to be only 15% higher than the value calculated by Hunt, Leacock, Peters, and Hecht [J. Chem. Phys. 42, 1931

(1965)]. Considering the complexity of their model and uncertainties in parameters required for input for their calculations, the agreement with our experimental value may be considered excellent.

7. Future Plans

In the coming year an atlas of absorption line frequencies and intensities will be completed for the ν_5 and $2\nu_9$ bands of HNO_3 near 880 cm^{-1}. This atlas will include all the transitions to these two states from the ground state including those transitions that are strongly perturbed by the effects of the Fermi resonance between these two states. We also expect to complete a paper describing the analysis of the spectrum of the ν_5 and $2\nu_9$ bands and also to complete a paper on the analysis of the ν_3 and ν_4 bands near 1300 cm^{-1}. This work is needed by various laboratories that are studying the concentration of nitric acid and nitrogen oxides in the atmosphere in connection with the ozone problem as well as the greenhouse effect.

By using a long path cell we should also like to make some heterodyne measurements on some of the weaker bands of OCS such as 11^10-00^00 (1372 cm^{-1}) 03^10 - 00^00 (1573 cm^{-1}) and 00^01-02^00 (1015 cm^{-1}). These measurements would locate more energy levels with respect to the ground state and would give us frequency data for the 520 cm^{-1} and 2100 cm^{-1} regions, as well as other regions.

We also expect to have new Fourier transform spectra of the lowest frequency fundamental band of SO_2 near 500 cm^{-1}. Both frequency and relative intensity measurements will be made on this band and the goal will be to produce a set of band constants that will enable us and others to accurately calculate the infrared spectrum of SO_2 in the 400-600 cm^{-1} region for any temperature appropriate to an atmospheric path. Understanding atmospheric SO_2, is, of course, important for understanding the acid rain problem.

C. Spectroscopy of Hydrogen-bonded and van der Waals Complexes

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 BOMEM Fourier transform spectrometer in both the mid- and far- infrared, and studies using the pulsed beam Fourier transform microwave spectrometer are reported. The major efforts this year deal with structural determinations of weakly bound dimers from microwave spectra and potentials derived from extensive infrared spectra. This program has benefitted greatly this past year from collaborations with guest workers. We certainly plan to continue work in this direction for the forseeable future.

1. Rotational Spectrum and Structure of CF_3H-NH_3
(G. T. Fraser, F. J. Lovas, R. D. Suenram, D. D. Nelson, Jr., and W. Klemperer)

The rotational spectrum of CF_3H-NH_3 has been obtained using a pulsed nozzle Fourier transform microwave spectrometer. A symmetric top spectrum is observed that is consistent with free internal rotation of the NH_3 subunit against the CF_3H subunit. Rotational transitions have been measured for both the ground and first excited internal rotor state of the complex. The spectroscopic constants which have been obtained include: $B_0 = 1996.903(2)$ MHz, $D_J = 3.46(12)$ kHz, and $eQ_q{}^N = - 3.186(8)$ MHz. From the quadrupole coupling constant of the nitrogen nucleus, $eQ_q{}^N$, the bending amplitude of the NH_3 unit is determined to be 22.57(10)°. The hydrogen bond length is 2.314(5) A and the weak bond stretching force constant is 0.066(2) mdyn/A. The bond length and stretching force constant for CF_3H-NH_3 are similar in value to those determined for $HCCH-NH_3$ (2.33 A and 0.070 mdyn/A, respectively).

2. Rotational Spectrum of the Hydrogen-bonded Formamide-water Dimer
(R. D. Suenram, F. J. Lovas, G. T. Fraser, J. Zozom, and C. W. Gillies)

The characterization of hydrogen bonding between peptides and water molecules is one of the most challenging problems in modern science. The fundamental peptide-water hydrogen bonding may be exemplified by the prototypical formamide-water species. To date most of the information available on these systems has been provided by ab initio calculations. Now for the first time the complex of these two species has been investigated experimentally by employing a pulsed molecular beam Fabry-Perot microwave spectrometer with a heated pulsed nozzle.

Based on the ab initio calculations of Jasien and Stevens, [J. Chem. Phys. 84, 3271 (1986)], we have investigated the rotational spectrum of the lower energy form of the formamide-water complex. A planar cyclic double hydrogen bonded structure was calculated to be the lowest energy form, and the observed spectrum is in excellent agreement with this conclusion. The rotational constants obtained are listed in Table 2.1. Comparison of the ^{14}N nuclear electronic quadrupole coupling constants between the complex and formamide indicates that the complex is slightly non-planar with an angle of 16.8° between the planes of the subunits. The structure of the complex is illustrated in Fig. 2.6.

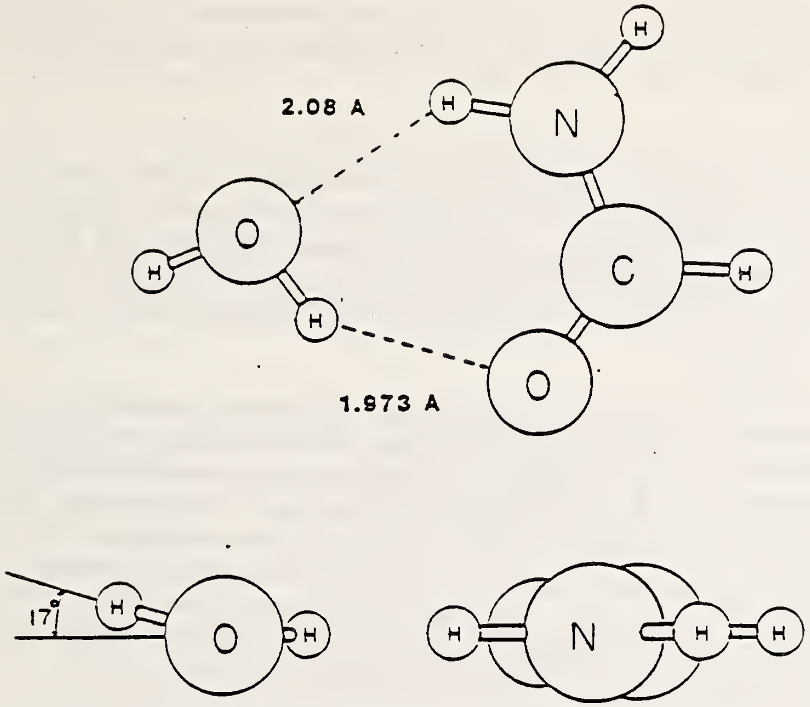


Fig. 2.6 Structure of the formamide-water dimer.

Table 2.1 Molecular constants determined from the microwave spectra of $NH_2CHO\cdots H_2O$ and $NH_2CHO\cdots HOCH_3$

Parameter	$NH_2CHO\cdots H_2O$ Value (MHz)	$NH_2CHO\cdots HOCH_3$ Value (MHz)
A	11227.913(34)	10186.69(15)
B	4586.997(2)	2088.86(8)
C	3258.872(3)	1764.18(6)
eQq_{aa}	1.330(5)	1.287(7)
eQq_{bb}	2.038(5)	2.026(6)
eQq_{cc}	-3.3685(5)	-3.313(6)
Δ $(=I_c-I_a-I_b)$	-0.1095 μA^2	-5.05 μA^2

3. Microwave Spectrum and Properties of the Methanol-Formamide Dimer

(F. J. Lovas, R. D. Suenram, G. T. Fraser, J. Zozom, and C. W. Gillies)

Recent *ab initio* calculations on formamide-water and formamide-methanol performed by Jasien and Stevens of the Quantum Chemistry Group [J. Chem. Phys. 84, 3271 (1986)] indicated that the most stable form of each is a double hydrogen bonded planar ring structure. The results of the formamide-water study discussed above are quite consistent with the theoretical structure, although evidence for slight non-planarity is given.

Since the methanol complex is expected to have a structure similar to that of the water complex, we have examined formamide-methanol. The spectra were obtained in a pulsed beam Fabry-Perot microwave spectrometer with a heated nozzle containing liquid formamide. Rotational assignments were considerably aided by the unique hyperfine structure. The rotational analysis provided the rotational and hyperfine constants shown in Table 2.1. The rotational constants are consistent with the ring structure, but the out-of-plane moment and hyperfine constants indicate that the complex is non-planar (disregarding the methyl group).

With the monomer geometries fixed, a rotation of 15° about the HO axis (moving the CH_3 group out of the plane of the remaining atoms) provides good agreement with the observed moments of inertia. The structure of the complex is shown in two views Figs. 2.7. The internal rotation of the methyl group has also been observed. Analysis of the A-E splittings provides a barrier to internal rotation of 231 cm^{-1}, which is about 38% lower than in free methanol.

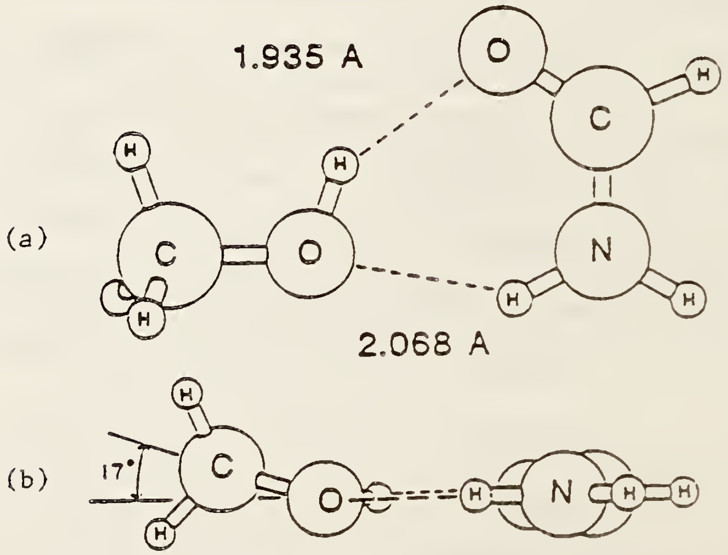


Fig. 2.7 Structure of the formamide-methanol dimer (a) top view (b) side view.

4. Microwave Spectra and Structures of the van der Waals Complexes Ar-Formamide and Ar-Methanol

(C. W. Gillies, J. Zozom, G. T. Fraser, R. D. Suenram, and F. J. Lovas)

During the course of characterizing the formamide-water and formamide-methanol complexes, we detected the spectra of two additional complexes. One of these showed ^{14}N nuclear quadrupole hyperfine structure while the second exhibited no splittings. By using Ne as the carrier gas in place of Ar in the pulsed beam expansion, it was clear that each species contained Ar.

Assignment of the hyperfine structure on the first species provided a unique rotational state assignment for the Ar-formamide complex. Spectral fitting provides the distortion free rotational constants A = 10725.32 MHz, B = 1771.58 MHz and C = 1549.53 MHz. These constants indicate a non-planar structure as shown in Fig. 2.8 with the Ar at 45° to the formamide plane.

Based on chemical evidence we identify the second species as Ar-methanol and have assigned the J = 3 - 2 and J = 4 - 3 a-type R-branch transitions. The rotational constants are consistent with a T- shape structure as illustrated in Fig. 2.9. A number of strong unassigned lines remain which we believe is evidence for near free internal rotation of the methanol subunit.

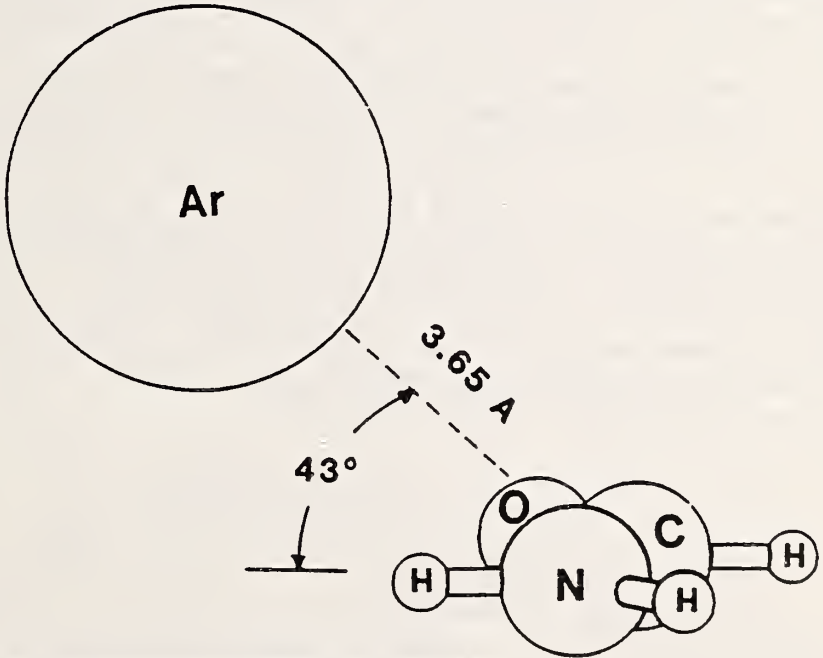


Fig. 2.8 Structure of the Argon formamide complex.

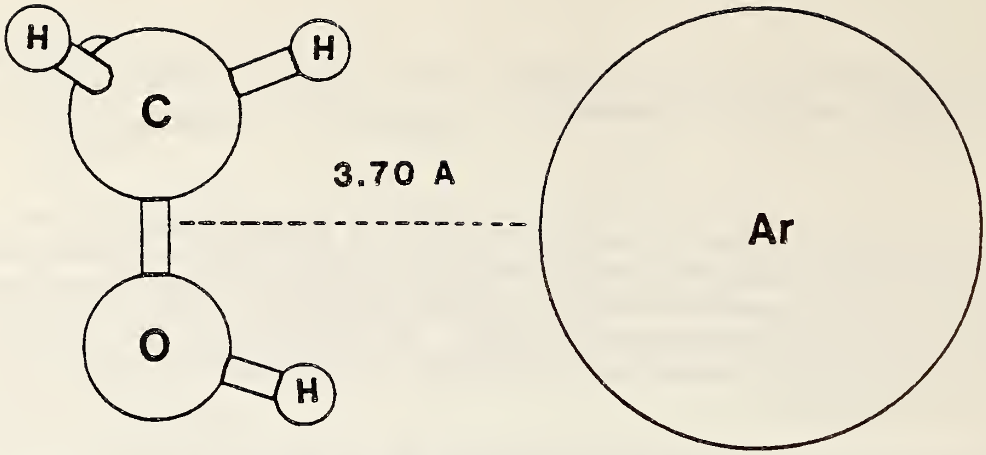


Fig. 2.9 Structure of the Argon-methanol complex.

5. Nearly Free Internal Rotation in Ar-CH_3Cl Determined from its Microwave Spectrum

(G. T. Fraser, R. D. Suenram, and F. J. Lovas)

Rotational spectra of Ar-CH_3Cl, for both Cl isotopes, have been observed, at 4 kHz resolution, using a pulsed nozzle Fourier transform microwave spectrometer. The observed spectra are consistent with a T-shaped complex in which the methyl group is undergoing nearly free internal rotation. Analysis of the ground (A-state) internal rotor state spectrum for Ar-CH_3Cl using an asymmetrical top Hamiltonian produces the spectroscopic constants listed in Table 2.2 for both the ^{35}Cl and ^{37}Cl isotopic forms. A combined analysis of the ground and excited internal rotor states (E-state) places an upper bound of 20 cm^{-1} on the three fold barrier to internal rotation. The Coriolis interactions in the E-state also allow the determination of $|eQq_{ab}|$ for Ar-$CH_3{}^{35}Cl$ as 13.0(3) MHz. The symmetry axis of the CH_3Cl subunit is nearly perpendicular (-82°) to the line joining the centers of mass of the two binding partners. The isotopic data indicate that the Cl end of the methyl chloride is tilted toward the argon. The distance between the centers of mass of the two subunits is 3.7825 A for Ar-CH_3 ^{35}Cl and 3.7839 A for Ar-CH_3 ^{37}Cl implying an Ar-Cl distance of 3.750 A. Centrifugal distortion analysis yields a weak bond stretching force constant of 0.0157 mdyn/A and stretching frequency of 34.6 cm^{-1} for Ar-CH_3 ^{35}Cl.

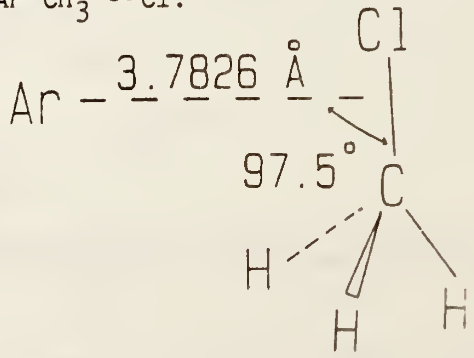


Fig. 2.10 Structure of the Argon-methylchloride complex.

Table 2.2 Asymmetric rotor constants (in MHz) for the A internal rotor states of $ArCH_3{}^{35}Cl$ and $ArCH_3{}^{37}Cl$.

	$ArCH_3{}^{35}Cl$	$ArCH_3{}^{37}Cl$
A	13633.020(14)[a]	13436.8700(56)[a]
B	1593.5683(79)	1565.075(12)
C	1420.4572(52)	1395.6126(36)
Δ_J	0.01216(14)	0.01280(41)
Δ_{JK}	0.1381(48)	0.1392(13)
δ_J	0.00096(17)	0.00150(15)
H_{JJK}	-0.00058(25)	. . .
eQq_{aa}	34.895(30)	27.432(27)
eQq_{bb}	-72.185(25)	-56.799(19)
eQq_{cc}	37.290(35)	29.367(25)

---

a. Experimental uncertainties are reported as two standard deviations from the least squares fits.

6. The Microwave Spectrum of the K=0 States of $Ar-NH_3$

(D. D. Nelson, Jr., G. T. Fraser, K. I. Peterson, K. Zhao, W. Klemperer, F. J. Lovas, and R. D. Suenram)

The microwave spectrum of $Ar-NH_3$ has been obtained using molecular beam electric resonance spectroscopy and pulsed nozzle Fourier transform microwave spectroscopy. The spectrum is complicated by nonrigidity and most of the transitions are not yet assigned. A $\Delta J=0$, K=0 progression is assigned, however, and from it the following spectroscopic constants are obtained for $Ar-{}^{14}NH_3$: $(B + C)/2 = 2876.849(2)$ MHz, $D_J = 0.0887(2)$ MHz, $eqQ_{aa} = 0.350(8)$ MHz, and $\mu_a = 0.2803(3)$ D. For $Ar-{}^{15}NH_3$ we obtain: $B + C)/2 = 2768.701(1)$ MHz, and $D_J = 0.0822(1)$ MHz. The distance between the Ar atom and the ${}^{14}NH_3$ center of mass, R_{CH}, is calculated in the free internal rotor limit and obtained as 3.8358 Å. The weak bond stretching force constant is 0.00840(2) mdyn/Å which corresponds to a weak bond stretching frequency of 34.6(1) cm^{-1}. The NH_3 orientation in the complex is determined primarily on the basis of the measured dipole moment projection and the quadrupole coupling constant. It is concluded that the $Ar-NH_3$ intermolecular potential is nearly isotropic and that the NH_3 subunit undergoes practically free internal rotation in each of its angular degrees of freedom. Spectroscopic evidence has been obtained which indicates that the NH_3 subunit also inverts within the complex. These conclusions concerning the internal dynamics in the $Ar-NH_3$ complex are in complete agreement with the model initially proposed in preliminary report concerning the microwave and infrared spectra of this species (Fraser et al., J. Chem. Phys. 82, 2535 (1985)).

7. Van der Waals Potentials from the Infrared Spectra of Rare Gas-HF Complexes

(G. T. Fraser and A. S. Pine)

The rare gas-hydrogen halide (Rg-HX) van der Waals complexes provide a simple, systematic series for studying weak molecular interactions pertinent to collisional and condensed phase properties. Last year we reported high-resolution tunable infrared laser spectra of the rare gas-HCl species including the observations of rotational predissociation, manifest as a sharp cutoff of the J progression within a band, and of the large-amplitude bending or librational motion from the anomalously strong bend-stretch combination band. In the present work we have extended the study to the rare gas-HF species using a difference-frequency laser to record the HF stretching fundamentals, ν_1, of Ar-, Kr- and Xe-HF under thermal equilibrium conditions at $T \cong 211$ K for path lengths up to 80 m. The observed Xe-HF spectra are shown in Fig. 2.11 along with simulations calculated from the measured and predicted rovibrational constants for the ν_1 fundamental nd $\nu_1 + \nu_3 - \nu_3$ hot band.

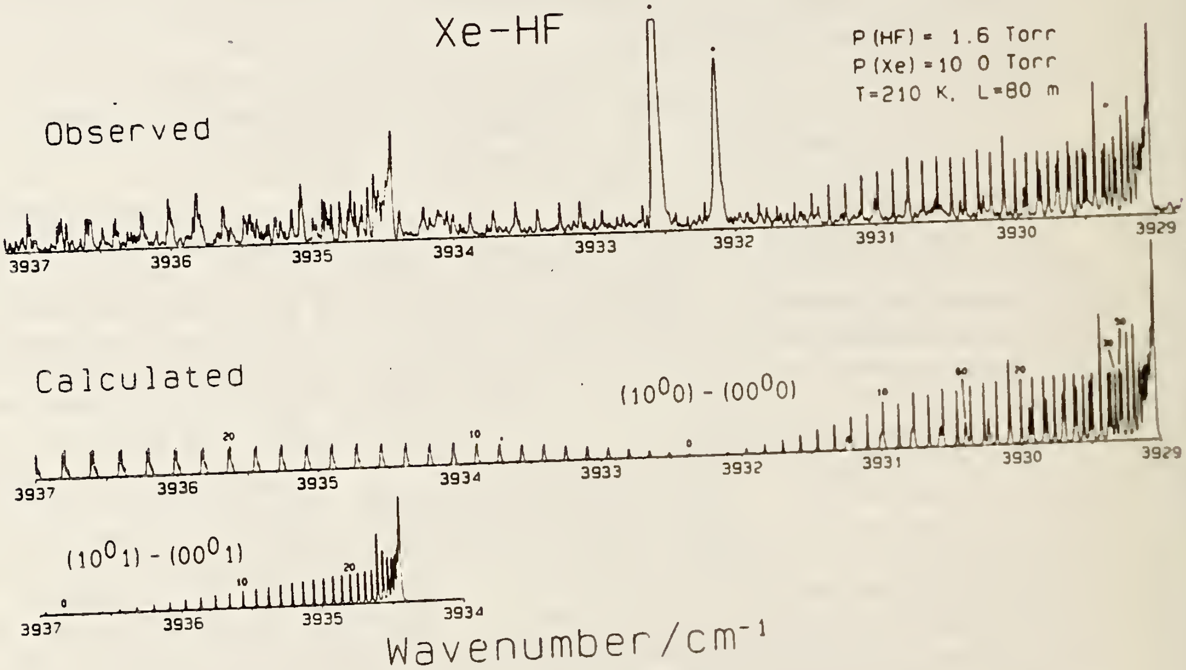


Fig. 2.11 Spectrum of the Xe-HF van der Waals complex for an absorption path length of 80 m and a temperature of $T = 211$ K; observed (top) and calculated (bottom).

Rotational structure has been observed up to or approaching rotational predissociation, permitting us to model the effective radial van der Waals potentials for these complexes. For example, Ar-HF is found to predissociate by tunneling through the centrifugal barrier at J=40 in the ground vibrational state, leading to the empirical potentials shown in Fig. 2.12. These potentials provide good estimates for the binding energies, D_0, and the van der Waals stretching frequencies, ν_3, in the ground (v_1=0) and excited (v_1=1) states of the molecules. For v_1=0 in Ar-HF, Kr-HF and Xe-HF, we find D_0 = 102, 133, and 181 cm^{-1} and ν_3 = 39.2, 41.1, and 43.4 cm^{-1} respectively. The ν_3 modes characterized by the model potentials aid in the assignment of the $\nu_1 + \nu_3 - \nu_3$ hot bands observed in our spectra. The band centers for the ν_1 fundamentals are all down-shifted in frequency from the isolated HF monomer by $\Delta\nu$ = -9.654, -17.518 and -29.185 cm^{-1} for the Ar, Kr, and Xe complexes respectively, indicating that the van der Waals bonds are some 10 to 15% stronger in the excited vibrational state. This increased vibrational attraction also results in a contraction of the van der Waals radial coordinate manifest in the larger rotational constants observed for ν_1; $\Delta B/B_0$ = +0.35, +1.00 and +1.75% for Ar-, Kr-, and Xe-HF. We have also observed the Q branch of the $\nu_1 + \nu_2$ stretch-bend combination band in Ar-HF some 70.2 cm^{-1} above the ν_1 fundamental with a large negative $\Delta B/B_0$ = -2.00% implying a strong anisotropy in the potential.

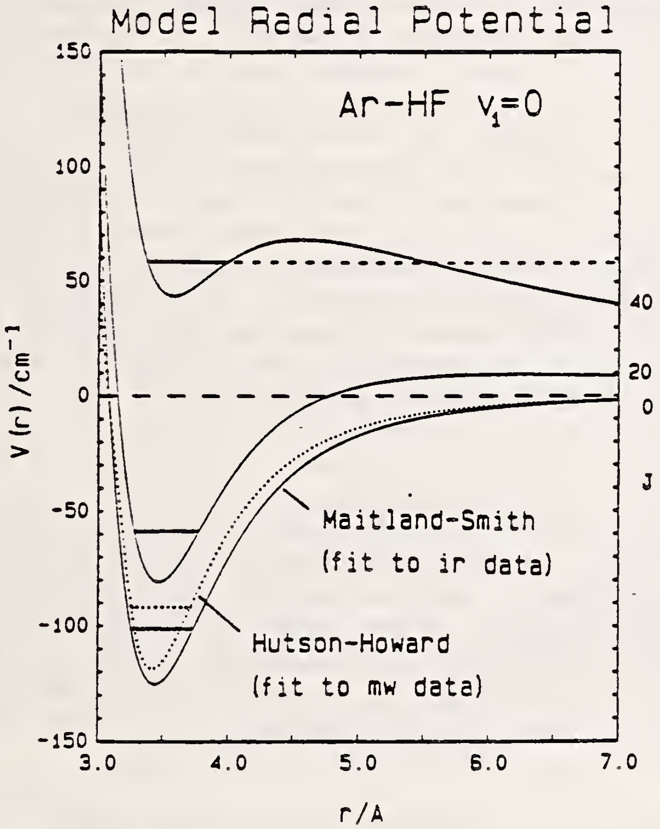


Fig. 2.12 Empirical potentials for Ar-HF derived from spectroscopic data.

8. NATO-Advanced Research Workshop
(A. Weber)

A NATO-Advanced Research Workshop on "Structure and Dynamics of Weakly Bound Molecules Complexes was conducted in Acquafredda di Maratea, Italy in September 1986. The purpose of this Workshop was to bring together researchers active in the field of high resolution spectroscopy and dynamics of van der Waals and hydrogen-bonded molecular complexes in order to assess the present state of knowledge, to communicate directions and progress of research already underway and to indicate directions, potential and level of effort needed for future research. Seventy scientists from nearly all NATO countries participated in this Workshop. The topics taken up included the determination of structures by microwave, molecular beam electric resonance, high resolution infrared, and visible spectroscopy, rotational and vibrational predissociation determined from spectral line widths and from time dependent photodissociation experiments, determination of potential energy surfaces from experimental data and from ab initio calculations, as well as stability and dissociation dynamics. The proceedings of the Workshop will be published in the NATO-ASI series of publications.

9. Future Plans

During the past year the pulsed beam Fourier transform microwave spectrometer (FTMWS) has provided rotational spectra of both new dimers and van der Waals complexes. Further work in this direction will continue next year. A number of dimer studies have been started, but are not yet complete due to the complexity of the observed spectra. These include studies of CH_3NH_2-H_2O, CH_3OH-NH_3 and several new species observed in Ar/O3 expansions. We hope to complete the assignment of these spectra during the coming year.

We will also test several new molecular beam designs. One design allows mixing two beams in the nozzle exit channel for the study of dimers of species which react, e.g., ammonium halides. A second design will provide a dc electric discharge in the beam exit channel which we hope will generate free radical species.

One of the major thrusts during FY87 will be the development of a pulsed laser ablation system which can be used in conjunction with the FTMWS to study molecular species that are normally non-volatile. The high power pulsed laser has been ordered and the pumping system is in place. All that remains is to design a vacuum chamber to allow the laser-target to be interfaced with a pulsed nozzle and the FTMWS.

A second area of major emphasis will be to investigate the feasibility of incorporating a cryogenically cooled, extremely low noise mixer device in the FTMWS. Theoretically improvements in signal-to-noise with this type of device could be two or three orders of magnitude.

Infrared investigations will also be performed on molecular-beam adiabatically-cooled systems. A pulsed molecular beam apparatus is now under construction and will be used for absorption spectroscopy with the aid of various tunable lasers. A cw-molecular-beam laser resonance apparatus is now under development and scheduled for completion during the coming year for vibrational predissociation measurements. Also under development is a high resolution tunable F-center laser system for high power excitation of van der Waals complexes for vibrational predissociation studies.

D. Matrix Isolation Spectroscopy

1. Fluorine-Atom Reaction Study

(M. E. Jacox)

Some years ago, the infrared spectra of cis- and trans-HOCO were obtained in this laboratory by the reaction of photolytically generated OH with a CO matrix. These species are of considerable interest to the combustion scientist, since the OH + CO reaction is the principal process by which CO_2 is formed in combustion systems. Because HOCO can hydrogen-bond to the CO matrix, it was desirable to obtain the spectra of its rotamers in an argon matrix. However, molecules cannot diffuse through solid argon under the conditions necessary for effective matrix isolation. Therefore, it was not feasible to study the OH + CO reaction in solid argon. Preliminary studies, outlined in the Annual Report for FY85, have shown that the reaction of F atoms with HCOOH provides a suitable source of trans-HOCO. Early in FY86, further isotopic studies on the F + HCOOH system were conducted using the Beckman IR-9 infrared spectrophotometer.

2. Excited Argon-Atom Reaction Studies

(M. E. Jacox)

As was reported in the Annual Report for FY85, a good yield of trans-HOCO can also be obtained by codepositing the Ar:HCOOH sample with a beam of argon atoms excited in a low-power microwave discharge. This method of preparation of trans-HOCO has the advantage of eliminating contributions of HOCO•••HF from the spectrum. Detailed isotopic studies of trans-HOCO formed in this system were also performed using the Beckman IR-9. However, the product yield on deuterium substitution was relatively low. Therefore, completion was deferred until the BOMEM Fourier transform system can be used. The greater frequency accuracy of this experimental system will be valuable for the determination of carbon-13 and oxygen-18 isotopic shifts. In turn, these isotopic data will permit derivation of an improved vibrational potential function for trans-HOCO.

The accessibility of the near infrared spectral region using the BOMEM system made possible a detailed series of experiments on the interaction of excited argon atoms with acetylene. Previous studies in this laboratory have shown that this sampling configuration provides a consistently high yield of the HC_2 free radical, an important intermediate in astrophysical and combustion systems. Extensive deuterium- and carbon-isotopic substitution studies spanning the 700-7900 cm^{-1} spectral region were conducted at a resolution of 0.2 cm^{-1}.

The mid-infrared studies yielded a more precise value of 1846.2 cm^{-1} for the CC-stretching frequency of HC_2. Several weak absorptions between 2100 and 3400 cm^{-1} were also assigned to HC_2. An absorption at 3610 cm^{-1} has previously been assigned (M. E. Jacox, Chem. Phys. 7, 424 (1975)) as the CH stretching fundamental of HC_2. Although this value is anomalously high for a CH-stretching fundamental, the observation of Fermi resonance with the first overtone of the CC-stretching fundamental for $H^{12}C^{13}C$ and for $H^{13}C_2$ indicates that the energy level of HC_2 which contributes this absorption must be of Σ^+ vibronic symmetry.

Recently, Curl, Carrick, and Merer (R. F. Curl, P. G. Carrick, and A. J. Merer, J. Chem. Phys. 82, 3479 (1985)) have assigned prominent gas-phase absorptions at 3796, 4012, and 4108 cm^{-1} observed by color-center laser spectroscopy in a discharge through polyacetylene to combination bands arising from the ground state of HC_2. Counterparts of these three bands at 3806, 4022, and 4134 cm^{-1} are prominent in the matrix experiments, consistent with such an assignment. The corresponding absorptions for the carbon-13 substituted species were also observed in the matrix experiments.

The matrix studies have provided the first observation of the A $^2\Pi$ - A $^2\Sigma^+$ absorption band system of HC_2 in the 4200-7900 cm^{-1} spectral region. As is evident from Fig. 2.13, a rich spectrum is obtained. The product absorptions shown in trace (b), the spectrum obtained in an

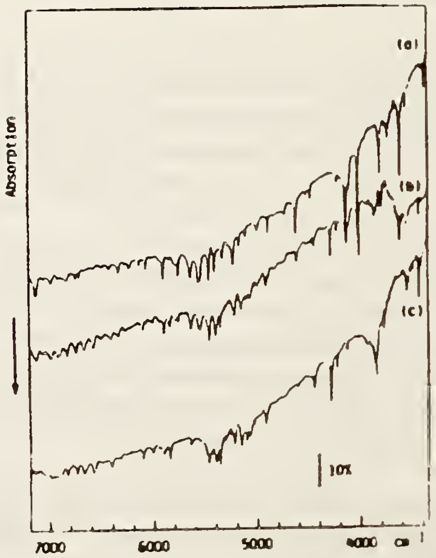


Fig. 2.13 HC_2 (DC_2) absorption spectrum between 3500 and 7200 cm^{-1} observed on codeposition of Ar: C_2H_2-d_n sample with a beam of excited argon atoms. (a) Ar: C_2H_2 = 800 + Ar^*; (b) Ar: HCCD = 200 + Ar^*; (c) Ar: C_2D_2 = 150 + Ar^*.

experiment using an HCCD sample, are the sum of those characteristic of C_2H_2 samples (trace (a)) and C_2D_2 samples (trace (c)), supporting the assignment of all of the peaks in this spectral region to HC_2 and DC_2. There are concentrations of peaks at intervals of approximately 1500 cm^{-1}, appropriate for a progression in the upper-state CC-stretching frequency. The superposed structure is contributed by extensive perturbation by high vibrational levels of the ground state. Although the ground-state bending vibration has not yet been directly observed, both it and the bending fundamental of HC_2 in the A $^2\Pi$ state are expected to occur at very low frequencies, as has been observed (C. Fridh and L. Asbrink, J. Electron Spectrosc. Relat. Phenom. 7, 119 (1975)) for the isoelectronic species HCN^+. Such perturbations in the spectrum of NO_2 are well known. Their occurrence for HC_2 helps to explain the properties of the emission spectrum observed on photolysis of acetylene in the gas phase. Depending on the photolysis wavelength, several workers have observed unstructured emission by HC_2 at wavelengths from the near ultraviolet to the cutoff of an InSb detector in the mid-infrared. Anomalously long lifetimes, between about 5 and 30 μs, are typical. Douglas (A. E. Douglas, J. Chem. Phys. 45, 1007 (1966)) has considered the increase in fluorescence lifetime which is associated with extensive interaction between two electronic states.

Although a detailed assignment of all of the matrix data has not been possible, the shifts on carbon-13 substitution appear to be sufficiently regular that correlations can be made with reasonable certainty. The isotopic shifts indicate that most of the peaks involve CC-stretching excitations. Of particular interest is a peak at 4622 cm^{-1}, which shifts by 103 cm^{-1} for $H^{13}C_2$. It is difficult to explain such a large shift except by postulating that two quanta of CC-stretching vibration are excited in the transition. Such an assignment would place the origin of the transition some 3000 cm^{-1} lower, or near 1600 cm^{-1}. A definitive assignment must await rotational analysis of the gas-phase absorption spectrum. Because all of the absorptions which are observed in the matrix experiments must arise from the X(000) state of the molecule, the data should be useful in the analysis of spectra of HC_2 obtained in future gas-phase studies in other laboratories.

3. Reaction Intermediates in the Decomposition of Energetic Materials (M. E. Jacox)

As a part of a project on the spectroscopic characterization of reaction intermediates in the decomposition of energetic materials, supported in part by the Army Research Office, studies of the products of the H + HCN reaction were also conducted on the BOMEM system. This reaction is of especial interest because H_2CN is a potential intermediate in the decomposition of the solid propellants HMX and RDX. Preliminary studies had provided evidence for the formation of CN and of three CH_2X species (presumably H_2CN and cis- and trans-HCNH) when H atoms produced by a microwave discharge through an $Ar:H_2$ mixture react with HCN in an argon matrix. BOMEM observations between 700 and 4000 cm^{-1} were conducted with a resolution of 0.2 cm^{-1}. The peak at 1336.6 cm^{-1}, which appeared even when low-energy H atoms were formed by the mercury-arc photolysis of HI, was shifted by only 0.1 cm^{-1} on carbon-13 substitution, but by 3.0 cm^{-1} on nitrogen-15 substitution. This behavior is similar to that of the 1500 cm^{-1} CH_2 "scissors" fundamental of H_2CO. Since H_2CN is calculated to be the most stable isomer and since it has been identified in earlier studies of the esr spectrum of products of the mercury-arc photolysis of Ar:HCN:HI samples, the assignment of the 1336.6 cm^{-1} peak to the CH_2 "scissors" fundamental of H_2CN is strongly indicated. The carbon-13 isotopic shift of the 3104 cm^{-1} peak, tentatively attributed to a HCNH species, requires its assignment to a CH-stretching fundamental. Carbon-13 and nitrogen-15 isotopic shifts were also observed for the 886.3 cm^{-1} absorption, contributed by a photochemically unstable HCNH species, probably the cis-rotamer. Despite the greater sensitivity of the BOMEM interferometer, other infrared absorptions which can be assigned to these three products have not been identified. The interferometer system was also used for survey scans of the 4000-8000- and 10,000-20,000 cm^{-1} spectral regions, but no absorptions which could be assigned to the analog of the red bands of the isoelectronic species HCO were detected.

In a preliminary Ebert scan of the ultraviolet spectrum which results on 122-nm photolyis of an Ar:HCN sample, moderately intense absorptions appeared at 34990 (overlapped by the OH A-X 1-0 absorption) and 35436 cm^{-1}. These two peaks correspond closely with gas-phase absorptions previously attributed to H_2CN, formed on flash photolysis of several more complicated precursor molecules. Several less intense peaks extending to 37764 cm^{-1} may have been contributed by previously unidentified bands of H_2CN. Further studies are needed to confirm this identification.

In an earlier study in this laboratory, the nitromethyl free radical, CH_2NO_2, was stabilized by the reaction of F atoms with CH_3NO_2 in an argon matrix, and the first spectroscopic data for this species were reported. Most of the vibrational fundamentals were observed for five isotopic species of nitromethyl, and a tentative vibrational assignment was proposed. The wealth of data available from these experiments suggested that a detailed normal coordinate analysis should be feasible. Among the important questions which such an analysis would address are whether the molecule is asymmetric, as had been proposed as a result of a recent ab initio calculation, and whether the unpaired electron contributes to partial double-bond character for the CN bond. A least-squares force constant adjustment calculation has recently been conducted. All of the observed frequencies can be fitted very well for a planar C_{2v} molecular structure. The vibrational assignment proposed in the earlier experimental paper has been somewhat revised. The magnitude of the CN-stretching force constant is appropriate for a single bond. A manuscript presenting the detailed results of the normal coordinate calculations is being prepared for publication.

A manifold has been designed and constructed to permit matrix isolation sampling of low vapor pressure materials by controlling the pressure of argon with which they are in equilibrium. This manifold will be used for studies of the spectra of products of the photolysis of phenol and nitrobenzene, also a part of the current ARO project.

4. Future Plans

During the coming year, highest priority must be given to the completion of a number of important projects which have already been discussed. These projects include BOMEM studies of the infrared spectrum of trans-HOCO and Ebert studies of the electronic spectra of the H + HCN reaction products. Detailed studies of products of the photolysis of benzene, phenol, and nitrobenzene be conducted using the BOMEM system. Studies of the products of the reaction of O atoms with these three molecules will also be conducted.

Studies begun in 1985 on the reaction of SiH_4 with H, Cl, and O atoms produced in a discharge are also planned. The potential stabilization of SiH_n and SiH_nO species is of interest in relation both to basic chemical research and to applied studies of plasma etching.

Infrared studies of interesting and important F-atom reaction systems- e.g., F + cyclopropane--will continue to be conducted. However, emphasis will now be placed on UV-visible studies of F-atom reaction products, for which there is a substantial backlog.

For some time, it has been planned to use a beam of excited neon atoms as a source of 16.6-16.8 eV energy for the production of small molecular ions, to be trapped in a neon matrix. This energy range should make possible the preparation of significant concentrations of such small molecular cations as HCO^+, H_2O^+, NH_3^+, and CH_4^+, not accessible in the 11.5-11.8 eV energy range provided by a beam of excited argon atoms. It is hoped that later in FY87 the excited neon atom experiments, which may provide much previously inaccessible information on the vibrational and electronic spectra of molecular ions, can begin.

E. General Spectroscopy and Theory

In addition to the previously described programmatic activities a variety of research problems are pursued in response to special opportunities, and special interests of the staff and outside guest scientists. The following are descriptions of such projects of a general nature.

1. Fourier Transform Measurements of High Temperature Species; Infrared Gas Phase Spectra of LiCl, LiH, and LiD

(W. B. Olson, G. A. Thompson, A. G. Maki, and A. Weber)

The new transfer optics for the BOMEM described below have allowed us to make high temperature measurements of the infrared spectrum of several compounds produced in a high temperature oven. So far we have measured the $\Delta v=1$ transitions of the two species LiH and LiD and the four naturally abundant isotopic species of LiCl.

A portion of the spectrum of LiCl containing 95% ^{6}Li is shown in Fig. 2.14. The complete spectrum contained over 2500 identified transitions for the various isotopic species. Vibrational transitions ranged from v=1-0 to v=8-7 and rotational transitions for J values up to 75. These transitions were fit to a set of Dunham potential constants that included 9 isotopically invariant terms and 4 terms to allow for isotopic shifts due to the break-down in the Born-Oppenheimer approximation. The standard deviation of the fit was 0.00027 cm^{-1} which is what we expect considering the slightly larger than normal Doppler linewidth of these high temperature spectra.

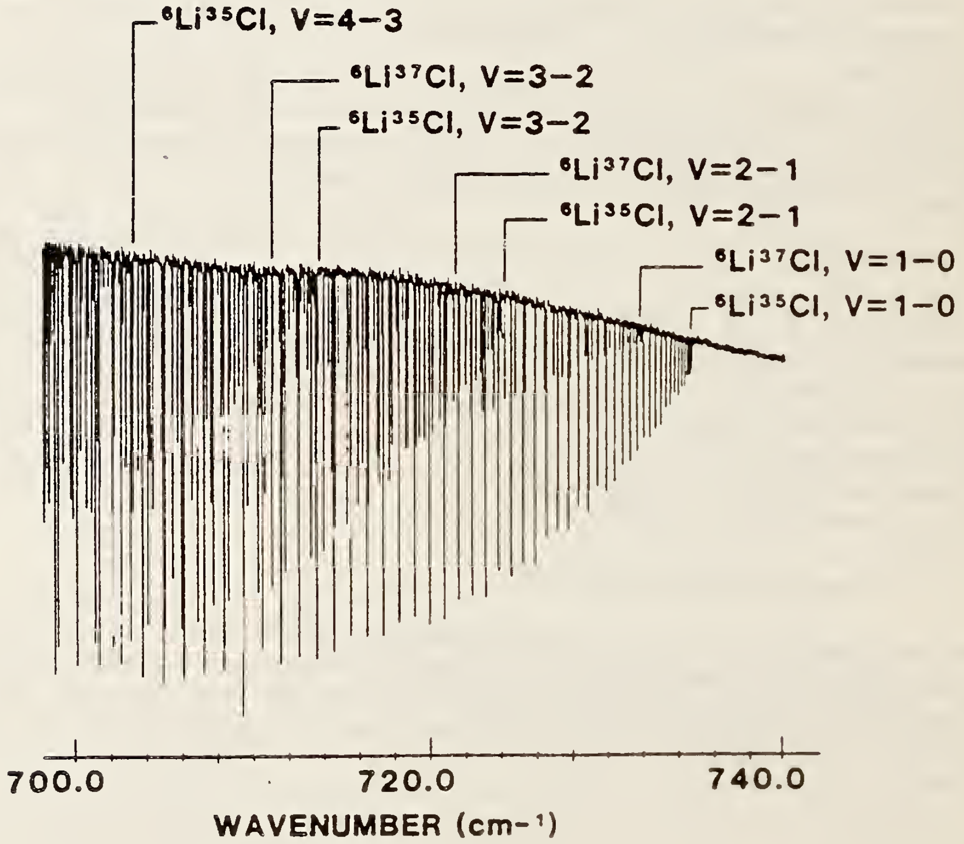


Fig. 2.14 A portion of the spectrum of ^{6}LiCl at 830°C. The locations of a number of band heads are indicated above the spectrum.

A portion of the spectrum of LiD is shown in Fig. 2.15. This spectrum is much more sparse than that of LiCl and shows the advantage of using a broad-scanning FTS instrument for making these measurements. Earlier measurements using a diode laser spectrometer were very slow because the lines were so far apart, the electronic tuning range of the spectrometer was quite small, temperature tuning was slow, and there were many gaps in the coverage.

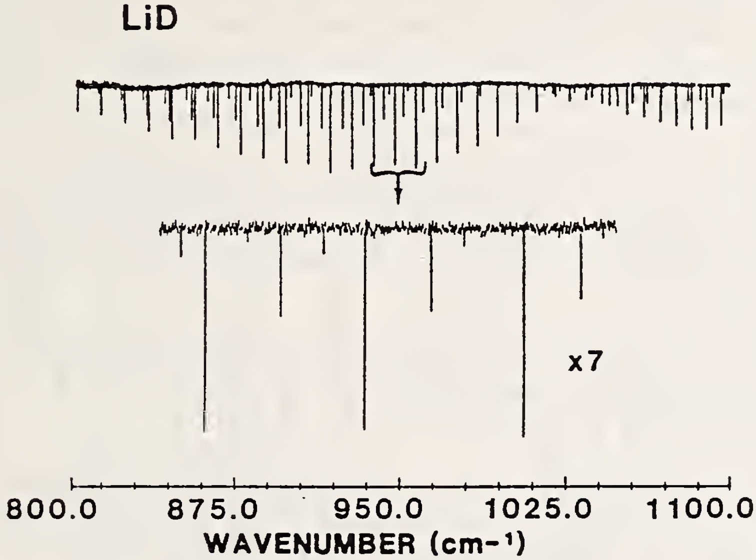


Fig. 2.15 A portion of the absorption spectrum of LiD at 750°C. The wave number scale applies to the upper spectrum.

The standard deviation of the fit of the LiH and LiD spectra (0.0076 cm^{-1}) was worse than that of LiCl because the Doppler width was larger and there seems to be more of a problem with break-down of the Born-Oppenheimer approximation. To investigate this further, we hope to measure the pure rotational spectrum of LiH at high J values to get better measurements on the higher centrifugal distortion constants.

2. Hydrogen Migration Tunneling Effects in the Rotational and Vibrational Spectrum of Protonated Acetylene $C_2H_3^+$

(J. T. Hougen)

The influence of a possible hydrogen atom migration in protonated acetylene, $C_2H_3^+$, on the high-resolution vibration-rotation spectrum of this ion was investigated. The migration model, which derives from ab initio calculations, consists of a planar structure with the three hydrogen atoms moving on an elliptical path around the two carbon atoms. Symmetry considerations for this ion were considered in terms of the permutation-inversion group G_{24}. A method for calculating energy levels for a highly idealized model of this ion can be found in the early microwave literature. In this idealized model, an equilateral triangle of three hydrogen atoms performs internal rotation about a dumbbell of two carbon atoms, with all atoms remaining in the same plane. This model gives rise to a symmetric rotor top, an asymmetric rotor frame, and a six-fold barrier to the internal rotation motion. An alternative method of calculating the energy levels of this ion, involving a more recently proposed algebraic tunneling formalism, shows that qualitatively similar results are obtained even when the hydrogens do not retain the form of a rigid equilateral triangle during their migration motion. Energy level diagrams, nuclear spin statistical weights, selection rules for electric dipole transitions, etc. were developed. It is hoped that the patterns described in the present work will aid in identifying and interpreting any spectrum of $C_2H_3^+$ obtained as a result of ongoing efforts elsewhere to record its spectrum.

3. The Torsional-Wagging Tunneling Problem and the Torsional-Wagging Rotational Problem in Methylamine

(N. Ohashi and J. T. Hougen)

A theoretical formalism is presented for fitting rotational energy levels in isolated (unperturbed) vibrational states of methylamine. This formalism is obtained by recasting and extending theoretical studies in the earlier literature, which were undertaken to help analyze the methylamine microwave spectrum. The present formalism is applicable when both the NH_2 umbrella (wagging) motion and the CH_3 internal rotation (torsion) motion take place near the high-barrier limit and leads to the usual Fourier sine and cosine series expansions for molecular energy levels. The derivation is separated into two parts, one treating the large-amplitude vibrational problem (the torsional-wagging problem) by itself, the other treating the torsional-wagging-rotational problem. In both treatments, permutation-inversion group and extended group ideas are used to determine the allowed terms in an effective rotational-tunneling Hamiltonian operator and to block diagonalize the matrix representation of this operator for a near-prolate symmetric top. Application of the method in detail to the methylamine spectrum is planned for a later study.

4. Far-Infrared Spectrum of Methylamine

(N. Ohashi, W. J. Lafferty, and W. B. Olson)

The far-infrared spectrum of CH_3NH_2 has been recorded in the region 50 to 350 cm^{-1} on the NBS BOMEM Fourier transform spectrometer with a resolution of about 0.004 cm^{-1}. The torsional band as well as pure rotational transitions originating in higher K_a levels fall in this region of the spectrum. This molecule is of more than passing interest since it has two large amplitude motions, the NH_2-wag and the CH_3-torsion, and the spectrum is rather complex as a result. Assignment of the pure rotational transitions is complete at this point, and the stronger $B_1(B_2) \leftarrow B_2(B_1)$ and $E_1 \leftarrow E_1$ components of the torsional band have been assigned. A small portion of the spectrum of the torsional band is given in Fig. 2.16 where the line assignment of two components of the ${}^rQ_4$- and ${}^rQ_5$- transitions is indicated. Ohashi and Hougen have recently derived approximate energy level formulas for CH_3NH_2, and a computer program is being written to fit the data and extract the molecular constants. Preliminary fits show that the torsional splitting in the torsional vibrational state is about 30 times larger than in the ground state, and, somewhat suprisingly, the inversion splitting in the excited state is about 3 times greater than it is in the ground state.

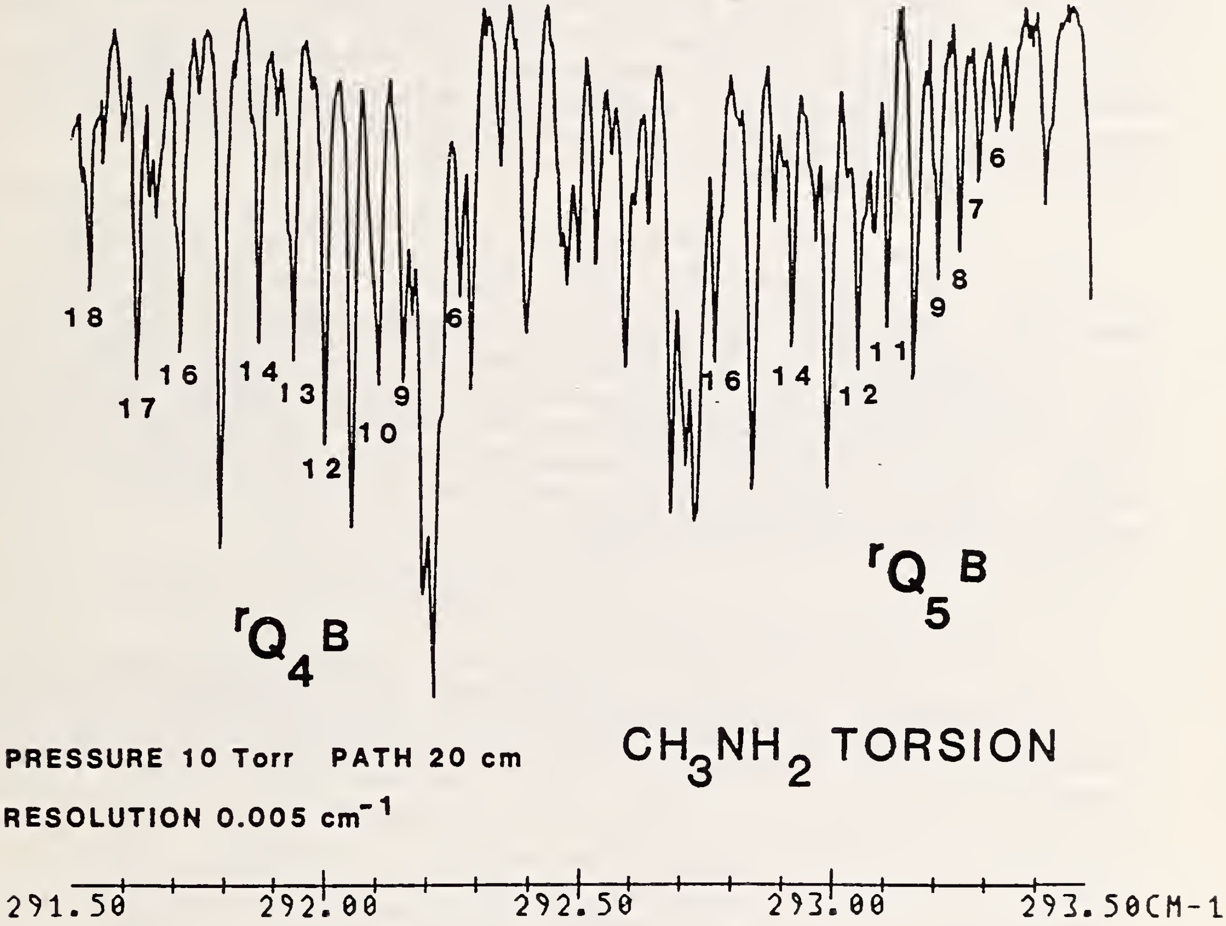


Fig. 2.16 A small portion of the torsional band of CH_3NH_2 taken with a resolution of 0.005 cm^{-1} showing the line assignments of the Q-branches of two components of the K=5-4 and K=6-5 subbands.

5. Transfer Optics System Design

(W. B. Olson)

An efficient transfer optics system has been designed and constructed to couple the BOMEM FTS to an existing heat pipe in order to obtain infrared absorption spectra of species which can only be seen in the gas phase at high temperatures. This system has enabled the high resolution observation of several bands of LiCl and LiH leading to improved vibrational and rotational constants for these species.

The necessity of efficient and practical transfer optics for the heat pipe was the "mother of the invention" of a fairly general and powerful approach to transfer optics design via a "system" concept of first order design, through analytical equations directly coupling required throughput or entendue to the ray transfer matrix of an optical system. The necessary ray transfer matrix for the system is uniquely determined (except for sign), and one can relatively rapidly calculate required distances and focal lengths of spherical mirrors required to implement a practical system.

With a single optical element, in our applications a concave spherical mirror, one has no degrees of freedom with which to make the design convenient. With each added optical element one gains two degrees of freedom to adjust features. With three optical elements one can specify all four distances in the system to convenient or practical values, and from these calculate the focal lengths required for each of the three mirrors. This is the method used for the heat pipe transfer optics system design. The resultant optical system for the heat pipe works well, but no precise explanation can be given of the function of the individual optical elements in simple, familiar terms.

6. Analysis of Infrared Spectra of SiH_3D
(R. Schaefer, R. Lovejoy, W. B. Olson, and G. Tarrago)

An analysis of the ν_2 parallel band of $^{28}SiH_3D$ has been nearly completed through the collaborative efforts of Ron Schaefer and Roland Lovejoy of Lehigh University, W. B. Olson of NBS, and Ginette Tarrago of the University of Paris, South. For a complete analysis the interactions of ν_2 with the parallel and perpendicular components of $2\nu_6$ had to be taken into account by simultaneous solution of a secular determinant containing all three vibrational states. Three different types of perturbations giving readily evident displacements of absorption line positions in ν_2 were found to be due to perturbations with the perpendicular component of $2\nu_6$.

The perpendicular component of $2\nu_6$ proved difficult to assign because it was so weak, and additional spectra were run with a pressure-pathlength product a factor of ten higher than that used for the initial runs. This also increased the intensity of many other weak lines from unidentified hot bands and silicon isotopes. Two techniques for getting assignments, and checking them through the quality of the least squares fit, and the success of using molecular parameters from the fit to calculate new line positions at higher values of J and K eventually lead to a reasonably complete set of assignments for this weak band. Many of the strongest lines in $2\nu_6$ are actually perturbation allowed transitions which get their intensity from the parallel component of $2\nu_6$ through the l-type doubling matrix element.

The secular determinant used for this work contained all possible matrix elements through the fourth order of the twice transformed Hamiltonian. A number of the higher order terms were found to be insignificant, while others of high order are significant, but did not make major contributions to the energies of any of the levels.

The values of the major low order molecular parameters of $2\nu_6$ are in quite satisfactory agreement with those of the ν_6 fundamental. The origin of the ν_2 band is at 1593.962 cm^{-1}, and that of $2\nu_6$ is at 1557.258 cm^{-1}. An article describing this work in detail is being prepared for publication.

7. Future Plans

In the coming year we plan to exploit the optical system used for the high temperature Fourier transform experiments to obtain Fourier transform measurements of other systems unstable under normal room temperature conditions. We shall try to observe the far infrared spectrum of several systems such as the pure rotational spectrum of LiH and the spectrum of compounds with low frequency vibrations (e.g., NaCl). We shall also try to observe the spectrum of compounds produced in an electric discharge with the hope that this may enable us to look at the spectrum of some metal oxides or hydrides.

Theoretical studies will focus further on large amplitude motions. Topics to be examined are the CH_3NH_2 microwave and far infrared spectra both in terms of pure rotational spectra and torsional spectra. The water dimer Hamiltonian and spectral consequences will be examined in further detail.

3. LASER PHOTOCHEMISTRY GROUP

D. F. R. Burgess, Jr., M. P. Casassa, R. R. Cavanagh, L. B. Elwell,
E. J. Heilweil, D. S. King, and J. C. Stephenson

This group primarily does quantum-state specific studies of molecular dynamics. A common factor in the research described below is the role of energy transfer in the spectroscopy and kinetics of molecules. Research on molecular dynamics of molecules on surfaces is done in collaboration with the Surface Science Division.

A. Condensed Phase Energy Transfer

(M. P. Casassa, R. R. Cavanagh, L. B. Elwell, E. J. Heilweil, and J. C. Stephenson)

The major effort in the condensed phase energy transfer program has been directed at the study of vibrational energy transfer (VET). During the past year we have successfully measured the rates of energy transfer from vibrationally excited chemical bonds in liquids, solids, and in molecules bound to surfaces.

This research area was extensively discussed in the 1985 Annual Report. The present report does not repeat last year's lengthly discussion of experimental detail and program rationale. In summary, we used a picosecond infrared pump/probe method to perform time-resolved measurements of the vibrational energy relaxation rate (T_1^{-1}) for the high frequency modes of species chemisorbed on a silica (SiO_2) surface in a variety of chemical environments. Previously, energy transfer rates have been measured for the vibrations of many molecules in the gas phase, and for a few molecules in liquids and low temperature solids. However, our experiments were the first to measure vibrational energy transfer rates for vibrations on surfaces.

A summary of some surface T_1 results is given in Table 3.1. These data were limited to vibrations with frequencies $\nu > 2500$ cm^{-1} since the psec ir pulses necessary to cause transient bleaching of the surface vibrations were generated in a Nd-YAG-pumped $LiNbO_3$ OPA ($LiNbO_3$ only transmits $\nu > 2500$ cm^{-1}). The data suggest the following conclusions. T_1 times are longer than most people expected prior to these measurements. Energy relaxation rates (T_1^{-1}) are much slower by factors of 100-2000, than would be deduced from spectral bandwidths of these surface vibrations. At the vacuum interface, the MOH (M=B, Si, Al, Zn) and MOD stretching vibrations relax via anharmonic coupling to spatially adjacent vibrational modes, particularly the M-O-H bending mode. One reason BOH relaxes faster than SiOH is that its local accepting modes are higher in frequency and hence a better match to the OH stretch. The faster relaxation of NH_2 and OCH_3 vibrations is consistant with energy transfer from the NH stretches to the NH_2 bend and similarly from the CH stretches to the CH bends (with which the CH stretches are known to couple strongly via Fermi resonance). It is reasonable that T_1 of OH in the commercial zeolite ZSM-5

Table 3.1 T_1 decay times at room temperature for various surface vibrations

System	$\nu(cm^{-1})$	$T_1(ps)$	$k(10^9\ s^{-1})$	Notes
SiOH/vacuum	$\nu_{OH}=3750$	220±20	4.9	Pressed SiO_2 disk
SiOH/CCl_4	$\nu_{OH}=3690$	159±16	6.3	Dry SiO_2 dispersion
SiOH/CF_2Br_2	$\nu_{OH}=3690$	140±30	7.1	"
SiOH/CH_2Cl_2	$\nu_{OH}=3660$	102±20	9.8	"
SiOH/C_6H_6	$\nu_{OH}=3625$	87±30	11.0	"
SiOH/C_6D_6	$\nu_{OH}=3625$	80±30	12.0	"
SiOH/H_2O/CCl_4	$\nu_{OH}=3690$	56±10	18.0	SiOH T_1, $-5H_2O/100Å^2$ physisorbed
SiOD/vacuum	$\nu_{OD}=2760$	155±16	6.5	OD T_1 with 67% OH replaced by OD
BOH/vacuum BOH/CCl_4	$\nu_{OH}=3700$	-70	-14.3	
$SiNH_2$/vacuum $SiNH_2$/CCl_4	$\nu_{NH}=3460$ 3520	≤20	≥50	Pulsewidth limited signal, ΔT/T -5% for both stretches
$SiOCH_3$/vacuum	$\nu=2860$ 3000	<5(?)	>280(?)	No pulse saturation observed for any CH-stretching mode
OH on zeolite ZSM-5/CCl_4 (Si/Al=3600)	$\nu_{OH}=3690$	140±25	7.1	Pressed disk CCl_4 saturated
OH on ZnO	$\nu_{OH}=3485$	≤10	≥100	$\Delta T/T_o \approx 12\%$ pulsewidth limited
ZnO, no OH	3600-3750	≤10	≥100	Electronic excitation of free carrier absorption ΔT/T ≈10%.

is the same as on fumed SiO_2, since the high Si/Al ratio ($\approx$3600) of this particular sample precluded any appreciable bonding of OH on aluminate sites. The very rapid relaxation of OH on the semiconductor ZnO surface may not be caused by anharmonic coupling to adjacent vibrational modes but by coupling to electronic excitations of impurity states in the ZnO.

Relaxation rates for the surface vibrations increase in the presence of solvents (solid/liquids vs. solid/vacuum interface). The increase in rate is minor for solvents like CCl_4 which have no resonant high frequency modes, (ν^3_{C-Cl} = 770 cm^{-1} is the highest fundamental). An increase in rate of about a factor of 2.5 occurs for benzene which has many nearly resonant ($\nu_{OH} \rightarrow$benzene $\nu_1 + \nu_4$, etc.) internal vibrational states which could accept some or all of the OH quantum. Alternatively, vibrational relaxation rates may increase in the presence of solvents which perturb the OH($v=0 \rightarrow 1$) absorption through hydrogen bonding or van der Waals interactions. The dependence of T_1 for surface vibrations on chemical environment, temperature, and other factors previously mentioned is always qualitatively in the direction expected by analogy to T_1 data in homogeneous phases. However, standard first order perturbation theory calculations (e.g., solid state multiphonon relaxation theory) do not quantitatively agree with these trends.

During the past year a new picosecond dye laser was constructed for the purpose of generating tunable ir pulses for $\nu < 2500$ cm^{-1}. This enables us to pump and probe interesting surface vibrations such as CO bound to metals. For vibrational relaxation on a metal surface, it is thought that a qualitatively different energy transfer mechanism, damping by excitation of electron-hole pairs in the metal, may be dominant. If this is true, then perhaps the broad spectral bandwidths (~5-50 cm^{-1} FWHM) observed for high frequency vibrations on metals are really due to T_1 broadening, as has often been assumed. A direct time-resolved measurement of vibrational relaxation for a molecule on a metal surface is crucial to assessing the importance of this damping mechanism, and for understanding surface spectroscopy and kinetics.

The new laser is a synch-pumped tunable dye laser pumped by the second harmonic (532 nm) of the rejected trains of ps pulses from our actively-passively modelocked 10 Hz ps Nd-YAG laser. A single pulse from the dye laser is cavity-dumped, amplified to ~500 μJ/pulse and mixed in a $LiIO_3$ crystal with a single 532 nm pulse derived from the same 10 Hz YAG. Typically pulses of ~25 ps duration, 20 μJ, and tunable throughout the CO stretching region (~4 cm^{-1} FWHM), are generated by this system. These pulses are sufficient to perform pump/probe ir saturation measurements of T_1 for CO(v=1) bound to small metal particles (e.g., Pt) on an insulator support (e.g., SiO_2). The Pt particle size (or other transition metal) can be controlled so that CO will chemisorb to either isolated metal atoms or larger crystallites. Measurement of T_1 for CO on the surface of supported metal particles should begin mid October 1986.

Initial experiments with the new laser system have involved measuring T_1 for stretching vibrations of CO bound to transition metal atoms (metal carbonyl complexes) dissolved in CCl_4 and other solvents. In terms of vibrational spectroscopy, the inorganic carbonyls are analogous to surface-bound CO (the assignment of surface CO sites as "bridge-bonded" on "terminal" frequently involves comparing the surface vibrational frequencies with corresponding metal carbonyls). Figure 3.1 shows ir pump-probe saturation data giving T_1 for the F_{1u} CO(v=1) mode of $Cr(CO)_6$ in carbon tetrachloride and hexane solutions. T_1 is very long ($T_1 \cong 490$ ps corresponds to 20,000 vibrational periods) and is clearly unrelated to the 8 cm^{-1} FWHM infrared Lorentzian bandwidth. We expect a similar T_1 lifetime for CO bound to isolated surface metal atoms on a dielectric support. A wide variety of metal carbonyls and nitrosyls are available and are excellent model compounds to answer questions about VET mechanisms, such as: is there a "heavy atom effect"; is T_1 for bridge-bonded CO different from terminal CO?; how is vibrational energy exchanged among modes of different ligands (adsorbates) bound to the same or neighboring metal atoms?

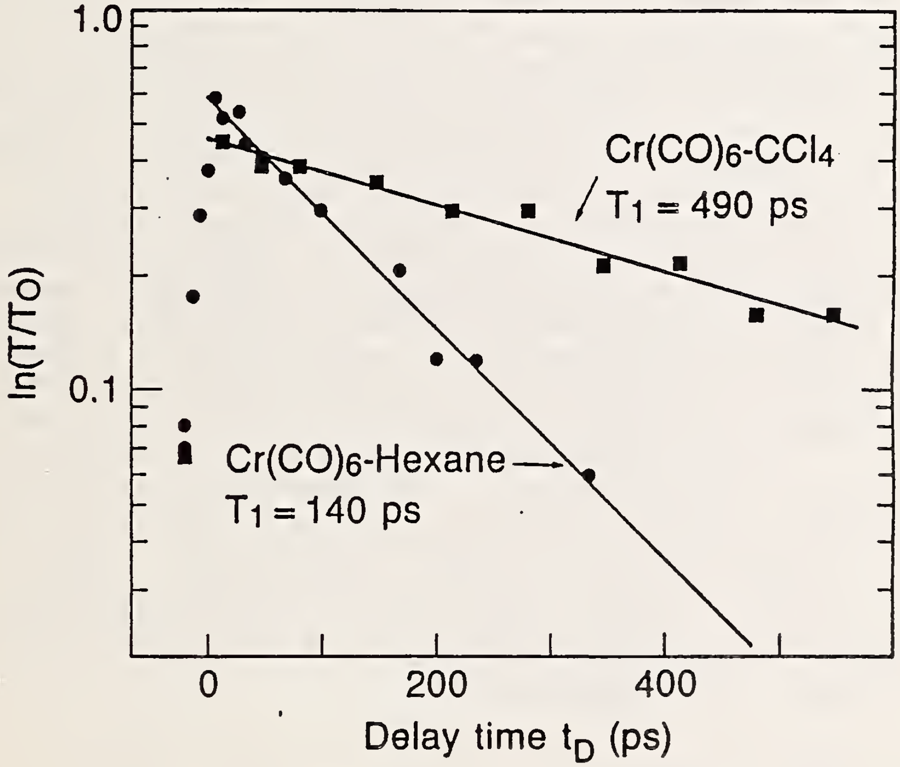


Fig. 3.1 Vibrational relaxation times for the F_{1u} CO(v=1) mode of $Cr(CO)_6$ in solutions of hexane and carbon tetrachloride.

Studies of related energy transfer processes at semiconductor surfaces have also recently begun in collaboration with Dr. Claude Sandroff of AT & T Bell Laboratories. The luminescence decay times of "exciton-like" electronic states of extremely small (≤ 30Å diameter) and planar PbI_2 and $PbBr_2$ colloidal particles suspended in organic solvents are being measured. Preliminary experiments for PbI_2 and $PbBr_2$ in alcohol, using the third harmonic of the picosecond Nd^{+3}:YAG (355nm for PbI_2) and the second harmonic of the synchronously pumped dye laser (310 nm for $PbBr_2$) as excitation pulses, have yielded ca. 1100 and 900 ps lifetimes, respectively. These emission lifetimes were measured with a streak camera system. It is believed that measurements of this sort will reveal mechanisms for light-induced chemical reactions occurring at the liquid-surface interface. These include, for example, charge-transfer and oxidation-reduction reactions that are known to occur at semiconductor surfaces.

Using the $LiNbO_3$ OPA system, a study of the T_1 relaxation times of OH(v=1) and OD(v=1) vibrations of silanol, R_3SiOH, and alcohol, R_3COH, molecules in solution was completed. The results are summarized in Table 3.2. They may be compared to the surface OH results in Table I and the OH in crystalline mica results in Table 3.3. Most of the liquid phase results can be understood in terms of an isolated binary collision (IBC) model frequently used to interpret gas phase collisional VET rates. The fact that T_1 for $(CH_3)_3SiOH \leq T_1$ for $(C_6H_5)_3SiOH$, even though the latter molecule has 500 times the total density of vibrational states, shows clearly that factors other than the total vibrational state density are important in determining T_1. The deactivation of hydroxyls of R_3MOH and R_3MOD (M=C,Si) were simply modelled using the assumption that OH(v=1) or OD(v=1) energy is initially transferred to the eleven vibrations involving the OH bond and the neighboring four tetrahedral bonds of the central M atom. Data were analyzed by considering the frequencies of those particular accepting modes, and by using the propensity rules that energy transfer will be nearly resonant, and that processes involving the fewest vibrational quantum number changes (n=number changing) will be most probable. Because of their different vibrational frequencies, there are many more nearly resonant relaxation channels, involving lower values of n, for the alcohols (n ≥ 4) than for the silanols (n ≥ 5). This may explain why the R_3COH and R_3COD molecules relax much faster than corresponding silanols. The observation that the R_3SiOD molecules relax more slowly than the R_3SiOH species is consistent with energy transfer occuring predominantly to the SiOH bending motion, and is not consistent with transfer primarily to the Si-O stretching vibration. Similar analysis for the methanols (CH_3OH, CH_3OD, CD_3OH, CD_3OD) suggests that energy transfer to the CH (CD) stretching vibrations or to the C-O stretch are probably not dominant relaxation channels.

Table 3.2 T_1 lifetimes for the OH and OD(v=1) stretching vibration in alcohols and silanols in dilute CCl_4 solution ($\leq$0.007 mole fraction) at 298 K. Error limits are $\pm\sigma$, or 10% of T_1, whichever is greater.

SILANOLS[a]	$\nu_{OH,OD}$(cm^{-1})	T_1 (ps)	ALCOHOL[a]	$\nu_{OH,OD}$(cm^{-1})	T_1 (ps)
Me_3SiOH	3690	205 ± 21	Me_3COH	3614	< 6[b]
Me_3SiOD	2722	245 ± 25			
Et_3SiOH	3689	185 ± 19	Et_3COH	3622	< 6[b]
Et_3SiOD	2722	224 ± 22	Et_3COD	2673	< 20[b]
ϕ_3SiOH	3675	206 ± 21	ϕ_3COH	3609	< 15[b]
ϕ_3SiOH	2712	292 ± 29			
$\phi_2Si(OH)_2$	3610,3679	80 ± 15	CH_3OH	3641	15 - 30[b]
$\phi_2Si(OD)_2$	2665,2710	134 ± 14	CH_3OD	2685	52 ± 17
			CD_3OH	3642	73 ± 7
			CD_3OD	2690	79 ± 17
			EtOH	3625	70 ± 10
			ϕOH	3610	5 - 20[b]
			ϕOD	2665	15 - 25[b]
			C_6F_5OD	2640	< 15[b]

[a] Me=$-CH_3$, Et=$-CH_2CH_3$, ϕ=$-C_6H_5$

[b] Limits on T_1 were deduced from computer simulation.

Table 3.3 T_1 vibrational lifetimes of the OH(v=1) stretching fundamental mode of hydroxyl ions in natural crystalline micas at 298 K. Uncertainties in T_1 are $\pm 1\sigma$. Where applicable, the samples are labelled by their Smithsonian Institution identification numbers.

Muscovite	ν_{OPA} (cm^{-1})	T_1(ps)	Biotite	ν_{OPA} (cm^{-1})	T_1(ps)
104935	3591	88 ± 16	82063	3691	198 ± 15
105013	3648	90 ± 15	C3647	3691	244 ± 15
105051	3591	83 ± 18	C3675-1	3691	220 ± 18
	3675	85 ± 8		3575	125 ± 11
B16862	3675	105 ± 36	Ruggles	3591	72 ± 20
Ruggles	3591	79 ± 8	Unknown	3540	64 ± 5
	3675	114 ± 13			

For comparison to the surface (Table 3.1) and liquid (Table 3.2) phase results, new results were obtained for the OH(v=1) T_1 lifetime of hydroxyl ions located within the two-dimensional crystalline layers of natural Muscovite and Biotite micas. Briefly, these silicate crystals are composed of a sheet of metal cations octahedrally coordinated to OH^- ions which is in turn sandwiched between two covalently linked SiO_4 tetrahedral layers. This composite layer is further stacked upon others (creating several polymorphs) to form the mica. Excess negative charge in these stacked layers is neutralized by intercalated K^+ ions which give micas their easily cleaved sheet-like character. With Al^{+3} ions in the octahedral layer, the chemical composition of Muscovite is best represented as $[KO_3<Si_{3/2} + Al_{1/2}>O_2(OH)Al_2(OH)O_2<Si_{3/2} + Al_{1/2}>O_3]_n$. Since its aluminum ions occupy two of three possible octahedral sites (two Al^{+3} and one vacancy), Muscovite is called a dioctahedral mica. Because Biotites generally have all three octahedral sites filled (e.g., by Mg^{+2} in Phlogopite), their chemical composition may be written as $[KO_3<Si_{3/2} + Al_{1/2}>O_2(OH)Mg_3(OH)O_2<Si_{3/2} + Al_{1/2}>O_3]_n$ and they are called trioctahedral micas. Substitutions for Mg^{+2} in Phlogopite (by Fe^{+3} and Al^{+3}, for example) gives rise to other forms of the Biotite family.

T_1 values for the micas are given in Table 3.3. At room temperature, the average OH(v=1) vibrational population lifetime ($T_1 \pm \sigma$) for OH^- in Muscovite is 92 ± 13 ps. For Biotite samples, absorptions arising from two distinct lattice sites yield T_1 = 221 ± 23 and 87 ± 33 ps, respectively. These energy dissipation times are comparable to those observed for the surface OH, liquid silanols, and OH in amorphous fused silica. In the micas the MOH bending frequency is in the 800-900 cm^{-1} range (like surface OH) while the M-OH stretch in the micas is lowered to 400 - 500 cm^{-1} (much lower than the stretch in silanols or for surface OH). Thus the similarily of T_1 may again be consistent with energy transfer to the MOH bend being a dominant channel. The observed trends in T_1 (Muscovite and Biotite low frequency site vs. Biotite high frequency site) can be rationalized in terms of local site structure and hydrogen bonding. The high frequency trioctahedral Biotite sites have the longest T_1 (221 ps) and are least hydrogen bonded because their out-of-plane orientation leads to little O-HO interaction with the octahehral layer oxygens. The Muscovites and lower frequency Biotite hydroxyl sites are dioctahedral sites with broader, lower frequency absorption, reduced O-HO distance (3.5Å) and increased H-bonding and a correspondingly shorter T_1.

The crystalline micas are also attractive samples for measuring transient vibrational populations by picosecond coherent anti-Stokes Raman scattering (CARS). Such measurements will give independent confirmation that the ir pump-probe experiments yield correct T_1 times. Also the CARS probing may determine what vibrational modes accept the energy following deactivation of the high frequency OH(v=1) mode. The 10 Hz dye laser described above and the 532 nm doubled Nd-YAG form the CARS probe pair. The OH(v=1) level is initially pumped by the $LiNbO_3$ OPA. Large CARS signals have been produced from crystalline mica when the dye laser was tuned to make the pulse pair resonant with the OH $v=0 \rightarrow v=1$ transition. We do not yet (mid September 1986) have time-resolved population data using this approach.

The preceeding successfully completed experiments and those now being done are all steps toward answering the questions 1) What is T_1, for a molecule on a metal surface? 2) What are the pathways of energy transfer (i.e., where does the energy go)? 3) How is VET at surfaces related to chemistry? With continued support from the Air Force Office of Scientific Research, we anticipate continuing progress toward understanding these and other important questions in condensed phase energy transfer.

The most significant questions for us to answer in the area of energy transfer for molecules on surfaces are: 1) What is T_1, for a molecule on a metal surface? 2) What are the pathways of energy transfer (i.e., where does the energy go)? 3) How is VET at surfaces related to chemistry? The experiments outlined below are planned to answer these questions.

We have several different strategies for measuring T_1 for a molecule on a metal surface. One approach is to perform our usual one color IR pump/probe time-resolved bleaching experiment for molecules on supported metal clusters. Another approach involves IR excitation of a molecular (e.g., pyridine) bound to the surface of a metal (e.g., Au) particle suspended in liquid as a sol; this would be followed by anti-Stokes Raman scattering (surface enhanced) as a time dependent probe of vibrational population. These experiments require infrared and visible laser pulses of suitable energy, bandwidth, frequency, and duration. We have two suitable laser systems which generate the difference frequency, ω_{IR}, = $\omega_1-\omega_2$, between two visible laser pulses in non-linear crystals. For frequencies $\omega_{IR} \geq 1800$ cm^{-1} we use $LiIO_3$ and for lower frequencies $900 < \omega_{IR} < 1800$ we have tried $AgGaS_2$. In addition, a new hybrid 10 Hz pulsed Nd-YAG laser, presently under construction, should generate ~8 ps, 1.06 micron pulses, and hence much shorter dye, 532 nm, difference frequency ir, and OPA ir pulses than the present apparatus produces. These shorter pulses should improve the time resolution by more than factor of four compared to the current 10 Hz ps laser system. Ir pump-probe measurements of T_1 for CO(v=1) on dispersed supported small metal particles are being attempted with this new laser source. The successful T_1 experiments on "model compounds" like the metal carbonyls will continue. Anti-Stokes Raman scattering measurements to determine the pathways (accepting modes) involved in the VET will be done, first for homogeneous model compounds such as metal carbonyls in solution and crystalline micas. It is possible that the dispersed supported metal samples may scatter so much light as to make any anti-Stokes experiments impossible. If so, we may still be able to perform such time-resolved measurements on molecules bound to the surface of colloidal metal particles in liquid suspensions.

B. Laser Diagnostics of Surface Dynamics
(D. Burgess, Jr., R. R. Cavanagh, L. B. Elwell, and D. S. King)

This program is directed at understanding energy transfer and chemical dynamics occuring at metal surfaces at a fundamental level. The approach is to apply state-resolved diagnostics, shown over the last decade in gas phase reaction and beam scattering experiments to provide a tremendous wealth of information about intermolecular potential energy surfaces to issues in surface chemistry. Thermally driven processes that have been characterized (i.e., kinetics, binding site occupation, etc.) by more conventional surface science techniques have been chosen for study because of their ubiquitous role in heterogeneous chemistry. From the viewpoint of chemical physics, elucidation of the rates and mechanisms for energy flow from a molecule into a nearby surface (dissipation) or vice versa (fluctuation) are key to a fuller, fundamental knowledge of surface controlled chemical processes.

A collaboration between CCP Molecular Spectroscopy and Surface Science Divisions has resulted in the creation of an experimental facility to perform such state-resolved studies of thermal, molecular processes at well characterized surfaces. The facility includes two ultra-high vacuum (UHV) chambers. The major chamber, for oriented single crystal work, includes traditional surface sensitive analytic tools such as mass spectrometry, ion sputtering, low-energy electron difraction and Auger electron spectroscopy. The second chamber, a test chamber for laser desorption experiments, is much smaller in scale. Two laser systems are currently available. A near transform limited excimer-pumped dye laser is dedicated to measurements of vibrational, rotational, spin-orbit, and lambda doublet distributions, orientational effects, and kinetic energy distributions for molecules (e.g., NO) desorbing from surfaces. This system is used as the state-resolved diagnostic both for thermal and laser-induced desorption. For the laser-induced thermal desorption (LITD) studies we are using a YAG laser (temporarily borrowed from the Center for Radiation Research) capable of producing either nanosecond or picosecond duration pulses to probe the time scale required to achieve equilibrium.

1. Adsorbate-Adsorbate Interactions: (NO + NH_3)/Pt(111) Thermal Desorption

In FY85 measurements of the internal state distributions for NO thermally desorbing from Pt(111) were measured both for an extensive (10-fold) range in NO coverage and under the influence of co-adsorbed CO. Unlike the earlier, apparently non-equilibrium dynamics exhibited by the NO/Ru(001) system, the results of the work on the NO/Pt(111) system may be summarized as follows: 1) the rotational levels and spin-orbit states are characterized by a common rotational temperature; 2) although the kinetic parameters describing the desorption process change significantly with coverage and the presence of co-adsorbed CO, the rotational degree of freedom of the desorbing NO is always nearly fully accommodated with the surface temperature; 3) there was no measurable alignment of the desorbing species.

In terms of the observable dynamics there was no manifestation of adsorbate-adsorbate interaction, i.e., no substantial deviation from full accommodation. In both the NO-NO and NO-CO systems the adsorbate interactions are weak-to-moderate in strength. The co-adsorption system (NO+NH_3)/Pt(111) was chosen for study in FY86 since it had been shown by TPD and EELS studies that there is a stable, surface bound complex formed upon co-adsorption of NO+NH_3 on cold Pt(111). Thermal desorption of NO and of NH_3 occurs simultaneously at a temperature much higher than characteristic of either species, implying that the rate-limiting step in the co-adsorbed system is dissociation of the more strongly bound complex.

Although the kinetics for NO desorption from Pt(111) were significantly altered by the interaction with co-adsorbed NH_3 there was no significant deviation from near-complete rotational accommodation with the surface. For surface temperatures of 150 to 400 K and NO coverages of 5% to saturation, the rotational temperature of the desorbed NO was 90 ± 5% of the instantaneous surface temperature and independent of the amount of co-adsorbed NH_3. This imples that disruption of the NO/NH_3 complex leads to NO molecules which are able to accommodate with the surface prior to desorption.

2. Laser-induced Desorption: NO/Pt(foil)

Thermal desorption techniques probe surface processes occuring under conditions of thermodynamical equilibrium. This is to say that external heating rates of 1-10 K/s are much slower than rates for energy transfer in condensed phases. To attempt to learn the important time scales for molecular energy transfer at surfaces we have implemented a program in laser-induced thermal desorption. Here it is hoped that sufficiently rapid temperature jumps (heating laser pulse durations of 10^{-8} to 2×10^{-11} s) will allow desorption or other surface processes to compete favorably with energy exchange or relaxation processes characteristic of thermal processes.

A major concern in all experiments where a laser is used to heat a surface is the accurate determination of the surface temperature. Classical heat conduction equations have been employed to establish the surface temperature in the past, and are currently being used to analyze the desorption yields obtained in this laboratory. However, experimental efforts to validate the surface temperature actually achieved due to laser heating are sparse. A direct measure of the laser perturbation of the surface properties would offer the most satisfactory probe of the heating effects. Attempts at exploiting the resulting time dependent black-body radiation as a signature of the surface temperature have not been successful. The choice of our initial system for study, NO/Pt using 3-8 nanosecond heating-laser pulses, was based on our earlier results for NO/Pt thermal desorption wherein we have always observed near-complete rotational accommodation. Our naive expectation was that desorbed NO would exhibit rotational and translational accommodation and thereby give us an in situ probe of the response of such a surface in other laser-heating experiments.

The experiments were performed on a 25 x 12 x 0.25 mm polycrystalline Pt foil in a small UHV test chamber (base pressure 2×10^{-10} torr). A frequency-doubled, 3 ns FWHM YAG laser was used to heat the surface. A spatially homogeneous portion of the collimated laser beam irradiated a 1.5 mm diameter portion of the surface with 0.5 mJ/pulse at near normal incidence. The density of desorbed NO in specific (V, J, Ω) states above the surface was probed using a frequency-doubled dye laser (0.05 cm^{-1} bandwidth, 9 ns FWHM) tuned to the (0-0) or (1-1) vibronic bands of the NO A-X electronic transition. The 1 mm diameter probe beam was aligned parallel to the surface at a distance of 4 mm. LEF from desorbed molecules in a 1.5 mm long portion of the probe beam was detected with f/2.5 collection optics, spatial masks, spectral filters, and a solar-blind photomultiplier.

The platinum surface was initially flashed clean to 1300 K, cooled to 200 K, and then exposed to a saturation dose of NO. A background pressure of 4×10^{-9} torr NO was maintained during the experiments to stabilize the surface NO concentration, which would otherwise have been slowly depleted by the LITD process. Time of flight (TOF) distributions were obtained by scanning the time delay between the desorption laser and the probe laser in 0.1 μsec increments. At the 30 mJ/cm^2 incident energy density used, the surface temperature jump was calculated to be 120 K from the optical and thermal properties of platinum and the laser pulse FWHM. This implies a maximum surface temperature of T_m=320 K.

Representative TOF distributions for desorbed NO in v=0 with low (25 cm^{-1}) to moderate (662 cm^{-1}) rotational energy are shown in Figure 3.2. The observed LEF/TOF signals correspond to maximum molecular densities of about 5×10^{-8} torr in the probed region as determined by comparison to LEF signals with NO flowing through the chamber. The prompt onset and early maximum exhibited by the molecules in the J=19.5 rotational state became increasingly more apparent as higher quantum states were probed. These data and TOF spectra for 16 other rotational states with $25 < E_R < 2162\ cm^{-1}$ suggest that there are at least two distributions of NO desorbing from the surface: a "fast" component with moderate internal excitation and a slower component with a "colder" internal energy distribution. To characterize the translational and rotational energy distributions of the desorbed NO, all of the TOF spectra were fit to the sum of two velocity distributions, each of the form $P(v) = v^4 \exp[-(a+bv+cv^2)]$, which reduces to a Maxwell-Boltzmann distribution for b=0.

For all quantum states with $25 < E_R < 2162\ cm^{-1}$, the slow component was fit by a distribution with a mean kinetic energy of $\langle E_T \rangle = 52 \pm 5$ meV, while $\langle E_T \rangle$ for the fast component continuously increased from 240 ± 35 meV to 460 ± 50 meV with increasing E_R. Maxwell-Boltzmann distributions with these average energies are characterized by effective translational temperatures $\langle E_T \rangle / 2k$ of 300 K and ranging from 1400 to 2650 K, respectively. However, the observed distributions were not Boltzmann. Each had a slightly larger energy spread $\langle E_T^2 \rangle / \langle E_T \rangle^2$ than would a Maxwell-Boltzmann distribution. The relative populations for the rotational levels were determined by their magnitudes in the TOF fits. The rotational populations for states with $25 < E_R < 662\ cm^{-1}$ were well characterized by Boltzmann distributions with temperatures of 410 ± 50 and 170 ± 20 K for the fast and slow components, respectively. The energetic NO molecules contributed 21 ± 3% to the integrated desorption flux under these experimental conditions.

TOF distributions were measured for desorbed NO(v=1,J) states with $E_R < 133\ cm^{-1}$. These were dominated by a single velocity distribution with $\langle E_T \rangle = 290 \pm 25$ meV. The NO(v=1) rotational distribution was estimated from an excitation spectrum taken at 3 μsec delay and including transitions from 7 different rotational levels. A value of $T_R(v=1) = 155 \pm 75$ K was obtained. Comparison of the integrated population in v=1 to the v=0 fast component yielded a ratio of 0.054 ± 0.027, consistent with $T_V \approx 900$ K.

To summarize the NO/Pt(foil) laser-induced thermal desorption results, at near saturation coverage from a platinum foil two components were observed. Although the mean kinetic energy of the less energetic component is comparable to the maximum surface temperature, its rotational temperature is significantly lower than the surface temperature. Such incomplete rotational energy accommodation has been observed in conventional TDS experiments for NO/Ru(001) and discussed in terms of dynamical factors in the adsorption potentials. A dramatic departure from accommodation was exhibited by the energetic NO, with its high translational energy. While this is consistent with exit channel effects which have been invoked for thermally activated H_2 recombination and CO oxidation reactions at metal surfaces, it is also consistent with a sudden (non-thermal) desorption channel. Apparently, at heating rates of 10^{10} K/s new desorption channels compete favorably with thermalizing energy relaxation pathways even under mild temperature jump conditions. This work is supported in part by the U.S. Department of Energy.

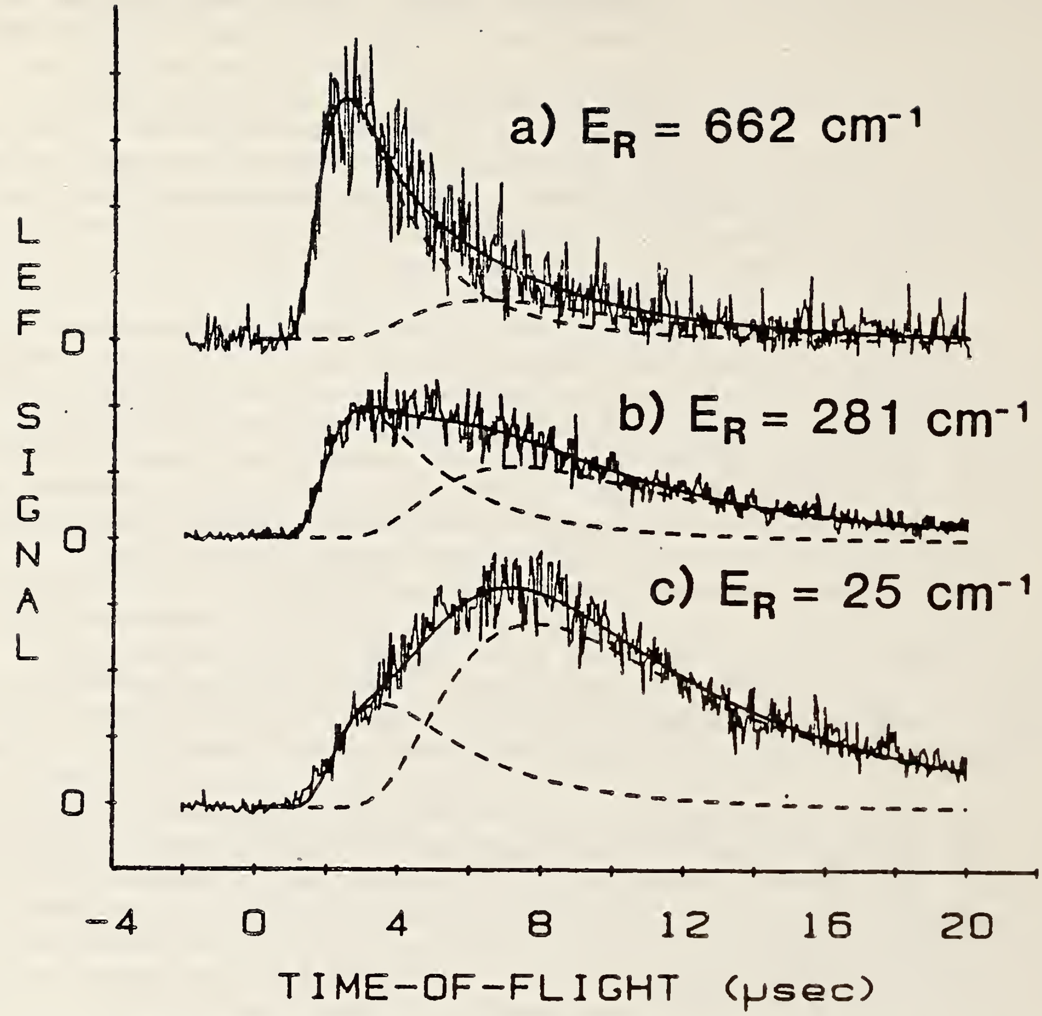


Fig. 3.2 Desorbed nitric oxide LEF signal as a function of time delay between heating and probe laser pulses for different quantum states. Spectra are normalized to NO at 294 K. Two-component fits to the data are also shown. a) J=19.5, $\langle E_T \rangle$ = 450 and 60 meV; b) J=12.5, $\langle E_T \rangle$ = 330 and 53 meV; c) J=3.5, $\langle E_T \rangle$ = 235 and 47 meV.

3. Future Plans

This work will be directed towards exploring in more detail laser-induced thermal desorption (LITD). "Non-equilibrium" behavior has been observed for NO desorbing from Pt foils at low initial surface tempeatures when driven by 3 ns, visible heating-laser pulses. We hope to answer speculations regarding the physical origin of this non-equilbrium dynamics (i.e., secondary desorption channels, recombinatory desorption, coverage dependent adsorbate interactions, binding site effects, or electronic effects) by exploring LITD results as a function of heating-laser pulse length, wavelength and energy, of surface morphology using single crystals, and of initial surface temperature, coverage and co-adsorbates.

One of the long range goals of this program is to study recombination reactions on surfaces. For technical reasons, this is difficult by thermal desorption techniques. Experiments currently underway entail the use of a variable pulse length heating laser (10 ns to 25 ps on loan from Radiation Physics for four months). These experiments should ellucidate the contribution from recombinatory desorption to the observed NO/Pt(foil) LITD signals (described above). It is anticipated that LITD will provide a powerful technique for detailed study of recombination rections.

C. Dynamics of van der Waals Molecules

(M. P. Casassa, L. B. Elwell, D. S. King, and J. C. Stephenson)

There has been substantial recent theoretical interest in the vibrational predissociation of van der Waals (vdW) molecules, but very few experiments that have looked at either the final product state distributions or obtained real time measurement of the dissociation lifetimes. We have recently studied the vibrational predissociation of the nitric oxide vdW dimer, including picosecond time-resolved measurements of the lifetime following excitation of the symmetric (v_1) and antisymmetric (v_4) stretching modes, and measurements of the complete distribution of energy in NO product fragments following v_1 excitation.

Vibrational predissociation of van der Waals molecules occurs because, in general, the constituent molecular vibrational levels lie above the vdW bond energy. Vibrational excitation and subsequent vibrational energy flow lead eventually to rupture of the weak van der Waals bond. While such systems have had great appeal as models for vibrational dynamics, the previously available lifetime data are based on indirect measurements. In our experiments, picosecond infrared pulses excited the symmetric ($\nu_1 = 1$) or antisymmetric ($\nu_4 = 1$) stretching modes of the NO dimer. The formation times of the NO fragments ejected upon vibrational predissociation were measured by laser excited fluorescence (LEF) using picosecond time-delayed ultraviolet laser pulses. A remarkable dependence of the predissociation lifetime on the vibrational mode initially excited was observed.

The NO dimer has C_{2V} symmetry with a 2.236 A N-N separation and a 99.6° O-N-N bond angle. The dimer bond energy is 800 ± 150 cm^{-1}. Photodissociation spectra have been reported for excitations of the symmetric ν_1 (vibrational symmetry A_1) and antisymmetric ν_4 (B_2) N-O stretching fundamentals at 1870 cm^{-1} and 1789 cm^{-1}, respectively. The low frequency modes associated with the vdW bond are 90 (A_2), 170 (A_1), 198 (B_2), and 263 (A_1) cm^{-1}. We used laser-excited fluorescence (LEF) spectroscopy (using a frequency doubled CO_2 laser for photolysis and a 10 ns probe dye laser) to determine the internal state distribution and kinetic energy of the NO photofragments. For fragments with internal energy $E_{int} \leq 400$ cm^{-1} (representing ≥ 97% of all products), the rotational states were adequately represented by a Boltzmann distribution with $T_{Rot} = 110$ K, for both spin orbit states. The two spin orbit states, F_1 = NO $^2\Pi_{1/2}$ and F_2 = NO $^2\Pi_{3/2}$, were formed with equal probability. The lambda doublet states were formed with equal probability. The average product internal energy was $\langle E_{int} \rangle = 135 \pm 25\ \mathrm{cm}^{-1}$.

Doppler profile measurements were made for fragments in the F_2 (J=3.5) state. Profiles measured with the propagation direction of the probe laser parallel or perpendicular to the electric vector of the photodissociation laser were indistinguishable. This indicates the angular flux of the NO photodissociation fragments was essentially isotropic. The observed Doppler profiles were "top hat" (rectangular) in shape with $0.165 \pm 0.01\ \mathrm{cm}^{-1}$ FWHM. The top hat shape implies a narrow kinetic energy distribution, a condition imposed by the photon energy and E_{int} distribution [assuming the dimers initially equilibrated with the beam (T ~ 1K)]. Computer modeling (including the fragment internal state distributions) of the observed Doppler profiles gave an average kinetic energy $\langle E_K \rangle = 400 \pm 50\ \mathrm{cm}^{-1}$ for each NO. Conservation of energy gives a bond energy $D_o = 800 \pm 150\ \mathrm{cm}^{-1}$, which may be compared to the value $D_o = 590 \pm 80\ \mathrm{cm}^{-1}$ calculated from infrared intensity measurements.

For the lifetime measurements, dilute mixtures of NO in He or H_2 were expanded through a pulsed valve operating at 4 Hz with a .75 mm diameter orifice. The observed LEF signals scaled with expansion conditions as $X^2P^{2.9}$, for NO mole fractions $0.005 \leq X \leq .02$ and nozzle stagnation pressures $3 \leq P \leq 10$ atm. This is the same scaling behavior attributed to $(NO)_2$ previously. The conditions used for the lifetime measurements were shown by mass-spectrometry and final-state energy distribution measurements to produce cluster signals dominated by NO-dimer, and exhibit rotational cooling (of uncomplexed monomer) to ~1 K.

Picosecond infrared (ir) and ultraviolet (uv) laser pulses were derived from two visible dye lasers synchronously pumped by a frequency-doubled, modelocked cw YAG laser. One dye laser was set at ω_1=17, 341 cm^{-1}. The second dye laser was tuned to ω_2 = 15,471 or 15,552 cm^{-1} so that the frequency difference, $\omega_3 = \omega_1 - \omega_2$, coincided with either the ν_1 or ν_4 fundamental. Dye amplifiers pumped by a frequency-doubled, 2 ns Q-switched YAG laser amplified both lasers to produce visible picosecond pulses at 20 Hz with typical pulse energies of 0.7 mJ (ω_1) and 0.3 mJ (ω_2). Bandwidths of these pulses were 3 cm^{-1} FWHM with autocorrelation widths of 7.5 ps FWHM and a cross - correlation width of 10 ps FWHM. Infrared pump pulses of 4μJ were obtained by difference frequency mixing ω_1 and ω_2 in $LiIO_3$. The ir pulses were focused to a 0.3 mm diameter beam waist to vibrationally excite the beam-cooled $(NO)_2$. Ultraviolet probe pulses were produced by frequency-doubling ω_2 in KDP and then summing $2\omega_2$ with residual 1.064 nm from the Q-switched YAG in KD^*P. These pulses traversed a variable optical delay and were focused to a 0.15 mm beam waist colinear with the ir pump beam.

Probe pulses polarized at the magic angle to the ir pump pulses traversed the beam at a time t_D, relative to the pump pulses, exciting those NO fragments formed in the J = 1.5-7.5 levels of the $X^2\Pi_{3/2}$ state (P_2 band head region), resulting in LEF signals directly proportional to the number of NO fragments formed during the time t_D. Previous studies showed that these probed states 1) are not appreciably populated by uncomplexed monomer in the expansion, 2) are formed with high probability in the $(NO)_2$ ν_1 photolysis, and 3) are not favorably formed in the 1870 cm^{-1} photolysis of other NO complexes. The LEF signal and pump and probe pulse energies were recorded for each shot with a computer based data acquisition system. LEF signals were normalized to the uv probe energy. Shots with ir energy falling outside a ±20% acceptance window were rejected. For each data point, a delay setting was randomly selected and 100 accepted shots were averaged.

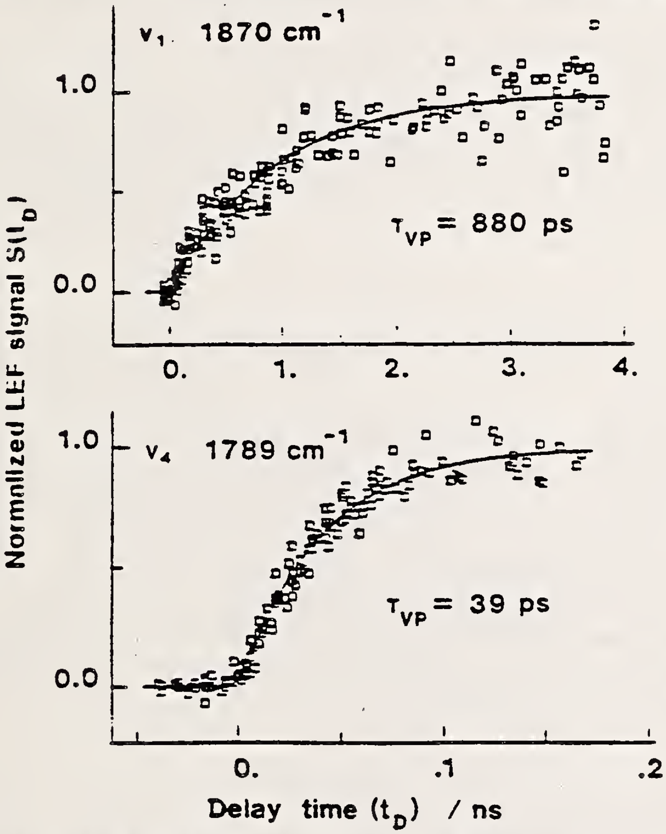


Fig. 3.3 Time-resolved appearance of NO fragments following excitations of either the symmetric (ν_1) or antisymmetric (ν_4) stretching fundamentals of the NO dimer. Note the 20-fold difference in time axes. The solid curves are least-squares fits of a simple exponential decay function with unimolecular decay rate $k_{uni} = 1/\tau_{VP}$. Although only short time measurements are included for the rapidly rising ν_4 data, there was no change in signal for delays between 150 ps and 4 ns.

Results for $(NO)_2$ $\nu_1(v=1)$ and $\nu_4(v=1)$ photodissociations are shown in Fig. 3.3. A dramatic difference in dissociation rates for these two modes of nearly equal energy is immediately apparent (Note the 20-fold difference in time axes). Only short-time measurements are shown for the rapidly rising ν_4 data; no further increase in signal was observed for delays between 150 ps and 4 ns.

If the ir laser excited an ensemble which dissociated with a single unimolecular rate constant, $k_{uni} = 1/\tau_{VP}$, the expected fragment appearance behavior would be:

$$S(t_D) = S(t_D = \infty)\ [1-\exp(t_D/\tau_{VP})].$$

Of course non-exponential or multi-exponential decay could occur. Non-linear least-squares fits of single exponential decays to the data, shown as solid curves, yield lifetimes of 880 ± 260 ps for ν_1 and 39 ± 8 ps for ν_4. These lifetimes represent average values for a distribution of rotational levels. Assuming that the ir bandwidth is 4-5 cm^{-1} (convolution of two 3 cm^{-1} Gaussians), the pump laser interacts with all $(NO)_2$ rotational levels expected to be populated in the molecular beam (If T_{ROT} = 1 K, levels with $J'' \leqq 3$, $K_a'' \leqq 2$ account for 95% of the population). Each vibrationally-excited rotational level could have a distinct predissociation lifetime. However, with the present signal-to-noise, the data at many different expansion conditions are adequately fit by the same single exponential time constant. Including additional exponentials with different decay times did not significantly improve the fit to the data (i.e., reduce chi square).

That ν_4 (1789 cm^{-1}) decays much faster than ν_1 (1870 cm^{-1}) is inconsistent with standard statistical theories of unimolecular reaction which predict unimolecular rates to increase with reactant internal energy. On the other hand, models of vibrational predissociation involving pure V-T energy transfer correlate increased lifetime with increased energy release, and predissociation from ν_1 releases 81 cm^{-1} more energy than ν_4. However, theory quantitatively predicts a much smaller difference (factor of ≤ 2) between ν_1 and ν_4 than was observed. In the case of $(NO)_2$, the predissociation might be nonadiabatic since the $^2\Pi$ configurations of the NO fragments combine to form several low-lying electronic states in the dimer. Nonadiabatic effects have been suggested to explain the anomalously large collisional cross-section observed for vibrational deactivation of NO(v=1) by NO(v=0). The different overall symmetries of the ν_1 and ν_4 levels of the dimer $^1A_1$ ground state may constrain coupling to low lying repulsive state(s), causing the observed difference in lifetimes. Ongoing measurements of product energy distributions following ν_4 dissociation and lifetimes for states of different vibrational symmetries (e.g., combination bands involving the vdW modes) might elucidate the source of the difference in ν_1 and ν_4 predissociation rates.

Future progress in this area depends critically on our ability to obtain additional funds, either internal or from other agencies, to cover staff salaries and operations. During 1987 we hope to measure the vibrational predissociation rates following excitation of particular vibrational modes of several vdW dimers, and also to measure the distribution of energy (electronic, vibrational, rotational, translational) in the products. Candidate molecules are:

$$\begin{array}{llll}
C_2H_4\cdot NO & \xrightarrow{1900\ cm^{-1}} & C_2H_4(\nu_7+\nu_8)\cdot NO & \xrightarrow{\tau} C_2H_4 + NO\ (J,\Omega,\Lambda) \\
 & \xrightarrow{1870\ cm^{-1}} & C_2H_4\cdot NO(v=1) & \xrightarrow{\tau} C_2H_4 + NO\ (J,\Omega,\Lambda) \\
CO\cdot NO & \xrightarrow{2046\ cm^{-1}} & CO(v=1)\cdot NO & \xrightarrow{\tau} CO(0)+NO(v=1 \text{ or } v=0,J,\Omega,\Lambda) \\
C_2H_2\cdot C_2D_2 & \xrightarrow{3282\ cm^{-1}} & C_2H_2(\nu_3=1)\cdot C_2D_2 & \xrightarrow{\tau} C_2H_2(v,J) + C_2D_2\ (v,J).
\end{array}$$

Many other vibrations in C_2H_2, C_2D_2, and C_2HD complexes can be studied. In several systems vibrational energy transfer across the vdW bond (a fast process according to some theoretical calculations) may occur and can be readily detected by LEF. A high resolution (e.g., transform limited, 15 ns pulses) tunable infrared laser source, similar to the low resolution ps ir difference frequency system, is necessary for obtaining good photodissociation spectra on the same molecular beams used for the time-resolved measurements.

D. Photophysical Studies of Photosensitizers

(D. S. King, in collaboration with D. F. Heller and J. Krasinski of Allied Corporation and R. S. Bodaness of National Center for Health Services Research, OHTA)

Many photosensitizers, such as hematoporphyrin derivative (HPD), are known to produce excited-singlet molecular oxygen which is then responsible for ensuing oxidation reactions. Chemically, HPD has received significant interest because it preferentially binds to tumor tissue and can be used for tumor localization (fluorescence) and photochemotherapy. Conventional tumor photolocalization techniques use blue to ultraviolet excitation sources which are severly attenuated by tissue absorptions, limiting detection and treatment to exposed surface layers. We have persued a more universal approach which takes advantage of the two-photon spectroscopy of HPD.

Two-photon excited fluorescence spectra were taken using either a Q-switched YAG with a 20 ns output pulse duration at 1064 nm or a Q-switched alexandrite laser with 55 ns pulse duration, tunable in the 730 to 780 nm range. Second harmonic generation was also used to directly excite the sample at 532 or 375 nm. The evidence for two-photon excitation consists of both the similarity of the fluorescence spectra recorded following, for example, excitations at 1064 nm (two-photon absorption) and at 532 nm (one-photon absorption), and the quadratic intensity dependence of the two-photon fluorescence signals. Calibrations to determine the two-photon cross-sections were made from single-photon fluorescence data, using the known single-photon absorption coefficients and fluorescence quantum yields. The two-photon excitation cross-section at 750 nm (of 1.5×10^{-49} cm^4 s) was approximately 100-fold greater than that at 1064 nm; we attribute this to a resonant enhancement contribution from the HPD S_1 state.

In the alexandrite laser excitation experiments the HPD two-photon fluorescence was of sufficient intensity to be observed by eye in a darkened room through a single dielectric filter. This implies potential usage of such two-photon techniques for tumor localization at substantial tissue depths since there is an approximately one-thousand fold increase in tissue transmission at 750 nm as compared to 400 nm. Since the two-photon absorption rate is proportional to the square of the laser intensity, the application of picosecond laser pulses should greatly increase the efficiency of the two-photon absorption process, permitting the use of substantially reduced laser pulse energies to achieve equivalent ends. Use of 50 ps, 1 mJ pulses available from a pulsed, mode-locked alexandrite laser oscillator will only deliver 2% of the energy dose used in the present two-photon experiments, however the two-photon excitation rate should be enhanced a million-fold in relation to excitation by a 50 ns pulse of the same energy. This should lead to complete saturation of the HPD two-photon absorption. Such experiments are planned for Spring 1987.

4. QUANTUM CHEMISTRY GROUP

H. Basch, D. Beveridge, W. Fink, N. Goldgaber, P. J. Jasien, P. S. Julienne,
M. Krauss, B. Lengsfield, M. Mezei, F. H. Mies, K. J. Miller,
R. Osman, W. J. Stevens, and L. Vahala

The Quantum Chemistry Group develops and applies atomic and molecular structure and scattering methods to chemical and spectroscopic problems where experiments are difficult to perform or so complicated that the theory is needed to model the results. The activities of the group encompass three broad areas: the study of the structures and properties of large biomolecules, accurate quantum mechanical calculations on small molecules, and atomic and molecular scattering theory.

The biomolecular research is a result of the NBS biotechnology initiative and represents a new direction for the group. Initial work in this area has focussed on the development of methods for accurately predicting the electronic structure, energetics, and properties of small pieces (eg., active sites) of large molecules. This research has resulted in new techniques for the decomposition of molecular electrostatic potentials and polarizabilities into transferrable fragment components that will be used to construct effective Hamiltonians for the small parts of the biomolecules to be studied quantum mechanically. During the past year, several collaborations with other groups have been initiated which will concentrate on applications of newly developed theoretical techniques to interesting problems in biochemistry. The Molecular Structure and Modeling Facility IBM4381 computer is used for these large scale calculations.

The determination of accurate electronic structures and properties for small molecules has been a central focus of the group's activities for many years. Our unique capability for handling heavy atoms through the use of effective core potentials has allowed the study of a variety of interesting molecules including transition metal oxides and heavy rare-gas dimers. The accomplishments for this year include state-of-the-art calculations on chromium oxide and silicon carbide, and a complete set of calculations of the van der Waals potentials for the homonuclear and mixed rare-gas dimers.

In the area of scattering theory, new methods have been developed for the determination of cross-sections and fragment state distributions associated with the collisonal broadening and photodissociation of small molecules in the presence of both weak and strong radiation fields. In addition, significant progress has been made in the area of multichannel quantum defect theory and non-adiabatic half-collision amplitudes, with specific applications to broad-band continuum spectroscopy.

A. Theoretical Calculations on Biomolecules

1. Development of an Ab Initio Reaction Field Program

(W. J. Stevens, H. Basch, and M. Krauss)

Although the methods of modern quantum chemistry and the machines on which calculations are carried out have evolved dramatically in the last ten years, it is still not feasible to determine the geometric and electronic structures of very large molecules (> 20-30 atoms) by ab initio techniques. However, in large molecules such as proteins, it may be possible to learn a great deal about chemical properties by looking at the detailed electronic structure of a small part of the molecule (the active site), while treating the remainder of the system as a perturbing environment that plays only an indirect role in the chemistry. During the past year we have modified the HONDO electronic structure program to include a reaction-field Hamiltonian that allows the study of an active molecular fragment, "A", in the field of a molecular "spectator" environment, "S". The Hamiltonian is written

$$H_A = H_A^0 + V_{AS}$$

where V_{AS} describes the interaction of the active electrons with the spectator part of the system. Assuming the interaction of "A" with "S" is non-bonding (i.e., no covalent bond, no charge-transfer), the interaction term in the Hamiltonian may be broken down into three pieces: electrostatic, polarization, and orthogonality and exchange repulsion. Our desire is to represent each of these interactions by one-electron operators in the Hamiltonian of the active part, so that the difficulty of the calculation is primarily dictated by the complexity of the active fragment "A".

Our analysis of the electrostatic potentials of the spectator molecules is based on localized molecular orbitals (LMO). Accurate SCF calculations are carried out for prototypical molecules containing specific functional groups. The molecular orbitals of the prototype are localized by some appropriate method (e.g., the Boys method). The electronic contribution to the electrostatic potential is the sum of the contributions from each LMO. The electrostatic potentials of LMOs catagorized by functional groups are found to be reasonably transferrable from one molecule to another. The electrostatic potential of each LMO is approximated by a multipole expansion at its center of charge. The molecular potential is then represented by a distributed set of LMO expansions. This distributed expansion produces an accurate representation of the molecular electrostatic potential for LMO expansions that include only the centers of charge and the first few moments. We have modified the HONDO code to include the potentials of such distributed charges and second moments in the Hamiltonian, and test calculations are now being done to determine the accuracy for a variety of prototypical systems.

The polarization of "A" by "S" occurs naturally when the Schroedinger equation is solved for the wavefunction of "A" using a Hamiltonian that contains the electrostatic potential of "S". However, the determination of accurate interaction energies requires that "S" also is polarized by the electrostatic potential of "A". In addition, there is a self-consistent effect in the mutual polarization of the two parts of the system. Fortunately, the self-consistent part of the polarization has been found to be small (~10%). For the energy contribution due to the dipole polarizability of "S" we evaluate the expression

$$< \Psi_A \left| \sum_{i,j} \vec{f}_i \cdot \vec{f}_j \ \alpha\,(\text{"S"}) \right| \Psi_A >$$

where $\vec{f}_i$ is the electric field due to electron i in fragment "A", and α("S") is the dipole polarizability of fragment "S". This energy term is evaluated as a perturbation once the wavefunction for "A" is known. Putting the operator directly into the Hamiltonian of "A" is not possible, because second order effects related to dispersion are improperly introduced. The polarizability of the fragment "S" is constructed from fragment LMO polarizabilities. We have developed a coupled Hartree-Fock scheme which allows the total calculated polarizability of a molecule to be rigorously represented as a sum of LMO polarizabilities. A series of calculations has shown the LMO polarizabilities for functional groups to be reasonably transferrable from one molecule to another. Distributing the LMO polarizabilities in the fragment "S" helps take into account the inhomogeneous nature of the electronic field due to "A". Higher order polarizabilities may be added in the same fashion if necessary. Currently, the HONDO code inccorporates spherically averaged LMO polarizabilities in the Hamiltonian of "A", and work is proceeding to incorporate tensor representations.

Exchange repulsion and orthogonality between "A" and "S" must be included in the Hamiltonian of "A" in order to prevent the collapse of the "A" wavefunction into the "S" region. A rigorous evaluation of the exchange interaction requires two-electron operators and a knowledge of the wavefunctions of "A" and "S". In the case of atoms, it has been shown that a one-electron effective potential can be constructed which accurately mimics the exchange repulsion between the valence electrons and the frozen core. Our group has used such potentials extensively in calculations on systems containing heavy atoms. We are developing analogous procedures for molecular systems where the fragment "S" is treated like the frozen core in the atomic case. A prototypical all-electron calculation is done in which the fragment "A" is optimized with the fragment "S" held frozen. The wavefunction of "S" is taken as a product of frozen LMOs which are obtained from independent calculations on "S" alone. Then the frozen LMO exchange operators in the Hamiltonian of "A" are replaced by one-electron effective potentials. The parameters defining the potentials are adjusted until the orbitals and energies of "A" match those obtained from the all-electron calculation using the frozen "S" and the correct exchange operators. Since the derivation of the effective potentials is based on LMOs, transferability from molecule to molecule is expected. Calculations are underway to test this hypothesis.

2. Modeling of Fe and Mn Superoxide Dismutases

(R. Osman, W. J. Stevens, M. Krauss, and H. Basch)

This research is part of a long term objective to understand the biochemical and biophysical role of metals in enzymatic mechanisms of metallo-enzymes. Quantum mechanical calculations are carried out on models of the enzymes active site, with and without the substrate, in order to ascertain whether proposed mechanisms are reasonable from an energetic point of view. The complexity of the model and the sophistication of the quantum mechanical approach are chosen to produce energetics that are reliable enough to determine which of several proposed pathways may be energetically the most favorable. The electronic structure of the model active site is analyzed to provide insight into the interactions that favor one pathway over another.

Three different superoxide dismutases have been chosen for study. They are Cu,Zn-SOD, Fe-SOD, and Mn-SOD. The availability of their crystal structures enables the construction of models of their active sites. Osman and Basch have previously studied Cu,Zn-SOD (J. Amer. Chem. Soc. 106, 5710 (1984)) and have suggested a new mechanism of action that is quite different from the ones proposed previously. Their quantum mechanical calculations indicate that a single superoxide (O_2^-) cannot reduce the cupric ion because of an arginine group (Arg-141), positioned near the copper, that forms a strong hydrogen bond with the superoxide. Thus, superoxide forms a relatively stable complex with Cu,Zn-SOD that is subsequently reduced by another superoxide in solution. The reduced complex undergoes an internal oxidation-reduction coupled to a proton transfer that results in regeneration of the original enzyme and the formation of the products of the dismutation reaction. The proposed mechanism is in agreement with all known kinetic measurements of the enzymatic reaction. The mechanism is based on the special poperties of the copper ion in the active site and its surroundings in the protein (particulary Arg-141).

Fe-SOD and Mn-SOD, while similar in structure to each other, are quite different in structure from the Cu,Zn-SOD. The proposed mechanism of action of these enzymes is also based on the reduction-oxidation cycle which is consistent with the kinetic studies of the dismutation reaction. However, the details of the reaction are not understood, and analogy to the Cu,Zn enzyme may not be warranted. The recent availability of crystal structures for these enzymes offers an opportunity to perform quantum mechanical calculations on models of the active sites.

We have begun the calculations by determining effective core potentials for the Fe and Mn atoms which allow their inclusion in the model active sites as valence-only systems. In addition, the core potentials have been modified to reproduce accurate $M^{+2} \rightarrow M^{+3}$ ionization potentials. Crystal structures indicate that the metal ion is pentacoordinate, with three hystidines, one aspartate, and one water (or OH^-) acting as ligands. In our initial models we have replaced the hystidines by ammonias and have considered only the five ligands directly bonded to the metal ion. More complex models will be developed using a reaction field approach to incorporate regions of the enzyme that do not participate directly in the reaction but do influence the energetics by virtue of their electrostatic potentials.

3. Frozen Fragment Studies of Hydrogen Bonding
(W. J. Stevens and W. Fink (UC Davis))

In a recent series of articles (J. Chem. Phys. 1983, 78, 4066; J. Chem. Phys. 1985, 83, 735; J. Chem. Phys. 1986, 84, 5687) Reed and Weinhold have proposed an energetic decomposition of hydrogen bonding interactions based on a "natural bond orbital" analysis. The conclusions reached through this analysis are that the electrostatic attraction and exchange repulsion energy components of the hydrogen bond nearly cancel each other, and the charge-transfer interaction determines the shape of the potential energy surface and the structure of the complex. The charge-transfer analysis is similar to the HOMO-LUMO charge-transfer interaction proposed by Klemperer and coworkers, but differs in that the orbitals involved are the localized lone-pair orbital as electron donor and the unoccupied X-H antibonding orbital as electron acceptor. The amount of charge transferred is very small (a few thousandths of an electron), but the energy contribution is said to be several kcals/mol. This analysis is contrary to the widely accepted proposal of Buckingham and others that the structure and energetics of hydrogen bonding is determined primarily by electrostatics.

One of the problems with a decomposition of the interaction energy between two molecules is that the orthogonlity, exchange, and charge-transfer components are difficult to unravel because they all involve the overlap of the molecular wavefunctions. The analysis is also confused by a superposition effect that occurs when the virtual orbitals from the basis set of one fragment help to improve the occupied orbitals of the other fragment. Even though the analysis of Reed and Weinhold appears to be remarkably consistent for a wide variety of hydrogen bonded complexes, it is not impossible that the component of the energy that has been assigned to charge-transfer is really a mixture of other effects.

In collaboration with the group at the University of California at Davis, we have modified the HONDO program to allow for the selective freezing of molecular fragments in an all-electron calculation. It is also possible to selectively eliminate unoccupied virtual orbitals from the basis set. We have used this program to study the water dimer and to assess the importance of charge-transfer in the hydrogen bond interaction. The molecules in the dimer are labelled "A" and "B". Using a fully optimized hydrogen bonding geometry at the double-zeta plus polarization level, the energy is calculated by selectively freezing the wavefunction of either "A" or "B" and optimizing the wavefunction of the unfrozen molecule. The frozen wavefunction is obtained from a calculation on an isolated water molecule. Charge-transfer cannot occur from the frozen water to the variationally active water. We have also eliminated the virtual orbitals from the frozen water basis set so that charge-transfer cannot occur from the variationally active water into the unoccupied space of the frozen water. With all of these constraints, our preliminary calculations have found that the hydrogen bond energy in the frozen molecule calculations is within 20% of a fully variational hydrogen bond energy. Also, a significant portion of the missing energy can be traced to the lack of polarization in the frozen molecule. Although many more hydrogen bonded systems need to be studied, our tentative conclusion is that charge-transfer does not determine the structure and energetics of hydrogen bonded complexes.

4. Monte Carlo Studies of Solvated Biomolecules

(D. Beveridge, M. Mezei, W. J. Stevens, and M. Krauss)

This research project has been initiated to explore the interface between ab initio quantum mechanical studies of large molecules and simulation of molecules in the liquid state using the Metropolis Monte Carlo method. The first step in this project has been to install the Hunter College MMC program for Metropolis Monte Carlo simulations on the Molecular Structure and Modeling Facility IBM4381 computer and the Consolidated Scientific Computing System CYBER205 computer. The MMC program, developed by Mezei and Beveridge, is a state-of-the-art program for simulation of a dilute aqueous solution with a force-bias option for convergence acceleration, and a proximity analysis option for assigning the solvent molecules in each N-particle configuration of the system to individual atoms of the solute. The MMC program uses intermolecular potential functions based on several current prescriptions. These functions are hardwired into the code, but the introduction of new potentials is easily accomplished. The results of the computer simulation include the calculated thermodynamic internal energies, heat capacities, and various structural and energetic molecular distribution functions. Some new methods for free energy simulations are also included.

The accuracy of the results of computer simulations of dilute aqueous solutions is dependent on the intermolecular potential functions that are used to evaluate interaction energies and energy derivatives between molecular constituents. The functions currently used in programs such as MMC are based on pairwise-additive interaction potentials between points in the molecules (usually the atoms) that are derived either empirically or from ab initio quantum mechanical calculations. The form of the potentials is kept simple (6-12 plus a coulombic term) because of the computer time required to carry out the simulations. Potentials derived by fitting quantum mechanically calculated potential energy surfaces have been restricted to low-level SCF calculations, such as STO-3G, due to the expense of accurate calculations on complex molecules. Our high-speed computing resources and recently developed methods for simplifying ab initio calculations on large molecules (such as the reaction field approach) will enable us to examine the dependence of the Monte Carlo simulation results on the accuracy of the potentials. Benchmark calculations are planned for several small amides in aqueous solution. We will also explore the use of distributed molecular polarizabilities in the evaluation of interaction energies as a method for incorporating many-body effects in the simulation. This will be particularly important in the study of solvated ions.

Quantum mechanical calculations of the properties and reactivities of molecules in solution or of molecular fragments imbedded in very large molecular systems are limited by the statistical nature of the perturbing environment at nonzero temperatures. Part of the collaboration between the NBS and Hunter College groups will be to explore the use of snapshot distributions from converged Monte Carlo simulations to construct models of the solvent environment in reaction field studies of prototypical molecules.

5. Binding of Pt Complexes to DNA

(H. Basch, M. Krauss, K. J. Miller (RPI))

Preliminary calculations on the binding of cis-Pt$(NH_2R_2)_2$, (R=H, methyl, and cyclopropyl) to a tetramer duplex were reported in last years report but research has expanded on this problem because of new experimental results reporting the binding of Pt$(NH_3)_2$ to a pGpG segment (S. E. Sherman et al., Science <u>230</u>, 412 (1985)), that suggested Pt(NH_3)•••OP H-bonds significantly stabilize the complex. This research was initiated to determine if binding energies could account for the very different anti-tumor potencies between the methyl derivative and both Pt$(NH_3)_2$ and the cyclopropyl derivative. We concluded in the preliminary results which combined SCF calculations of model binding energies with molecular mechanics conformational energy analysis that the binding energy varies smoothly with substitution. The constrained molecular mechanics energy minimization did not show direct hydrogen bonding between the amine ligand and phosphate which is a feature of the Pt-pGpG crystal structure.

Two directions are being pursued to determine if direct phosphate H-bonding is important in the duplex structure. Full cartesian coordinate geometry optimization is being pursued with a tetromer duplex bound to Pt. Achieving a global minimum is an almost impossible task but a number of local minimum structures have been examined and those which distort the H-bonding between the bases the least were examined for the substituted amines. Although a phosphate moiety is found to approach closer to ammonia (O•••H of the order of 3.5Å), an H-bond distance of approach has not been found. The second phase of this calculation is to examine SCF H-binding energies for Pt$(NH_3)(R)_2$ to phosphate with associated waters in order to examine the possibilities for water either externally bonded or as a bridged water. These calculations are still in progress. The results to date do not alter the earlier conclusion that potency and binding energy are not correlated if no chemical reaction other than ligand replacement is induced by the Pt interaction with DNA.

6. Electronic Structure of Phosphates, Phosphoranes, and Their Analogues

(H. Basch, M. Krauss and W. J. Stevens)

Is the stable five coordinate vanadium complex formed in the binding of uridine vanadate to ribonuclease an analogue for a five corrdinate phosphate transition state? By examining the comparative electronic structure and the proton affinities (PA) the concept of transition state analogues can be made more precise. The relative amount of d orbital contribution and the PA of different sites will determine whether proton transfer from the protein to the site as observed for the vanadium complex reflects the phosphorane situation. At the SCF level there is a substantial difference between the electronic structure and PA of PO_3^- and VO_3^-. Electron correlation has only a small effect on PO_3^- or $H_2PO_4^-$ but the comparable vanadium calculation has not yet been done.

Whether phosphorothioate anions will interact with proteins at either the S or O site will, in part, be determined by the electrostatic potential at each site. Although considerable experimental effort has been devoted to determining bond orders and ionicities for these molecules, the simplest way to determine the potential is to calculate it from a high quality wavefunction. Electrostatic potential maps are compared in Fig. 1 for $H_2PO_4^-$ and $H_2PO_3S^-$ in a plane determined by O-P-O or O-P-S. The outer potential contour which determines binding behavior is shifted for S relative to O by approximately in proportion to the longer bond in P-S, reflecting the comparable ionicity of O and S. This suggests zwitterionic or H-bonds will be made initially with S which would be reinforced by the larger polarizability of S. On the other hand, there is much less difference in the outer contours of PO_3^- and PO_2S^-, reflecting the smaller fractional charge found for S in this case. Optimized geometries and PA's have been determined for all these species. Calculations have been initiated on the NMR chemical shifts for ^{31}P to correlate shifts with electronic structure and conformation.

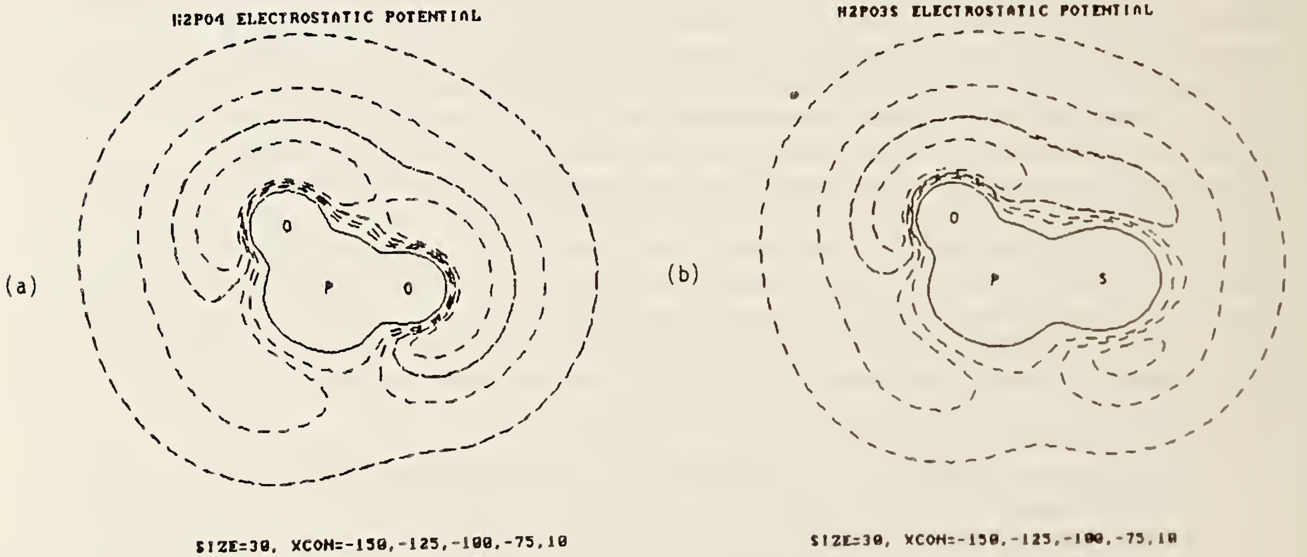


Fig. 4.1 A comparison of the electrostatic potentials of H_2PO_4 and H_2PO_3S. The dashed contours represent potentials of -150 (innermost), -125, -100, and -50 kcal.

7. Rotational Barriers in Formamide and Acetamide
(P. G. Jasien, W. J. Stevens, and M. Krauss)

The energy barrier to rotation about an amide bond is important in the modeling of protein conformation. There have been a number of ab initio attempts to calculate the inherent barrier, but a review reveals that the accuracy was significantly limited by a lack of a complete polarization basis. The present results indicate that the inclusion of polarization functions in the basis set leads to a substantial decrease of 5 kcal/mole in the barrier height at the SCF level. Considering electron correlation and the zero point energy correction, the in vacuo rotational barriers for formamide and acetamide are predicted to be 14.2 and 12.5 kcal/mole, respectively.

8. Future Plans

The major thrust in the biotechnology area is the development of the reaction field method. The reaction field method will be applied to the effect of solvation on the stability of amides, reactions of phosphates and their analogues, the binding of metals to DNA and protein model compounds, and the mechanism of reaction of Fe and Mn superoxide dismutase. A continuing effort is needed in evaluating the parameters and assessing the data (centroids, local polarizabilities, local quadrupoles, ...) required for the reaction field. The use of both molecular mechanics and statistical mechanics methods to determine the conformation of the environment region in the reaction field will be investigated.

B. Quantum Chemistry of Small Molecules

1. Accurate Calculations on Small Molecules
(W. J. Stevens, P. G. Jasien, and B. Lengsfield)

(a) CrO and CrO^+

Understanding the electronic structure of the transition metal oxides is a challenge for experimentalists and theoreticians alike. The multiple open-shell nature of the electronic wavefunction, highly degenerate constituent atoms, extreme covalent/charge-transfer mixing, and large spin-orbit splitting make the electronic states difficult to characterize theoretically and the spectra and thermodynamic behavior difficult to analyze. The CrO, CrO^+ system is interesting from a theoretical point of view because there are a number of experimental analyses available including high-resolution spectroscopy of the ground state, photoelectron spectroscopy determining the ionization potential, and several estimates of the dissociation energies. The ground state of CrO is a $^5\Pi$ state with the dominant valence configuration

$$\sigma_{Cr}^{1}\sigma_{O}^{2}\sigma_{b}^{2}\pi_{b}^{4}\pi_{a}^{1}\delta_{Cr}^{2}.$$

The molecule is best described as Cr^+O^-. The singly occupied σ orbital on chromium is strongly polarized away from both the O^- and the double occupied σ_b bonding orbital. The π_b bonding orbital is quite polarized toward oxygen, and the π_a orbital is only weakly antibonding. Ionization to form the positive ion will remove an electron from either the singly occupied sigma orbital or the singly occupied pi orbital. Dyke, et al. (J. Chem. Soc., Faraday Trans. 1983, 79, 1083) have analyzed the photoelectron spectrum of CrO in terms of a single $^4\Sigma^-$ state of the ion, while our calculations show a $^4\Pi$ state only 0.1 eV above the $^4\Sigma^-$ ion ground state. Our calculated ionization potential of 7.43 eV is in reasonable agreement with the experimentally deduced value of 7.85 eV, but our ion spectroscopic constants disagree with the experimental numbers. Our best calculations (singles and doubles CI from a multiconfiguration wavefunction) predict R_e = 1.64Å($^4\Sigma^-$), 1.62Å($^4\Pi$) and ω_e = 801 cm^{-1}($^4\Sigma^-$), 895 cm^{-1}($^4\Pi$) as opposed to 1.79Å and 640 cm^{-1} quoted by Dyke, et al. Our values for the $^5\Pi$ ground state of CrO of R_e = 1.647Å and ω_e = 850 cm^{-1} agree reasonably well with the values of R_e = 1.6179Å and ω_e = 898.50 cm^{-1} obtained from the analysis of rotationally resolved laser-induced fluorescence spectra by Hocking, et al. (Can. J. Phys. 1980, 58, 516). Since the theoretical calculations for the neutral and ion states were carried out at the same level of accuracy, we believe that the analysis of the photoelectron spectrum is in error.

(b) Silicon Carbide, SiC

The silicon carbide molecule, SiC, is of fundamental importance in astrophysics because of the role it may play in the formation of interstellar grains. Although the triatomic molecule, SiC_2, has been observed in the laboratory and in interstellar space, no observations of the SiC molecule have been reported. Recently, there have been a number of theoretical calculations on SiC which predict the infrared and electronic transition frequencies, but no accurate prediction of the microwave absorption frequency has been made. Radiotelescope observations of interstellar spectra are made in 128 MHz spectral windows which require several hours of data accumulation to develop a reasonable signal-to-noise ratio. At the absorption frequency of SiC (~18 GHz), the R_0 must be known to within ±0.004Å in order to predict the correct window for observation. Such a prediction is within the capability of modern quantum mechanical calculations.

We have performed singles and doubles CI calculations from multi-reference wavefunctions for the $^3\Pi$ ground state of SiC using a very large Slater-type basis set consisting of s,p,d, and f functions on each center. In addition to the usual d polarization functions, d and f functions were added for correlation, and their exponents were optimized in large-scale CI calculations. Five points around the bottom of the potential energy curve were calculated and fit to a Morse potential. The internuclear distances for the calculations were chosen to symmetrically surround the minimum and to cover an energy range surrounding the lowest vibrational level. Additional points were added to ensure that the predicted Morse parameters were not sensitive to the point distribution. In all cases, the Morse fit reproduced the calculated data points to within a few wavenumbers. Several curves were generated in this way using a variety of reference wavefunctions and CI selection criteria. In the largest calculations the wavefunction consisted of more than 300,000 configurations. The several largest calculations produced R_e values that were consistent to within 0.003Å and vibrational frequencies that agreed to within a few wavenumbers.

Spin-orbit coupling splits the ground state of SiC into Ω = 2,1, and 0 components. The $^3\Pi_2$ component is lowest in energy. Using ab initio effective spin-orbit operators developed in this laboratory, we have determined that the spin-orbit splitting in SiC is 34 cm^{-1} and nearly constant across the bottom of the potential curve. Thus, the predicted R_0 value will not be affected by spin-orbit coupling. There is a possibility that the $^3\Pi_2$ state could be perturbed by other low-lying Ω = 2 electronic states. In our calculations, the closest perturbing states are $^3\Delta$ and $^5\Pi$, both of which are several thousand wavenumbers higher in energy.

The results of this study have been communicated to Dr. Michael Hollis of NASA, who will compare the predictions to known interstellar microwave lines. If a sufficiently interesting comparison is found, an application will be made for viewing time at the Kitt Peak observatory.

2. Interaction Energy Curves of RR', (R,R' = He through Xe
(D. D. Konowalow and (Dept. Chem. SUNY Binghamton) M. Krauss)

Application of an ab initio hybrid model of the calculation of the rare gas dimers has yielded binding energies within 10-20% of experiment for these molecules. The discrepancy is attributed to the slow convergence in the attractive dispersion energy with high order multipoles. These calculations were performed to determine the applicability of the model to heavier systems to allow calculation of biomolecular models. Very recently an accurate correlated calculation of the binding energy of HeAr (W. Meyer et al., Phys. Rev. A33, 3807 (1986)) suggested that correlation of the fragments is important and the hybrid model potential may be questionable. Correlated atom calculations are now in progress to test this conclusion for a range of molecules. Since the hybrid model is widely used, it is necessary to examine the significance of correlation in model systems.

3. Future Plans

Accurate quantum chemistry calculations of model systems will be carried out to determine the level of accuracy required for predictive value in energetic conformations and spectroscopic properties. Electron correlation behavior in model compounds containing transition elements will continue to be studied by both ab initio and effective operator methods.

C. Scattering in the Presence of Radiation
(P. S. Julienne and F. H. Mies)

The general goal of this research is to provide calculations of radiative cross-sections and fragment state distributions associated with the collisional broadening and photodissociation of small molecules. We have developed extensive experience in calculating various nonadiabatic effects in the conventional weak-field limit, and are expanding our codes to treat the saturation of continuum transitions in intense, multiphoton fields.

Theoretical input into this program is provided by extensive sets of computer codes available to the quantum chemistry group. State of the art calculations of any necessary molecular potentials, couplings and radiative transition dipoles can be obtained. Our scattering programs have been expanded to allow for direct radiative interactions among many coupled channels. Preliminary calculations have been performed to study the pressure broadening of atomic lineshapes in both weak and strong laser fields. Our scattering codes presently provide the continuum-continuum scattering matrix elements needed in lineshape theory, and are being modified to provide the bound-continuum matrix elements required to describe photodissociation. In addition to these numerical procedures, the program involves extensive analysis of many new and exciting theoretical features introduced by very intense laser fields.

1. Non-adiabatic Theory of Atomic Broadening in Weak Fields

a) Redistribution Calculations for Sr($^1P \leftarrow {}^1S$) + Ar
(P. S. Julienne and F. H. Mies)

We completed our close-coupled calculations of polarized light redistribution in the Sr + Ar system. The calculations predict the polarization ratios of Sr(^1P) fluorescence following line wing excitation by either linear or circular polarized light. Ab initio calculations were used to obtain the ground and excited SrAr molecular potentials, which were adjusted modestly to give improved agreement with experiment. The radiative scattering theory gives a unified description of the absorption coefficient and subsequent fluorescence from the small detuning impact limit region to the far wings. The cross sections for depolarizing collisions of Sr(^1P) + Ar were also calculated. The calculated absorption coefficient, impact broadening rate, linear and circular polarization ratios, and depolarization rate coefficients are for the most part in good agreement with a diverse set of experimental data.

b) Redistribution Calculations for Na + Rare Gas
(P. S. Julienne and L. Vahala)

We have continued to calculate final state branching ratios for fine structure states and alignment/orientation for Na($^2P \leftarrow {}^2S$) + He,Ne,Ar systems, and have obtained good agreement with experimental measurements. In analysing the exact close-coupled data we uncovered a useful spin-uncoupling approximation of the collision dynamics and its dependence on collision velocity.

If the separation velocity of two colliding atoms is sufficiently large, the final state dynamics can be well approximated by the same recoil limit that has been successfully developed for photofragmentation. Our calculations show how the recoil limit for fine-structure branching ratios is approached for both red and blue detuning the separation velocity increases.

The recoil approximation for orientation/alignment only applies for collisions with small angular momentum (small impact parameter). The recoil limit applies when the separation time of the fragments is short compared to the characteristic times of axis rotation and spin-orbit coupling. However, by comparison to a pure ^1P atom we can develop a spin-recoil approximation which treats the spin projection as fixed in space during the rapid separation to fragments while accounting for the rotation of electronic angular momentum projection Λ with the internuclear axis. Comparison of the spin-recoil model with exact close coupling results for Na + rare gas shows the applicability of the approximation.

c) Lorentzian Pressure-Broadened Widths for Na
(P. S. Julienne and L. Vahala)

We have calculated the Lorentzian pressure-broadened widths for both the D1 and D2 lines of Na broadened by collisions with He, Ne, and Ar. In addition we have performed the first calculation of the so-called asymmetry parameter which has been widely observed in the impact regions of atomic lineshapes.

The absorption profile within the impact limit for one of the isolated ^2P_j fine structure lines may be written as

$$I(\Delta_j) = \frac{\nu_j(\Delta_j)/\pi}{(\Delta_j - \delta_J)^2 + \nu_j^2(0)}$$

where Δ_j and δ_j are the respective detunings and shift of the line. The detuning-dependent quantity $\nu_j(\Delta_j)$ may be shown to have a finite limit as $\Delta_j \to 0$ and exactly equals the usual impact limit broadening coefficient, including the effects of both elastic and inelastic collisions. The dependence on detuning give rise to the Lorentzian dispersion asymmetry which has been observed for Na + rare gas systems. We have calculated the radiative scattering cross section for detunings near the D1 and D2 lines for Na broadened by He, Ne, and Ar. The widths and asymmetry parameters are qualitatively in agreement with measured values. Deficiencies in the existing molecular potentials limit the expected accuracy of the scattering calculations.

2. Nonadiabatic Theory of Redistribution in Strong Fields

(a) Collisional Redistribution of Resonant Radiation

(F. H. Mies)

Close-coupling codes developed for scattering in the presence of radiation fields can be used to calculate the pressure broadening and collisional depolarization of the Sr resonance transition in both the weak field and the strong field limit,

$$Sr(^1S) + Ar + \hbar\omega_L \rightarrow Sr^*(^1P) + Ar \rightarrow Sr(^1S) + Ar + \hbar\omega.$$

As we increase the Rabi frequency Ω_L and decrease the detuning Δ_L of the incident laser three observable properties associated with optical collision processes are obtained from such calculations, 1) Impact Limit Lineshapes. As $\Delta_L \rightarrow 0$ we can demonstrate that proper pressure broadened half widths, which include both elastic and inelastic collisional effects, can be rigorously extracted from close-coupled radiative scattering matrix element. The first manifestations of a.c. Stark shifts associated with the dressing of fragments by the radiation field are extracted from the numerical results, and confirm the anticipated power broadening of the Lorenztian absorption profile. This suggests that normal perturbation theory as applied to radiative interactions must be carefully scrutinized. 2) Inelastic transitions involving dressed atomic states. As Ω_L increases and eventually exceeds Δ_L the asymptotic Sr atomic states become dressed. Our fully quantal inelastic cross-sections can be used to calculate population redistribution rates in the presence of intense fields. 3) Collisional redistribution spectra in saturating fields. In strong fields we obtain the redistribution spectra for $\hbar\omega_R$ in the impact limit and find the typical three-peaked Mollow lineshape due to fluorescence between dressed atomic states. Both the half-width and the polarization of the emission peaks are calculated.

(b) Analysis of Multiphoton Lineshape Theory in Intense Fields

(F. H. Mies and A. Ben-Reuven)

The theory of line broadening, collisional redistribution and collision-induced multiphoton phenomena is an interdisciplinary area of research. Particularly when adding the new ingredient of strong laser fields and the resultant non-linear effects induced by saturation of resonant transitions, the analysis of such phenomena requires the integration of several diverse fields of research.

Two complementary theoretical approaches are used to describe these phenomena. The first is represented by our "optical collision" approach here at NBS where we calculate the radiative scattering matrix elements for atom-atom scattering in the presence of intense monochromatic laser fields. The calculations incorporate many subtle and sophisticated non-adiabatic and inelastic effects which are often neglected in conventional lineshape theory. However, these data that we generate must then be incorporated into very subtle and complicated theoretical expressions for the density matrix of the interacting molecules in the field of the pumping laser fields. Only then do our calculations yield the proper description of the redistributed radiation.

The second theoretical approach, is exemplefied by the unique and outstanding theoretical approach developed by Professor Ben-Reuven at Tel Aviv University. The redistribution of radiation is expressed in terms of a tetradic formalism using a Liouvillian analysis of the molecular density matrix in the presence of collisions. Fortunatley, the formal ingredients of this sophisticated theory are the very scattering matrix elements that are generated by our optical collision approach.

We have begun a collaboration with Professor Ben-Reuven to explore the relationship between the tetradic description of redistribution and the close-coupled theory of scattering in strong multiphoton fields. So far we have succeeded in showing the explicit relationships required to analyze resonance fluorescence and resonant Raman lineshapes.

3. Future Plans

Our long range plans in the radiative scattering program require extensive code development combined with a careful theoretical analysis of strong field effects and multiphoton effects in the presence of collisions. In the immediate future we intend to complete the calculation of the pressure-broadening Mollow lineshape for Sr + Ar. At the completion of this relatively simple, near-resonant one-photon study we intend to explore the application of our close-coupled codes to multiphoton phenomena in strongly resonant laser fields with hopes of calculating collisional effects in four-wave mixing (PIERS-4) in Na. This will be studied in collaboration with A. Ben-Reuven at Tel Aviv University using his tetradic analysis of lineshapes.

D. Atomic and Molecular Scattering Theory

1. Half-Collision Amplitudes

a) Analysis of Exact Close-Coupled Codes
(F. H. Mies)

We have previously used a multichannel quantum defect analysis (MCQDA) of exact close-coupled radiative matrix elements to show that these can often be factored as follows:

$$S_{fi} = N^{-}_{ff'} \, S_{f'i'} \, N^{+}_{i'i}$$

where the 'incoming' half-collision matrix $N^{+}_{i'i}$ tracks the non-adiabatic scattering of the incident collision complex, and $N^{-}_{ff'}$ summarizes the inelastic behavior of the 'outgoing', radiatively excited collision complex.

We have speculated on the unitarity of these matrices which would justify the persistent use of the pure adiabatic Born-Oppenheimer matrix element $S^{BO}_{f'i}$, in evaluating total radiative cross-sections for continuum transitions. Based on a convincing but admittedly indirect numerical analysis of several previous studies we have been very confident in advancing the merits of this approximation. We have now modified our exact close-coupled codes to extract the exact half collision amplitudes without any commitment to unitarity. This new general capability of obtaining N^+ and N^- directly from close-coupled codes will enjoy a wide range of applicability in continuum spectroscopy and allow us to judge the validity of the unitarity condition.

(b) Multichannel Semiclassical Half Collision Amplitudes

(F. H. Mies and Y. Band)

In addition to solving the close-coupled equations exactly, we have developed a new simplified numerical procedures designed to obtain the half collision amplitude whenever the non-adiabatic couplings are restricted to classically accessible regions and the unitarity of N^+ is insured. This is equivalent to solving a set of coupled semiclassical equations. We begin by choosing a set of diagonal reference potentials tailored to the nature of the exact interaction matrix. These are used to generate a set of elastically scattered WKB reference wavefunctions. Two obvious choices that we have explored in some detail are either pure diabatic, or pure adiabatic reference potentials, although in any given situation the 'preferred' choice is usually self evident. By using a random phase approximation to neglect quickly oscillating contributions to the close coupled equations we can develop a set of first order differential equations for the half collision amplitudes which are perfectly unitary, and, in appropriate and well understood circumstances, reproduce the exact close-coupled amplitudes. This multichannel semiclassical approximation is presently being applied to a number of interest situations, including multichannel curve crossings, and asymptotic frame transformation among fine-structure states.

2. Multichannel Photodissociation Amplitudes

(P. S. Julienne)

The expansion of our multichannel close-coupling codes to calculate photodissociation cross-section is nearly complete. This gives very stable procedures for evaluating bound-continuum transitions, including all possible subtleties associated with non-adiabatic effects in molecular dissociation. A renormalized Numerov algorithm has been incorporated into the codes for the calculation of the usual continuum-continuum S-matrix elements needed for collisional problems, but more specifically for calculation of bound-continuum transition matrix elements needed for photodissociation. This algorithm is still being tested. In particular the code is designed to calculate the final state distribution of the photofragments. Ultimately these exact matrix elements can be compared to the predictions of our half collision amplitudes based on MCQDA.

3. Future Plans

Our first priority is to complete the development of the non-adiabatic photodissociation codes. The implementation of the photodissociation (and closely associated predissociation) codes will be stimulated by forthcoming studies of the Schumann-Runge predissociation of O_2 in collaboration with L. Vahala at Old Dominion University. The half collision amplitude studies will be continued and applied to an analysis of fine-structure distriutions in both continuum-continuum and bound-continuum transitions. Using our new semiclassical algorithm we intend to examine its application to polyatomic curve-crossing phenomena in collaboration with Y. Ban at Ben-Gurion University. In addition, we will continue to pursue our NCQDA studies of molecular dissociation in conjunction with Professor S-h. Pan from the Chinese Academy of Science in Beijing who will be spending a year with us at NBS. In particular we will analyse the charge transfer states of alkali-halide molecules.

5. PUBLICATIONS

(a) Publications of Past Year

Basch, H., Krauss, M., and Stevens, W. J., "Cation Binding Effect on H-Bonding," J. Am. Chem. Soc. 107, 7267 (1985).

Basch, H., Krauss, M., Stevens, W. J., and Cohen, D., "Electronic and Geometric Structures of $Pt(NH_3)_2^{2+}$, $Pt(NH_2)_3Cl_2$, $Pt(NH_3)_3X$ and $Pt(NH_3)_2XY$ ($X,Y = H_2O,OH$)," J. Inorg. Chem. 24, 3313 (1985).

Basch, H., Krauss, M., Stevens, W. J., and Cohen, D., "Binding of $Pt(NH_3)_2^{2+}$ to Nucleic Acid Bases," J. Inorg. Chem. 25, 684 (1986).

Bodaness, R. S. and King, D. S., "The Two-Photon Induced Fluorescence of the Tumor Localizing Photosensitizer Hematoporphyrin Derivative via 1064nm Photons from a 20ns Q-switched Nd-YAG Laser," Biochem. and Biophys. Research Commun. 126, 346 (1985).

Casassa, M. P., Heilweil, E. J., Stephenson, J. C., and Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation at Surfaces," J. Electron. Spec., 38, 257 (1986).

Casassa, M. P., Heilweil, E. J., Stephenson, J. C., and Cavanagh, R. R., "Time-Resolved Measurements of OH(v=1) Vibrational Relaxation on SiO_2 Surface: Isotope and Temperature Dependence," J. Chem. Phys., 84, 2361 (1986).

Casassa, M. P., Stephenson, J. C., and King, D. S., "Vibrational Predissociation of Nitrix Oxide Dimer: Total Energy Distribution in the Fragments," J. Chem. Phys., 86, 2333 (1986).

Chackerian, C., Jr., Bus, E. S., Olson, W. B., and Guelachvili, G., "Determination of $A_0 - B_0$ of CH_3D from Perturbation-Allowed Transitions," J. Mol. Spectrosc., 117, 355-360 (1986).

Dang-Nhu, M. and Pine, A. S., "Intensities des Raies d'Absorption dans la Bande Chaude $\nu_8 + \nu_{11} - \nu_{11}$ de l'Allene," Can. J. Phys. 64, 289-296 (1986).

Fraser, G. T., Nelson, D. D., Jr., Peterson, K. I., and Klemperer, W., "The Rotational Spectra of NH_3-CO and NH_3-N_2", The Journal of Chemical Physics, 84, 2472 (1986).

Fraser, G. T., Nelson, D. D., Jr., Gerfen, G. J., and Klemperer, W., "The Rotational Spectrum, Barrier to Internal Rotation, and Structure of NH_3-N_2O," The Journal of Chemical Physics, 83, 5442, (1985).

Fraser, G. T. and Coy, S. L., "Absorber Speed Dependence of the Coherence Relaxation Rate of the J=0-1 Transition of N_2O," The Journal of Chemical Physics, 83, 5687 (1985).

Fraser, G. T., Lovas, F. J., Suenram, R. D., Nelson, D. D., Jr., and Klemperer, "Rotational Spectrum and Structure of CF_3H-NH_3," The Journal of Chemical Physics, 84, 5983 (1986).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Time-Resolved Vibrational Energy Relaxation of Surface Adsorbates," J. Vac. Sci. Technol. B3, 1471 (1985).

Heilweil, E. J., Casassa, M. P. Cavanagh, R. R., and Stephenson, J. C., "Vibrational Energy Decay of Surface Adsorbates," Proceedings of Time-Resolved Vibrational Spectroscopy Conference (Springer-Verlag: Proceedings in Physics, A. Laubereau and M. Stockburger, eds., Vol. 4, pg. 71, 1985).

Hillman, J. J., Jennings, D. E., Olson, W. B., and Goldman, A., "High Resolution Infrared Spectrum of Hydrogen Peroxide: The ν_6 Fundamental Band," J. Mol. Spectrosc., 117, 46-59 (1986).

Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer," J. Mol. Spectrosc., 114, 395-426 (1985).

Hougen, J. T., "Symmetry beyond Point Groups in Molecular Spectroscopy," J. Phys. Chem. 90, 562-568 (1986).

Howard, B. J. and Pine, A. S., "Rotational Predissociation and Libration in the Infrared Spectrum of Ar-HCl," Chem. Phys. Lett. 112, 1-8 (1986).

Jacox, M. E., "Comparsion of the Ground-State Vibrational Fundamentals of Diatomic Molecules in the Gas Phase and in Inert Solid Matrices," J. Mol. Spectrosc., 113, 286 (1985).

Jacox, M. E., "Reaction of F Atoms with the Methyl Haildes. Vibrational Spectra of CH_3XF and of H_2CX--HF Trapped in Solid Argon," J. Chem. Phys. 83, 3255 (1985).

Jasien, P. G. and Stevens, W. J., "Ab Initio Study of the Hydrogen Bonding Interactions of Formamide with Water and Methanol," J. Chem. Phys. 84, 3271 (1986).

Jasien, P. G. and Stevens, W. J., "Calculated Proton Affinities for Some Molecules Containing Group VIA Atoms," J. Chem. Phys. 83, 2984 (1985).

Jennings, D. E., Weber, A., and Brault, J. W., "Raman Spectroscopy of Gases with a Fourier Transform Spectrometer: The Spectrum of D_2," Appl. Opt. 25, 284 (1986).

Julienne, P. S. and Mies, F. H., "Analytic Multichannel Theory of Molecular Dissociation," in Electron and Atomic Collisions, ed. D. C. Lorents, W. E. Meyerhof, and J. R. Petersen (North Holland, Amsterdam, 1986), p. 725.

Karpas, Z., Stevens, W. J., Buckley, T. J., and Metz, R., "Proton Affinity and Gas-phase Ion Chemistry of Methyl Isocyanate, Methyl Isothiocyanate, and Methyl Thiocyanate," J. Phys. Chem. 89, 5274 (1985).

Krauss, M., Stevens, W. J., and Basch, H., "Relativistic Effective Potential SCF Calculations of AgH and AuH," J. Comp. Chem. 6, 287 (1985).

Lovas, F. J., "Recommended Rest Frequencies for Observed Intersellar Molecular Microwave Transitions - 1985 Revision," J. Phys. Chem. Ref. Data, 15, 251-303 (1986).

Maki, A. G., Wells, J. S., and Hinz, A., "Heterodyne Frequency Measurements on the 12°0-00°0 Band of OCS," Int. Journal of Infrared and Millimeter Waves, 7, 909-917 (1986).

Mantell, D. A., Cavanagh, R. R., and King, D. S., "Internal States lDistributions of NO Thermally Desorbed from Pt(111): Dependence on Coverage and Co-Adsorbed CO," J. Chem. Phys. 84, 5131 (1986).

Mialocq, J.-C. and Stephenson, J. C., "Picosecond Laser Study of the Collisionless Photodissociation of Dimethylnitramine at 266 nm," Chem. Phys. Lett. 123, 390 (1986).

Mialocq, J.-C. and Stephenson, J. C., "Picosecond Laser Induced Fluorescence Study of the Collisionless Photodissociation of Nitrocompounds at 266 nm," Chem. Phys (1986).

Miller, K. J., Taylor, E. R., Basch, H., Krauss, M., and Stevens, W. J., "A Theoretical Model for the Binding of Cis-Pt$(NH_3)_2^{2+}$to DNA," J. Bio. Struct. Dynam. 2, 1157 (1985).

Nelson, D. D., Jr., Fraser, G. T., and Klemperer, W., "Ammonia Dimer: A Suprising Structure," The Journal of Chemical Physics, 83, 6201 (1985).

Ohashi, N., Lafferty, W. J., and Olson, W. B., "Fourier Transform Spectrum of the Torsional Band of Hydrazine," J. Mol. Spectrosc., 117, 119-133 (1986).

Perry, J. W., Woodward, A. M., and Stephenson, J. C., "Picosecond Coherent Anti-Stokes Raman Scattering (CARS) Study of Vibrational Dephasing of Carbon Disulfide and Benzene in Solution," SPIE Proceedings 620, (1986).

Pine, A. S. and Howard, B. J., "Hydrogen-Bond Energies of the HF and HCl Dimers from Absolute Infrared Intensities," J. Chem. Phys. 84, 590-596 (1986).

Rosenkrantz, M. E. and Krauss, M., "Damped Dispersion Interaction Energies for He-H_2, Ne-H_2, and Ar-H_2," Phys. Rev. A32, 1402 (1985).

Suenram, R. D., Lovas, F. J., and Pickett, H. M., "The Microwave Spectrum and Molecular Conformation of Peroxynitric Acid ($HOONO_2$)," J. Mol. Spectrosc., 116, 406-421 (1986).

Suenram, R. D., Lovas, F. J., and Pickett, H. M., "Fluoromethanol: Synthesis, Microwave Spectrum and Dipole Moment," J. Mol. Spectrosc. 119, (1986).

Thompson, G. A., Maki, A. G., and Weber, A., "Infrared Tunable Diode Laser Spectroscopy of the $\Delta\nu = 2$ Band of $^{7}Li^{127}l$, J. of Mol. Spectrosc. 118, 540-543 (1986).

Thompson, G. A., Maki, A. G., and Weber, A., "The Infrared Spectrum of GeO," J. Mol. Spectrosc., 116, 136-142 (1986).

Thompson, G. A., Maki, A. G., and Weber, A., "Infrared Spectrum of LiI," J. Mol. Spectrosc., 118, (1986).

Weber, A. (ed.), "Technical Activities 1985 - Molecular Spectroscopy Division," NBSIR 86-3313 (1986).

Wofford, B. A., Bevan, J. W., Olson, W. B., and Lafferty, W. J., "Rovibrational Analysis of ν_3 HCN---HF Using Fourier Transform Spectroscopy," J. Mol. Spectrosc., 83, 6188-6192 (1985).

Wofford, B. A., Bevan, J. W., Olson, W. B., and Lafferty, W. J., "Rovibrational Analysis and Vibrational Predissociation in the ν_2 Band of HCN Dimer," J. Chem. Phys. 85, 105-108 (1986).

Wofford, B. A., Jackson, M. W., Bevan, J. W., Olson, W. B., and Lafferty, W. J., "Rovibrational Analysis of an Intermolecular Hydrogen-bonded Vibration: The ν^1_6 Band of HCN---HF," J. Chem. Phys. 84, 6115-6118 (1986).

Vahala, L. L., Julienne, P. S., and Havey, M. D., "Nonadiabatic Theory of Fine Structure Branching Cross-Sections for NaHe, NaNe, and NaAr Optical Collisions," Phys. Rev. A 34, 1856 (1986).

(b) Publications in Progress

Basch, H., Krauss, M., and Stevens, W. J., "Cation Binding Effect on Imidazole Tautomerism, Intern. J. Quant. Chem. (in press).

Bodaness, R. S., Heller, D. F., Krasinski, J., and King, D. S., "Two-photon Laser-Induced Fluorescence of the Tumor Localizing Photosensitizer Hematoporphyrin Derivative: Resonance Enchanged 750nm Two-photon Excitation into the Near UV-Soret Band," J. Biol. Chem. (in press).

Burgess, D.,Jr., King, D. S., and Cavanagh, R. R., "Kinetics and Dynamics of the Ammonia/Nitric Oxide Coadsorbate System on Pt(111)," in preparation for submission to Surface Science.

Burgess, D., Jr., Mantell, D. A., Cavanagh, R. R., and King, D. S., "Dynamics of the Laser-induced Thermal Desorption of Nitric Oxide from a Platinum Foil," J. Chem. Phys. (in press).

Burkholder, J. B., Hammer, P. D., Howard, C. J., Maki, A. G., Thompson, G. A., and Chackerian, C., Jr., "Infrared Frequency and Intensity Measurements of the ClO Radical," (manuscript in preparation).

Casassa, M. P., Stephenson, J. C., and King, D. S., "Vibrational Predissociation of the Nitric Oxide Dimer," Faraday Discuss. Chem. Soc. 82, (1986) (in press).

Casassa, M. P., Stephenson, J. C., and King, D. S., "Picosecond Measurements of the Dissociation Rates of the Nitric Oxide Dimer ν_1(v=1) and ν_4(v=1) Levels," J. Chem. Phys. (submitted).

Fraser, G. T., and Pine, A. S., "Van der Waals Potentials from the Infrared Spectra of Rare Gas-HF Complexes," The Journal of Chemical Physics, (in press).

Fraser, G. T., Suenram, R. D., and Lovas, F. J., "Nearly Free Internal Rotation in Ar-CH_3Cl," The Journal of Chemical Physics (in press).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Population Lifetimes of OH(v=1) and OD(v=1) Stretching Vibrations of Alcohols and Silanols in Dilute Solution," J. Chem. Phys., (in press).

Heilweil, E. J., "Vibrational Population Lifetimes of OH(v=1) in Natural Crystalline Micas" Chem. Phys. Letters (in press).

Hinz, A., Wells, J. S., and Maki, A. G., "Heterodyne Frequency Measurements on the Nitric Oxide Fundamental Band," J. Mol. Spectrosc. (submitted).

Hinz, A., Wells, J. S., and Maki, A. G., "Heterodyne Measurements of Hot Bands and Isotopic Transitions of N_2O Near 7.8μm," Zeitschrift fur Physik D, (submitted).

Hougen, J. T., "Hydrogen Migration Tunneling Effects in the Rotational and Vibrational Spectrum of Protonated Acetylene $C_2H_3^+$," J. Mol. Spectrosc. (submitted).

Jackson, M. W., Wofford, B. A., Bevan, J. W., Olson, W. B., and Lafferty, W. J., "Infrared Spectrum of the Overtone Band $2\nu_5 0$ in the Hydrogen Bonded Complex HCN-HF," J. Chem. Phys. (in press).

Jackson, M. W., Wofford, B. A., Bevan, J. W., Olson, W. B., and Lafferty, W. J., "Rovibrational Analysis of the C-H stretching Band and its Overtone in the Hydrogen-bonded Heterodimer HCN---HF," J. Chem. Phys. (in press).

Jacox, M. E., "Comparison of the Electronic Energy Levels of Diatomic Molecules in the Gas Phase and in Inert Solid Matrices," J. Mol. Struct. (in press).

Jasien, P. G., Stevens, W. J., and Krauss, M., "Ab Initio Calculations of the Rotational Barriers in Formamide and Acetamide: The Effects of Polarization Functions and Correlation," J. Mol. Struct. Theochem. (in press).

Jasien, P. G. and Stevens, W. J., "Theoretical Studies of Potential Gas-phase Charge Transfer Complexes: NH_3 + HX (X = Cl, Br, I)," Chem. Phys. Letters (in press).

Jennings, D. E., Weber, A., and Brault, J. W., "FTS-Raman Flame Spectroscopy of High-J Lines in H_2 and D_2," (submitted).

Julienne, P. S. and Mies, F. H, "Nonadiabatic Theory of Atomic Line Broadening: Redistribution Calculations for Sr('P ← 'S) + Ar," Phys. Rev. A (in press).

Julienne, P. S. and Vahala, L. L., "Close Coupled Theory of Fine Structure Transitions in Collisional Redistribution," in Spectral Lineshapes, Vol. 4, ed., by R. Exton (in press).

Lafferty, W. J. and Olson, W. B., "The High Resolution Infrared Spectra of the ν_2 and ν_3 Bands of HOCl," J. Mol. Spectrosc. (in press).

Lafferty, W. J., Suenram, R. D., and Lovas, F. J., "The Microwave Spectra of the $(HF)_2$, $(DF)_2$, HFDF and DFHF Hydrogen Bonded Complexes," J. Mol. Spectrosc. (in press).

Lindsay, D. M., Thompson, G. A., and Wang, Y., "ESR Spectra of $Cu_3(^2A_1)$ in an N_2 Matrix, J. Phys. Chem., (in press).

Lovas, F. J., Suenram, R. D., Ross, S., and Klobukowski, M., "Rotational Structural Ab Initio and Semirigid Bender Analysis of the Millimeter Wave Spectrum of H_2CO-HF," J. Mol. Spectrosc. (in press).

Lovas, F. J. and Suenram, R. D., "Design and Operation of a Pulsed Beam Fourier Transform Microwave Spectrometer, Measurements on OCS and Rare Gas-OCS Complexes," J. Chem. Phys. (in press).

Maki, A. G., "High Resolution Measurements of the ν_2 Band of HNO_3 and the ν_3 Band of trans-HONO," (submitted).

Mies, F. H., Julienne, P. S., Band, Y. B., and Singer, S. J., "A Converged Analysis of Radiative Matrix Elements," J. Phys. B., (in press).

Monten, K. M., Walmskay, C. M., Henkel, C., Wilson, T. L., Snyder, L. E., Hollis, J. M., and Lovas, F. J, "Torsionally Excited Methanol in Hot Molecular Cloud Cores," Astron. Astrophys. (in press).

Nelson, D. D., Jr., Fraser, G. T., Peterson, K. I., Zhao, K., Klemperer, W., Lovas, F. J., and Suenram, R. D., "The Microwave Spectrum of the K=0 States of Ar-NH_3," The Journal of Chemical Physics (submitted).

Ohashi, N. and Hougen, J. T., "The Torsional-Wagging Tunneling Problem and the Torsional-Wagging-Rotational Problem in Methylamine," J. Mol. Spectrosc. (in press).

Olson, W. B., Hunt, R. A., Maki, A. G., and Brault, J. W., "Hydrogen Peroxide: Rotational Constants of the Ground State and the Lowest Torsional Component of the First Excited Torsional State," (submitted).

Pine, A. S. and Looney, J. P., "N_2- and Air-Broadening in the Fundamental Bands of HF and HCl," J. Mol. Spectrosc. (in press).

Schaeffer, R. D., Lovejoy, R. W., Olson, W. B., and Tarrago, G., "High Resolution Spectrum of $^{28}SiH_{3D}$ from 1450 to 1710 cm^{-1}," (submitted).

Suenram, R. D. and Lovas, F. J., "The Microwave Spectrum and Structure of the Argon --- Acrylonitrile van der Waals Complex," (submitted).

Thompson, G. A., Olson, W. B., Maki, A. G., and Weber, A., "Fourier Transform Infrared Spectrum of the Fundamental Band of LiCl at 830°C," (submitted).

Wofford, B. A., Bevan, J. W., Olson, W. B., and Lafferty, W. J., "Rovibrational Analysis of the ν_5 Vibrational Band in the HCN-HF Hydrogen Bonded Cluster," (submitted).

6. TALKS

Casassa, M. P., "Picosecond Measurements of Vibrational Relaxation of Chemisorbed Molecules," Laser Users Group Seminar, NBS, February 1986.

Casassa, M. P., "Time- and State-Resolved Studies of van der Waals Molecule Predissociation," Gordon Conference, August 1986.

Casassa, M. P., "Picosecond Measurements of Vibrational Predissociation of van der Waals Dimers," Symposium on Clusters and Cluster Ions, Baltimore, MD, September 1986.

Casassa, M. P., "Picosecond Studies of van der Waals Molecule Vibrational Predissociation," Surface Science Lunch Bunch Seminar, NBS, September 1986.

Casassa, M. P., "Picosecond Studies of Vibrational Predissociation in van der Waals Molecules," Symposium on State-to-state Chemistry, ACS National Meeting, Anaheim, CA, September 1986.

Fraser, G. T., "van der Waals Potentials from the Infrared Spectra of Rare Gas-HF Complexes," 41st Symposium on Molecular Spectroscopy, Columbus, OH, June 1986.

Fraser, G. T., "Rotational Spectrum, Internal Rotation, and Structure of Ar-CH_3Cl," 41st Symposium on Molecular Spectroscopy, Columbus, OH, June 1986.

Fraser, G. T., "van der Waals Potentials from the Infrared Spectra of Rare-Gas-HF Complexes," 41st Symposium on Molecular Spectroscopy, Columbus, OH, June 1986.

Fraser, G. T., "Infrared and Microwave Spectroscopy of Weakly Bound Complexes," 20th Mid-Altantic Regional Meeting of the American Chemical Society, Symposium on Clusters and Clusters Ions, Baltimore, MD, September 1986.

Fraser, G. T., "Nearly Free Internal Rotation in Ar-CH_3Cl," NATO-Advanced Research Workshop on Structure and Dynamcis of Weakly Bound Molecular Complexes, Maratea, Italy, September 1986.

Fraser, G. T., "Rotational Spectrum and Structure of CF_3H-NH_3," NATO-Advanced Research Workshop on Structure and Dynamics of Weakly Bound Molecular Complexes, Maratea, Italy, September 1986.

Heilweil, E. J., "Picosecond Vibrational Dynamics of Hydroxyl Groups in Condensed Phase Systems," National Institutes of Health, January 1986.

Heilweil, E. J., "Picosecond Vibrational Dynamics of Hydroxyl Groups in Condensed Phase Systems," Chemistry Department, Physical Chemistry Seminar, University of Illinois, Urbana, IL, February 1986.

Heilweil, E. J., "Population Lifetimes of OH(v=1) and OD(v=1) Vibrations in Alcohols, Silanols and Crystalline Micas," Ultrafast Phenomena Conference, Snowmass, CO, June 1986.

Heilweil, E. J., "Picosecond Vibrational Dynamics of Hydroxyl Groups in Condensed Phase Systems," Gordon Conference on Vibrational Spectroscopy, Wolfeboro, NH, August 1986.

Hougen, J. T., "Symmetry Beyond Point Groups in Molecular Spectroscopy," Duke University, Durham, NC, November 1985.

Hougen, J. T., "Hydrogen Migration Tunneling Effects in the Rotational and Vibrational Spectrum of Protonated Acetylene," University of California at Irvine, March 1986.

Hougen, J. T., "Overview of Molecular Spectroscopy at NBS," Jet Propulsion Laboratories, Pasadena, CA, March 1986.

Hougen, J. T., "Hydrogen Migration Tunneling Effects in the Rotational and Vibrational Spectrum of Protonated Acetylene," NBS, Boulder, CO, March 1986.

Hougen, J. T., "Hydrogen Migration Tunneling Effects in the Rotational and Vibrational Spectrum of Protonated Acetylene, $C_2H_3^+$," 41st Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 1986.

Hougen, J. T., "Far-Infrared Spectrum of Methylamine and the Group Theoretical Treatment of Its Large Amplitude Motions," 41st Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 1986.

Hougen, J. T., "Hydrogen Migration Tunneling Effects in the Rotational and Vibrational Spectrum of Protonated Acetylene, $C_2H_3^+$," 9th International Conference on High Resolution Infrared Spectroscopy, Liblice (near Prague), Czechoslovakia, September 1986.

Hougen, J. T., "The Role of Tunneling Models in Analyzing High-Resolution Spectra of Weakly Bound Molecular Complexes," NATO-Advanced Research Workshop on Structure and Dynamics of Weakly Bound Molecular Complexes, Maratea, Italy, September 1986.

Jacox, M. E., "Vibrational Spectra of Free Radicals Formed by the Reaction of F Atoms with Small Molecules," Department of Chemistry, Bryn Mawr College, Bryn Mawr, PA, November 1985.

Jacox, M. E., "Vibrational Spectra of Free Radicals Formed by the Reaction of F Atoms with Small Molecules," AT & T Bell Laboratories, Murray Hill, NJ, December 1985.

Jacox, M. E., "Vibrational Spectra of Free Radicals Formed by the Reaction of F Atoms with Small Molecules," Delaware Valley Section, Society for Applied Spectroscopy, Philadelphia, PA, February 1986.

Jacox, M. E., "Vibrational Spectra of Free Radicals Formed by the Reaction of F Atoms with Small Molecules," Department of Chemistry, University of Colorado, Boulder, CO, February 1986.

Jacox, M. E., "Matrix Isolation Spectroscopic Studies of the Reaction of F Atoms with Small Molecules," Symposium on Matrix Isolated Species, Central Regional American Chemical Society Meeting, Bowling Green, OH, June 1986.

Jacox, M. E., "Spectroscopy of Free Radicals Formed in the Early Stages of Nitramine Decomposition," U.S. Army Research Office Workshop on Combustion Probes for the Solid Nitramines, Combustion Research Facility, Sandia National Laboratory, Livermore, CA, June 1986.

Jacox, M. E., "Comparison of the Electronic Energy Levels of Diatomic Molecules in the Gas Phase and in Inert Solid Matrices," 41st Symposium on Molecular Spectroscopy, Columbus, OH, June 1986.

Jacox, M. E., "The A $^2\Pi$ - X $^2\Sigma^+$ Near Infrared Absorption Spectrum of HC_2 Isolated in Solid Argon," 41st Symposium on Molecular Spectroscopy, Columbus, OH, June 1986.

Julienne, P. S., "Close Coupled Theory of Fine Structure Transitions in Collisional Redistribution," 8th International Conference on Spectral Line Shapes, College of William and Mary, Williamsburg, VA, June 1986.

Julienne, P. S., "Close Coupled Theory and Analytic Models for Collisional Redistribution," Department of Atomic Physics, University of Newcastle, Newcastle-upon-Tyne, England, July 1986.

Julienne, P. S., "Close Coupled Calculations on Laser Assisted Collisions," Max Planck Institute for Quantum Optics, Garching, West Germany, July 1986.

Julienne, P. S., "Scattering Theory of Photoassisted Collisions: Application to Alkali and Alkaline Earth Atoms Colliding with Rare Gas Atoms," and "Half Collision Analysis of Photoassisted Collisions: Development of Physical Insight," Department of Physics, University of Kaiserslautern, Kaiserslautern, West Germany, August 1986.

Julienne, P. S., "Close Coupling Calculations of Atomic Line Profiles and Collisional Redistribution for ^1P and ^2P Transitions," Observatoire de Paris, Meudon, France, September 1986.

King, D. S., "Molecule-Surface Dynamics," Rice University, Department of Chemistry and Rice Quantum Institute, Rice University, Houston, TX, November 1985.

King, D. S., "Two-Photon Excitations of the Tumor-Localizing Photosensitizer HPD," International Laser Science Conference, Dallas, TX, November 1985.

King, D. S., "Dynamics of the Molecular-Surface Interaction," JILA Symposium, Boulder, CO, March 1986.

King, D. S., "Thermal and Laser-Induced Desorption Dynamics," Cornell University, Department of Chemistry, Cornell University, Ithaca, NY, March 1986.

King, D. S., "Dynamics of the Photodissociation of van der Waals Dimers," Virginia Commonwealth University, Chemistry Department, Richmond, VA, March 1986.

King, D. S., "Vibrational Predissociation of NO-containing van der Waals Dimers," ACS Symposium on Dynamics of Clusters, National Meeting, NY, April 1986.

King, D. S., "Photodissociation of van der Waals Dimers," Brookhaven National Laboratory, Chemistry Department, Long Island, NY, April 1986.

King, D. S., "NO/Pt Interactions: Thermal- and Laser-Induced Desorption," IBM, Yorktown Heights, NY, April 1986.

King, D. S., "Vibrational Predissociation Dynamics of the Nitric Oxide Dimer," NBS Staff Research Seminar Series, NBS-Gaithersburg, May 1986.

King, D. S., "Dynamics of the Vibrational Predissociation of the Nitric Oxide Dimer," Mid-Atlantic Regional Meeting of ACS, Baltimore, MD, September 1986.

King, D. S., "Vibrational Predissociation Dynamics of van der Waals Dimers," Faraday Soc. Disc. on Photodissociation Dynamics, Bristol, England, September 1986.

King, D. S., "Vibrational Predissociation Dynamics of van der Waals Dimers," NATO-Advanced Research Workshop on Structure and Dynamics of Weakly Bound Molecular Complexes, Maratea, Italy, September 1986.

Krauss, M., "Pt Binding to DNA," Chemistry Department, Drexel University, Philadelphia, PA, May 1986.

Krauss, M., "$Pt(NH_2R)_2$ Binding to a tetramer Duplex of DNA," Meeting of the American Society of Biological Chemists, Washington, D.C., June 1986.

Lafferty, W. J., "Sub-Doppler Resolution Infrared Spectroscopy of the Carbon Dioxide Dimer," Mid-Atlantic Regional Meeting of ACS, Baltimore, MD, September 1986.

Lovas, F. J., "Microwave Spectrum and Properties of the Methanol-Formamide Complex," Mid-Atlantic Regional Meeting of ACS, Baltimore, MD, September 1986.

Maki, A. G., "High Resolution Measurements and Analysis of the ν_2, ν_3, ν_4, ν_5, and $2\nu_9$ Bands of Nitric Acid," 41st Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 1986.

Maki, A. G., "New Infrared Frequency and Intensity Measurements on Chlorine Monoxide (ClO)," 41st Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 1986.

Mies, F. H., "Collisional Redistribution of Intense Laser Radiation," Department of Chemistry, Tel Aviv University, Tel Aviv, Israel, February 1986.

Mies, F. H., "Collisional Redistribution of Intense Laser Radiation," Department of Chemical Physics, Weizmann Institute, Rohovot, Israel, February 1986.

Mies, F. H., "Collisional Redistribution of Intense Laser Radiation," Department of Physics, Bar Ilan University, Ramat-Gan, Israel, March 1986.

Mies, F. H., "Collisional Redistribution of Intense Laser Radiation," Department of Chemistry, Ben Gurion University, Beer Sheva, Israel, March 1986.

Olson, W. B., "Experimental Values for the Rotational Constants of the 0G and 1G Torsional Components of the Vibrational Group State of H_2O_2, and the Matrix Element Coupling Them," 41st Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 1986.

Pine, A. S., "High-Resolution Infrared Spectroscopy of Hydrogen-Bonded and van der Waals Complexes," Department of Chemistry, Johns Hopkins University Baltimore, MD, November 1985.

Pine, A. S., "High-Resolution Spectroscopy of van der Waals and Hydrogen-Bonded Complexes," NBS Staff Research Seminar, NBS Gaithersburg, MD, May 1986.

Pine, A. S., "N_2 and Air Broadening in the Fundamental Bands of HF and HCl," 41st Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 1986.

Pine, A. S., "Vibrational Anomalies and Dynamic Coupling in Hydrogen-Bonded van der Waals Molecules," NATO-Advanced Research Workshop on Structure and Dynamics of Weakly Bound Molecular Complexes," Maratea, Italy, September 1986.

Stephenson, J. C., "Picosecond Studies of Vibrational Energy Transfer: Surfaces, Solids, and Liquids," AFOSR Contractors Meeting, Dayton, OH, November 1985.

Stephenson, J. C., "Picosecond Studies of Vibrational Energy Transfer: Surfaces, Solids, and Liquids," Department of Chemistry, University of Pittsburgh, PA, March 1986.

Stephenson, J. C., "Picosecond Studies of Vibrational Energy Transfer: Surfaces, Solids, and Liquids," Department of Chemistry, Cornell University, April 1986.

Stephenson, J. C., "Picosecond Studies of Vibrational Energy Transfer: Surfaces, Solids, and Liquids," Department of Chemistry, U. C. Berkeley, Berkeley, CA, June 1986.

Stephenson, J. C., "Picosecond Studies of Vibrational Energy Transfer: Surfaces, Solids, and Liquids," International Quantum Electrons Conference, San Francisco, CA, June 1986.

Suenram, R. D., "Rotational Spectra and Structural Determinations of Several van der Waals Complexes," Rice University, Department of Chemistry Colloquium, Houston, TX, March 1986.

Suenram, R. D., "Rotational Spectra and Structural Determinations of Several van der Waals Complexes," 11th Annual Austin Symposium on Molecular Structure, Austin, TX, March 1986.

Suenram, R. D., "Rotational Spectrum of the Hydrogen Bonded Formamide-Water Complex," Mid-Atlantic Regional Meeting of ACS, Baltimore, MD, September 1986.

Suenram, R. D., "Structures of the Ar···Acrylonitrile and Ar···Formamide van der Waals Complexes," NATO-Advanced Research Workshop on Structure and Dynamcis of Weakly Bound Molecular Complexes, Maratea, Italy, September 1986.

Suenram, R. D., "Rotational Spectrum of the Hydrogen Bonded Formamide-Water and Formamide-Methanol Complexes," NATO-Advanced Research Workshop on Structure and Dynamics of Weakly Bound Molecular Complexes, Maratea, Italy, September 1986.

Thompson, G. A., "Infrared Spectroscopy of High Temperature Diatomics," Rome Air Develpment Center, Griffisse Air Force Base, NY, May 1986.

Thompson, G. A., "High Temperature Spectroscopy of Alkali Halides and Hydrides at High Temperature," Advanced Fuel Research, Inc., East Hartford, CT, May 1986.

Thompson, G. A., "Infrared Spectroscopy of High Temperature Diatomics," Photometrics, Inc., Boston, MA, May 1986.

Thompson, G. A., "High Resolution Infrared Spectroscopy of LiCl at 800°C," 41st Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 1986.

Weber, A., "Research in High Resolution Molecular Spectroscopy at NBS," ENEA, Centre Ricerche Energie Frascati, Frascati, Rome, Italy, September 1986.

Weber, A., "Research in High Resolution Molecular Spectroscopy at NBS," Physics Deparment, University of Florence, Florence, Italy, September 1986.

Weber, A., "Research at NBS in High Resolution Spectroscopy of Weakly Bound Molecular Complexes," Physics Department, University of Giessen, Giessen, Germany, October 1986.

7. MOLECULAR SPECTROSCOPY DIVISION SEMINARS

Balasubramanian, K., Department of Chemistry, Arizona State University, Tempe, NJ, "Electronic Structure of Moelcules Containing Heavy Atoms" May 1986.

Ben-Reuven, A., School of Chemistry, Tel-Aviv University, Tel-Aviv, Israel, "New Challenges in the Study of Spectral Line Shapes," September 1986.

Bevan, J., Chemistry Department, Texas A&M University, College Station, TX, "Dynamical Behavior in Linear Hydrogen-Bonded Interactions," November 1985.

Beveridge, D., Department of Chemistry, Hunter College, New York, NY, "Aqueous Hydration of Biological Molecules: Free Energy Simulations," February 1986.

Clough, S. A., Air Force Geophysics Laboratory, Hanscom AFB, MA, "Line Shapes and Molecular Collisional Broadenings with Applications to Atmospheric Problems," February 1986.

Cook, M., Naval Research Laboratory, "Electronic Structure of the $MoFe_3S_4(SH)_6^{3-}$ Ion: A Model for the Nitrogenase Active Site," October 1985.

DeFrees, D., Molecular Research Institute, San Jose, CA, "Theoretical Studies of Interstellar Chemistry," November 1985.

Fink, W. H., Chemistry Department, National Science Foundation, Washington, D.C., "Influence of External Potentials of H-Bonding," December 1985.

Graner, G., Universite de Paris-Sud, Orsay, France, "Recent Work in Molecular Spectroscopy at Laboratoire d'Infrarouge," June 1986.

Harris, D., Chemistry Department, University of California, Santa Barbara, CA, "Spectroscopy and Structure of MgOH: A Quasi-Linear Molecule," December 1985.

Harrison, J., Chemistry Department, Michigan State University, East Lansing, MI, "Electronic and Geometric Structure of Transition Metal-Containing Cations," August 1986.

Herman, R., Department of Physics, Penn State University, PA, "Velocity-changing Effects on Collisional Lineshapes," May 1986.

Kok, R., University of Georgia, Athens, GA, "Molecular Mechanics and Ab Initio Calculations on Some Organic and Organo-metallic Compounds," October 1985.

Konowalow, D. D., Ballistics Research Laboratory, Aberdeen, MD, "High Spin States of He_2," July 1986.

Lester, W., Department of Chemistry, University of California, Berkeley, CA, "Quantum Monte Carlo of Electronic Structure," August 1986.

Lisy, J., Chemistry Department, University of Illinois, IL, "Vibrational Predissociation Spectroscopy of Molecular Clusters," March 1986.

Malvezzi, M., Gordon McKay Laboratory, Harvard University, MA, "Picosecond Laser Excitation, Melting, and Vaporization of Solid Surfaces," April 1986.

Mautner, M., Chemical Kinetics Division, NBS, Gaithersburg, MD, "Cluster Ions and The Ionic Hydrogen-Bond," January 1986.

Mialocq, J.-C., Centre d'Etudes Nucleaires de Saclay, Department de Physico-Chimie, France, "Ultrafast Molecular Dynamics Studied with Picosecond Lasers," June 1986.

Miller, A. E. S., Department of Chemistry, Bryn Mawr College, Bryn Mawr, PA, "Electronic Structure of Transition-Metal Hydrides," March 1986.

Mollendal, H., Universiteteti Oslo, Oslo, Norway, "Microwave Spectra of 1,4 defluoro -2-butyne and Several Molecules with Intra-molecular Hydrogen Bonds," March 1986.

Osman, R., Department of Physiology and Biophysics, Mt. Sinai School of Medicine, New York, NY, "A New Mechanism of Action of Superoxide Dismutase," November 1985.

Rappe, A. K., Department of Chemistry, Colorado State University, CO, "Studies on $2_\pi + 2_\pi$ Reactions: Allowed Reactions Involving Transition Metal Complexes," October 1985.

Rosenkrantz, M., Ballistic Research Laboratory, Aberdeen, MD, "Application of Quantum Chemistry to Molecules of Atmospheric Interest," October 1985.

Sandroff, C., AT & T Bell Communications, "Layered Semiconductor Colloids and Their Uses: Interfacial Science, Cluster Chemistry and New Solid Materials," December 1985.

Saykally, R., Chemistry Department, University of California, Berkeley, CA, "Laser Spectroscopy of Molecular Ions and van der Waals Molecules," May 1986.

Schrötter, H.-W., Sekton Physik, Universitat München, West Germany, "High Resolution CARS and Inverse Raman Spectroscopy," August 1986.

Scoles, G., Department of Chemistry, University of Waterloo, Waterloo, Canada, "Infrared Laser Molecular Beam Spectroscopy of Molecule-Noble Gas Clusters," April 1986.

Shapiro, M., Chemical Pnysics Department, Weizmann Institute of Science, Rehovot, Israel, "Coherent Control of Unimolecular Reactions," January 1986.

Shuker, R., Physics Department, Ben Gurion University of the Negev, Beer Shene, Israel, "Laser Induced Cherenkov and Non-linear Effects in Sodium Vapor," June 1986.

Smalley, R., Chemistry Department, Rice University, Houston, TX, "New Results with Supersonic Cluster Beams," November 1985.

Sutter, D. H., Institut für Physikalische Chemie, Universitat Kiel, Kiel, Olshausenstrasse, Germany, "Microwave Zeeman and Fourier Transform Studies at Kiel," February 1986.

Toennies, J. P., Max-Planck-Institut für Stromungesforchung, Gottingen, West Germany, "State Resolved Molecular Beam Scattering Experiments on Atom-molecule Inelastic Collisions," March 1986.

Vidal, C. R., Institut für Extraterrestrische Physik, Max-Planck-Institut für Physik und Astrophysik, Bayern, West Germany, "Laser Intracavity Absorption," April 1986.

Watts, R. O., The Australian National University, Canberra, Australia, "Molecular Structure and Dynamics from Molecular Beam Experiments," April 1986.

8. TECHNICAL AND PROFESSIONAL COMMITTEE PARTICIPATION AND LEADERSHIP

Hougen, J. T.

Member, Editorial Advisory Board, Journal of Molecular Spectroscopy.

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 a National Science Foundation panel for the review of proposals for Engineering Research Equipment Grants and Research Initiation Grants.

Member, Admissions Committee, NBS Chapter, Sigma XI.

King, D. S.

Member, DOE University Research Instrumentation Grant Award Review Panel.

Lovas, F. J.

Member, International Astronomical Union Commission 14: Fundamental Spectroscopic Data.

Maki, A. G.

Member, Editorial Advisory Board, Journal of Molecular Spectroscopy.

Weber, A.

Editoral Advisory Board, Journal of Raman Spectroscopy.

Chairman, Williams-Wright Awards Symposium, Coblentz Society, March 1986.

Member, Program Committee, 10th International Conference on Raman Spectroscopy, 1986.

Chairman, Welsh Symposium on High Resolution Spectroscopy, 10th International Conference on Raman Spectroscopy, University of Oregon, September 1986.

Director and Chairman, Organizing Committee, NATO Advanced Research Workshop on "Structure and Dynamics of Weakly Bound Molecular Complexes."

Editorial Advisory Board, Journal of Physical and Chemical Reference Data.

Member, Program Committee, International Conference on Infrared and Fourier Transform Spectroscopy, Washington, 1989.

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.

Consulted with Dr. K. C. Janda, University of Pittsburgh, on studies of the photodissociation of van der Waals molecules.

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 Professor R. M. Hochstrasser, University of Pennsylvania, on transient grating phenomena in molecular solutions.

Jacox, M. E.

Collaborated with Dr. J. Hudgens, Chemical Kinetics Division, NBS, on the assignment and normal coordinate analysis for Rydberg state of CH_2OH.

Consulted with Dr. P. Thaddeus, Institute for Space Studies, on the spectroscopy of C_3H_2, HCCNH.

Collaborated with Dr. R. F. Curl, Department of Chemistry, Rice University, on near infrared absorption spectrum of HC_2.

Consulted with Dr. G. Herzberg, National Research Council of Canada, on infrared spectra of trihalides and trihalide and anions.

Collaborated with Dr. J. Wormhoudt, Aerodyne Research, Inc., on infrared spectra of SiH_2 and SiH_3.

Consulted with Dr. K. Kawaguchi, Institute for Molecular Science, Okazaki, Japan, on infrared spectrum of BH_3.

Julienne, P. S.

Consulted with Dr. L.Vahala, Old Dominion University, Norfold, VA, on calculation of collisionally broadened line profiles and collisional redistribution of light for Na + He, Ne, Ar systems.

Collaborated with Dr. J. Weiner, University of Maryland, on theory of photoassociation 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, Imperial College, London, England, on the development of close coupled and semiclassical theories for collisional redistribution of light.

Consulted with Dr. H. Hotop, University of Kaiserslautern, West Germany, on the development of close coupled theory and half collision analysis of collision of oriented or aligned atoms.

King, D. S.

Collaborated with Dr. R. Bodanness, NIH, on the role of biphotonic processes in the photo-activated generation of singlet oxygen.

Consulted with Dr. D. F. Heller, Allied Chemical Corp., on uses of Alexandrile laser in biophysics.

Collaborated with Dr. R. R. Cavanagh and Dr. W. Gadzuk, on experimental and theoretical aspects of molecular dynamics of the gas-surface interface.

Krauss, M.

Collaborated with Dr. K. J. Miller, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, on Pt binding to DNA.

Collaborated with Dr. H. Basch, Bar Ilan University, Israel, on molecular orbital calculations of biomolecules.

Collaborated with Dr. R. Osman, Mt. Sinai Medical School, NY, on mechanisms of metalloenzymes.

Lafferty, W. J.

Collaborated with Dr. J. P. Sattler, Harry Diamond Laboratory, on optically pumped far infrared laser line assignments.

Collaborated with Professor N. Craig, Oberline College, on high resolution infrared studies of fluoroethylenes.

Collaboration with Drs. S. A. Clough and M. Hoke, Air Force Geophysics Laboratory, in the study of collisional interference on the spectrum of CO_2.

Lovas, F. J.

Collaborated with Professor L. E. Snyder, University of Illinois, and Dr. J. M. Hollis, NASA/Goddard Space Flight Center, on interstellar molecular searches.

Collaborated with Drs. C. W. Gillies and J. Zozom, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, on microwave spectral studies.

Maki, A. G.

Collaborated with Dr. A. Goldman, University of Denver, on studies of Nitric Acid spectra.

Collaborated with Dr. A. Fayt, Universite Catholique de Louvain, Belgium, on the analysis of the ν_2 and ν_4 bands of HNO_3 and on Lamb-dip measurements of laser-Stark spectra.

Collaborated with Dr. J. Wells, Time and Frequency Division, NBS-Boulder on the frequency measurements an analysis of N_2O and NO absorption lines using heterodyne techniques.

Collaborated with Dr. C. Chackerian, NASA Ames Research Center, Moffett, CA, on the use of the Herman-Wallis effect to measure the intensity of the ClO fundamental band.

Pine, A. S.

Collaborated with Drs. R. M. Herman and J. P. Looney, Department of Physics, Penn State University, University Park, PA, on line broadening mechanisms in HF and HCl.

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. B. J. Howard, Physical Chemistry Laboratory, Oxford University, Oxford, England, on the analysis of the spectra of the rare gas-hydrogen chloride van der Waals complexes.

Collaborated with Dr. L. L. Strow, Department of Physics, Unviersity of Maryland, Baltimore, MD, on line coupling and rotational collapse of Q-branches of N_2O.

Stephenson, J. C.

Collaborated with Dr. J.-C. Mialocq, Centre d'Etndes Nucleaires de Saclay, France, on picosecond laser photolysis of nitro compounds.

Stevens, W. J.

Collaborated with Dr. M. Dupuis, IBM Corporation, on quantum chemistry calculations for large molecules.

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 reaction 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. W. Fink, University of California at Davis, on frozen fragment calculations of molecular structures and interactions.

Suenram, R. D.

Collaborated with Professor L. E. Snyder, University of Illinois, on radio astronomy searches for interstellar molecules.

Collaborated with Dr. H. M. Pickett, Jet Propulsion Laboratory, on $HOONO_2$ and CH_2FOH rotational spectra.

Consulted with Professor C. W. Gillies, Rensselaer Polytechnic Institute, on construction of pulsed Fourier transform microwave spectrometer.

Consulted with Dr. D. D. Nelson and Professor W. Klemperer, Harvard University, on $Ar \cdots NH_3$, and $NH_3 \cdots NH_3$ van der Waals complexes.

Consulted with Professor R. L. Kuczkowski and Dr. K. W. Hillig, II, University of Michigan, on construction of pulsed Fourier transform microwave spectrometer.

Consulted with Professor S. G. Kukolich, University of Arizona, on construction of pulsed Fourier transform microwave spectrometer.

Collaborated with Professor S. Ross, University of Alberta, on data fitting for $H_2CO \cdots HF$ hydrogen bonded species.

Collaborated with Professor R. K. Bohn, University of Connetticut, on assistance in the high resolution rotational assignment of several molecular species.

Collaborated with Dr. R. Ruoff and Professor H. S. Gutowsky, University of Illinois, on the measurement of dipole moment of the HCN trimer.

Weber, A.

Collaborated with Dr. J. W. Brault, National Solar Observatory, Tucson, AZ, on Raman Spectroscopy of gases with Fourier transform techniques.

Collaborated with Dr. K. Narahari Rao, Ohio State University, Columbus, OH, on discussions of the organization of the 1986 Columbus Symposium.

Collaborated with Drs. P. Esherick and L. Rahn, Sandia National Laboratories, Professor B. P. Stoicheff, University of Toronto, Professor H. W. Schrötter, University of Munich, Professor W. Kiefer, University of Graz, Dr. G. Rasasco, Temperature and Pressure Division, NBS, and Dr. J. Nibler, Chemistry Department, Oregon State University, on the planning for the 10th International Conference on Raman Spectroscopy held in Eugene, OR, September 1986.

Collaborated with Dr. D. E. Jennings, NASA/Goddard Space Flight Center, Greenbelt, MD, on Raman spectroscopy of gases with Fourier transform techniques.

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.

Consulted with Professor K. Miller, Rensselaer Polytechnic Institute, on advice on vibrational spectra of hydrocarbons.

Consulted with Dr. W. H. Weber, Ford Motor Company, on advice on the calibration of spectrometers.

10. VISITING SCIENTISTS

The Molecular Spectroscopy Division has been host in the past year to the following scientists who have worked with NBS scientists on problems of mutual interest.

Adams, George, A., Ballistics Research Laboratory, works with M. Krauss on electronic structure codes for the chemistry and spectroscopy of large molecules.

Basch, Harold, Bar Ilan University, Israel, is engaged in research on metal interactions with biomolecules. He works with M. Krauss.

Bodaness, Robert S., National Institutes of Health, works with D. S. King on laser photosensitization processes in biological samples.

Craig, N., Oberlin College, works with W. J. Lafferty on the Fourier transform Infrared spectrum of 1,2-difluorethylene.

Fink, W. H., National Science Foundation, works with W. J. Stevens on the development of model potentials and their application to large molecules.

Gillies, C. W., Chemistry Department, Rensselaer Polytechnic Institute, works with F. J. Lovas and R. D. Suenram on pulsed beam Fourier transform microwave spectroscopy of hydrogen bonded molecules.

Hollis, Jan Michael, NASA/Goddard Space Flight Center, works with F. J. Lovas and R. Suenram on software development for automated microwave spectrometer and collaborates on astronomical studies.

Jennings, Donald E., NASA/Goddard Space Flight Center, works with A. Weber on a project to do Raman spectroscopy of gases with the Fourier transform spectrometer of the National Solar Observatory (Kitt Peak).

Konowalow, Daniel D., Professor at SUNY-Binghamton, New York, works with M. Krauss on studies of electronic structure of alkali and alkaline earth molecules.

Lengsfield, Byron H., Ballistic Research Laboratory, works with M. Krauss on electronic structure codes for the chemistry and spectroscopy of large molecules.

Ohashi, Nobukimi, Kanazawa University, Physics Department, Japan, works with J. T. Hougen, W. J. Lafferty, and W. B. Olson on high resolution infrared spectroscopy and theory of methylamine.

Osman, R., Mt. Sinai School of Medicine, New York, works with W. J. Stevens on the application of ab initio quantum chemistry to biochemical modeling.

Sattler, Joseph L., Harry Diamond Laboratories, U.S. Army, collaborates with W. J. Lafferty and A. Maki on precise line frequency measurements in the infrared.

Vahala, Linda L., Physics Department, Old Dominion University, Norfolk, VA, works with P. S. Julienne on the theory of molecular line broadening and final state branching ratios for the resonance transitions of alkali atoms perturbed by rare gas collision partnes.

Zozom, Jennifer, Chemistry Department, Rensselaer Polytechnic Institute works with Drs. F. J. Lovas and R. D. Suenram on pulsed beam Fourier transform microwave spectroscopy of hydrogen bonded molecules.

NBS-114A (REV. 2-8C)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 86-3470	2. Performing Organ. Report No.	3. Publication Date OCTOBER 1986

4. TITLE AND SUBTITLE

Technical Activities 1986
Center for Chemical Physics

5. AUTHOR(S)

Pierre Ausloos

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report summarizes research projects, measurement method development, testing and data evaluation activities carried out during Fiscal Year 1986 in the NBS Center for Chemical Physics. These activities fall in the areas of surface science, chemical kinetics, chemical thermodynamics and molecular spectroscopy.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Chemical kinetics; chemical physics; molecular spectroscopy; surface science; thermodynamics

13. AVAILABILITY

☒ Unlimited
☐ For Official Distribution. Do Not Release to NTIS
☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

366

15. Price

$28.95