NISTIR 4390

TECHNICAL ACTIVITIES 1989
MOLECULAR PHYSICS DIVISION

A. Weber
Chief

U.S. DEPARTMENT OF COMMERCE
National Institute of Standards
and Technology
National Measurement Laboratory
Center for Atomic, Molecular, and
Optical Physics
Molecular Physics Division
Gaithersburg, MD 20899

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ABSTRACT

This report summarizes the technical activities of the NIST Molecular Physics Division during the Fiscal Year 1989. The activities span experimental and theoretical research in high resolution molecular spectroscopy, quantum chemistry and molecular dynamics, and include the development of frequency standards, critically evaluated spectral data, applications of spectroscopy to important scientific and technological problems, and the advancement of spectroscopic measurement methods and techniques. A listing is given of publications and talks by the Division staff.

FOREWORD

This report is a summary of the technical activities of the NIST Molecular Physics Division for the Fiscal Year 1989. It was prepared as part of the Annual Report of the Center for Atomic, Molecular, and Optical Physics within the National Measurement Laboratory of NIST. The Molecular Physics Division is organized into three working groups comprised of permanent staff, postdoctoral fellows, guest researchers, and support personnel. An organizational chart of the Division is given at the end of this Foreword.

The goals and activities of the Division and the general nature of its technical programs are described in the Introduction, Section 1. Sections 2-4 present the descriptions of technical work done by the High Resolution Spectroscopy, Molecular Dynamics, and Quantum Chemistry Groups. Each group report gives project objectives, details of results obtained during the past year, and plans for future work.

The technical descriptions are followed by Sections 5 and 6 which list the publications and talks given during the past year, while Section 7 lists the seminars hosted by the Division. The Division has had a number of visiting scientists during the past year; these are identified in Section 8.

Further information on the activities of the Division can be obtained by contacting the scientists identified in each project report, or by writing to Dr. Alfons Weber, Molecular Physics Division, Physics Building, B268, National Institute of Standards and Technology, Gaithersburg, MD 20899.

MOLECULAR PHYSICS DIVISION

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A. Kuehl, Secretary
C. V. Kurtz, Division Technician

HIGH RESOLUTION

A. Weber, Group Leader
L. Coudert*
W. Fawzy*
G. Fraser
C. Gillies*
J. Gillies*
J. Hougen
M. Jacox
I. Kleiner*
W. Lafferty
F. Lovas
K. Matsumura*
S. Novick*
W. Olson++
A. Pine
G. Rotter
R. Suenram
W. Thompson*

QUANTUM CHEMISTRY

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H. Basch*
R. Dubs+
A. Giusti*
R. Heather
P. Julienne
F. Mies
K. Miller++
W. Stevens
L. Vahala*

MOLECULAR DYNAMICS

J. Stephenson, Group Leader
D. Beckerle+++
S. Buntin++
M. Casassa
R. Cavanagh+++
L. Elwell
B. Foy+
E. Heilweil
D. King

*	Guest Researcher
+	Postdoctoral Research Associate
++	Contractor
+++	NIST Surface Science Division Collaborator

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MOLECULAR PHYSICS DIVISION

FISCAL YEAR 1989 TECHNICAL ACTIVITIES

I. INTRODUCTION

The properties of molecules and molecular systems as determined by theoretical and experimental spectroscopic methods are a major part of the interdisciplinary field of chemical physics. Originally limited to the study of molecular properties per se, molecular spectroscopy is now ubiquitous in many areas of physics, chemistry, astronomy, biology, environmental science, and various branches of engineering, all of which require data, models, and theoretical concepts to meet their respective needs.

In recent years Molecular Physics has undergone many changes and NIST has both responded and contributed to them in response to the developments of new experimental techniques and theoretical predicitions, challenges posed by basic problems at the forefront of chemical physics, and the needs of the user community. At the present time the work of the Division is conducted in three broad areas: molecular dynamics, high resolution spectroscopy, and quantum chemistry. Although seemingly disparate, the conduct of research in these three broad areas is marked by collaboration, and sharing of equipment and expertise, by the staff.

Though the problems currently attacked bear the mark of fundamental investigations, all of them are pursued either in direct response to the needs of other government agencies, e.g., the Air Force Office of Scientific Research (AFOSR), the Department of Energy (DOE), the National Aeronautics and Space Administration (NASA), industry, or as long term research projects to establish data bases for newly emerging technologies and to meet the contemporary challenges implied in the mission statement of NIST, newly reformulated in the Omnibus Trade Bill of 1988.

A. GOAL

The goal of the Molecular Physics Division is to conduct research at the forefront of theoretical and experimental spectroscopy in order to provide NIST, other government agencies, industry, and the research community with:

- Critically evaluated reference spectroscopic data.
- State-of-the-art calibration frequency standards.
- Forefront spectroscopic results and expertise.
- Data on molecular species of importance to environmental and climatic concerns.

- Data and models on ultrafast molecular processes, intramolecular dynamics, energy transfer in dilute and condensed phase systems, and molecule-surface interactions.
- Properties and behavior of weakly bound molecular aggregates.
- Properties and behavior of atomic and molecular systems in the presence of strong laser fields, and at ultra low temperatures.
- Advanced spectroscopic measurement methods and techniques.
- Theoretical concepts and quantum theoretical methods for predicting properties and energetics of molecules, clusters, and systems of biological importance.

B. ORGANIZATION AND STAFFING

The Division is composed of 22 full time permanent staff members as well as post doctoral research associates, guest researchers and contractors from other institutions in the U.S. and abroad. During the past year several changes have occurred. Wm. Bruce Olson and Arthur G. Maki of the High Resolution Group have retired while Robert Heather has joined the Quantum Chemistry Group.

To carry out its research the Division is organized into three working groups: Molecular Dynamics, High Resolution Spectroscopy, and Quantum Chemistry.

GROUP REPORTS

The activities conducted during the past year by the three research groups are presented in the following three sections.

II. HIGH RESOLUTION SPECTROSCOPY GROUP

The work of this group covers a variety of spectroscopic topics, many of which are part of programmatic efforts. The research reports are divided into six general topics: Data Center Activities, Spectroscopic Studies of Environmental Species, Hydrogen-bonded and van der Waals Complexes, Matrix Isolation Studies and Spectroscopic Theory. A number of guest researchers or contractors participated in the work. They are identified by an asterisk affixed to their names.

A. Data Center Activities

We collect under this heading the work most closely connected with the core mission of NIST, namely, the production and dissemination of compilations of accurately measured frequencies or wavenumbers for use as secondary standards, and of critically evaluated molecular properties for use in other disciplines. The group devotes a significant portion of its effort each year to this program which serves the needs in the microwave, infrared, and ultraviolet spectral regions.

1. Microwave Spectral Tables
(F. J. Lovas, R. D. Suenram, and G. L. Rotter)

In June 1988 we submitted a manuscript entitled "Microwave Spectral Tables III. Hydrocarbons, CH to $C_{10}H_{10}$" to the J. Phys. Chem. Ref. Data for publication. The manuscript includes 135 tables of molecular constants and 91 tables of spectral frequencies. This critical review contains all of the rotational spectral lines observed and reported in the open literature for 91 hydrocarbon molecules. Progress in publishing this compilation has been slow owing to the need for substantial editing on the Bedford computer by OSRD staff and further proofing of the edited copy; however, this review will appear in the next issue of the journal. During FY 1989 we continued work on the Microwave Spectral Tables IV which treats organic species containing oxygen. Our reprint collection currently contains 171 species in this class with empirical formulas CHO through $C_7H_{12}O$. Spectral data for 55 species (262 isotopic forms) have been coded for spectral fitting and table generating programs. The first part of this review (about half of the species) is projected to be completed in the fall of 1990.

2. Rest Frequencies for Radio Astronomy
(F. J. Lovas and G. L. Rotter)

The objective of this effort is to provide astronomers with a convenient source of molecular transitions previously identified in stellar and interstellar objects, and to provide the most accurate transition frequency available, which may be a measured or calculated value. Since the 1985 revision of this publication, 18 new interstellar species have been identified and many new transitions of previously known species have been reported. We are currently updating the compilation for publication next year.

Quite often we have been called upon to assist astronomers in identifying new spectral features and occasionally asked to participate in new observational projects. Last year a project to carry out a survey of the Orion A molecular cloud in the 330 - 360 GHz frequency window was initiated by P. Jewell, NRAO, Tucson, AZ. He invited us to collaborate in this project by providing expertise in identifying and assigning new transitions in this spectral region which arise from known interstellar molecules. This project was successfully completed and resulted in the observation of about 190 transitions from 37 species and 30 transitions for which the molecular source could not be identified. These results have been published recently in Astrophys. J. Supplement.

3. Molecular Structures
(W. J. Lafferty)

In collaboration with J. H. Callomon (Univ. College, London), E. Hirota (Okazaki), and K. Kuchitsu (Univ. Tokyo), a compilation of molecular structures, reported in the literature though the end of this year is well underway. This compilation, which will be the third update--and probably the last--of this series, includes structures determined in the gas phase by IR, MW, and visible spectroscopy as well as electron diffraction techniques. The IR section of the compilation is being done here at NIST. This work will be published as one of the Landolt-Börnstein series of scientific data reports.

4. Vibrational and Electronic Energy Levels
(M. E. Jacox)

All of the data from the compilations of the vibrational and electronic energy levels of small polyatomic transient molecules and much more recent spectral data have been converted to dBase III format for distribution of a searchable disk version (named VEEL) through the Office of Standard Reference Data. More than 1000 molecules are included in VEEL. There has been a collaboration with OSRD staff on search algorithms and menu design for the finished database, which, together with the documentation, is currently in review.

A supplement to the earlier compilations of vibrational and electronic spectral data for transient molecules is in preparation. As of August 15, it contained new data for approximately 270 molecules. In late 1989 or early 1990 it will be submitted to the Journal of Physical and Chemical Reference Data. As new data are added to the transient molecule supplement, they will also be added to VEEL, in preparation for its second edition.

5. Frequency Calibration Benchmarks
(A. G. Maki)

This laboratory has been involved in a collaboration on frequency calibration measurements with J. Wells at the NIST/Boulder laboratory. New measurements on a number of bands of OCS have led to new frequency calibration data for the 490 to 3000 cm^{-1} region. Nearly all the energy levels of OCS below 3000 cm^{-1} have now been tied to the cesium frequency standard with an uncertainty of ±9 MHz (± 0.0003 cm^{-1}) or better.

New heterodyne measurements were also made on N_2O to provide improved accuracy for the frequency values for the ν_2 band in the 520 to 660 cm^{-1} region as well as to improve our knowledge of the lower energy levels of this molecule.

To fill a gap between the N_2O and OCS calibration data, the frequencies of a number of transitions of the strong ν_3 band of CS_2 were measured. By combining data on both $^{12}CS_2$ and $^{13}CS_2$, which are easily seen in a low pressure sample, calibration tables were prepared for the 1460 to 1550 cm^{-1} region.

The new far-infrared heterodyne measurements made on the high-J transitions in the rotational spectrum of OCS are a major new contribution for the preparation of calibration tables. These will give greater accuracy to our evaluation of the centrifugal distortion constants in the vibrational levels below about 1900 cm^{-1}.

B. Spectroscopic Studies of Environmental Species

Many molecular species play a significant role in the chemistry of planetary atmospheres, and are of significant interest to agencies like NASA, DOD and the CMA (Chemical Manufacturer's Association). The major interest of these agencies focusses on molecular spectroscopy as a remote sensing tool for the determination of concentration profiles. Thus the emphasis of the work described here is on band analyses and the important properties of line strengths, line shapes, and collisional line broadening.

1. FTIR Studies of CO_2, ClO_2 and $(CN)_2$

(W. J. Lafferty, A. Weber, and W. B. Olson++)

This year significant effort was spent on the study of the high resolution infrared spectra of molecules of atmospheric or stratospheric interest, both obtained in this laboratory as well as in other laboratories. A laborious, long term laboratory project, studying collisional broadening in the Q-branches in the region of the ν_2 bending mode of CO_2 has been completed. This Air Force sponsored project is of practical as well as scientific interest since several of the "hot band" Q-branch lines are used for satellite temperature sounding measurements. The NIST data is now being analyzed by M. L. Hoke and S. A. Clough at AFGL, and it is proposed to include the Y collisional mixing parameters in the next edition of the Air Force Atmospheric Tables.

Work has started on the fundamental and combination bands of the ClO_2 molecule. This molecule is postulated to be involved in the stratospheric chlorine cycle, but no direct observation of it has been made as yet. The spectra were obtained by J. Burkholder and C. Howard at NOAA in Boulder, who asked our lab to analyze them. Although ClO_2 is a simple near-prolate asymmetric rotor, the spectra are complicated by the fact that the molecule is a free radical and the lines are doubled by nuclear spin splitting. Unfortunately, programs written some years ago in this laboratory using Polo approximations, which work well for the NO_2 molecule, have been found to be inadequate to treat the spectrum of ClO_2 since this molecule is a bit more asymmetric than nitrogen dioxide. In collaboration with R. Escribano at the Instituto de Estructura de la Materia in Madrid, a fitting program using direct diagonalization techniques is being written to obtain the molecular constants of this species.

A study of the cyanogen molecule, C_2N_2, one of the many molecules found on the moons of Jupiter, is nearly completed. Both the IR active fundamentals, the bending band ν_4^1 at 225 cm^{-1} and the asymmetric stretching band near 2300 cm^{-1}, as well as a myriad of "hot" bands have been assigned. In addition a number of combination and difference bands have been studied in order to get a complete set of anharmonic constants for this molecule.

The infrared spectrum of methylene fluoride was recorded with the NIST BOMEM interferometer and analyzed by R. D'Cunha and collaborators of the Bhabha Atomic Research Centre, Bombay, India. The work on the ν_8 band is completed while new spectra of the ν_4 band were obtained at dry ice temperature to suppress the spectral congestion due to hot band transitions.

2. FTIR Studies of Nitric Acid and SO_x

(A. G. Maki)

The four low frequency fundamental bands of nitric acid (HNO_3) have been measured and analyzed for the first time. Both infrared and microwave measurements were combined to obtain values for the rovibrational constants that are needed to calculate the energy levels and transitions responsible for the infrared spectrum.

The moderately strong band at 1205 cm^{-1} was also measured and analyzed. It was shown to be due to the combination transition $\nu_8 + \nu_9$. These bands have been characterized for both line position and relative intensity.

Spectra of the two gases, SO_2 and SO_3, which are involved in the acid rain problem, have also been the subject of some studies. Many of the weaker transitions of SO_2 in the 450 to 600 cm^{-1} region have now been identified as due to the $^{34}SO_2$ species which comprises 4.2% of a normal sample. The low frequency ν_2 and ν_4 bands of SO_3 have also been studied and a complete set of constants have been determined that allow one to calculate the appearance of those bands with confidence.

3. Photoacoustic Measurement of Differential Broadening of the Λ Doublets in NO ($X^2\Pi_{1/2}$, v=2-0) by Ar

(A. S. Pine)

A differential broadening of the Λ doublets in the v=2-0 overtone band of the $^2\Pi_{1/2}$ ground electronic state of NO in an Ar buffer gas has been observed by photoacoustic spectroscopy using a tunable color-center laser. The broadening coefficients for the *f* symmetry components are larger than for the *e* symmetry components by up to ~6% for J~16.5. This differential depends on J and vanishes at low J, implicating the anisotropy of the unpaired electron Π orbital in the plane of rotation. The $^2\Pi_{3/2}$ transitions are slightly broader than the $^2\Pi_{1/2}$ as a result of spin-flipping collisional relaxation. The observed lineshapes also exhibit collisional or Dicke narrowing due to velocity-changing collisions.

4. Q-Branch Line Mixing in HCCH

(A. S. Pine)

Three Q branch profiles in the C-H stretch-bend combination region of HCCH have been measured as a function of pressure by transmission spectroscopy using a linear-scan-controlled difference-frequency laser. At low pressure, in the Doppler-limited regime, the J component spectral transitions can be accurately characterized to within about 0.0001 cm^{-1} in frequency and 0.2% in intensity. However, as the pressure is raised, up to about 1 atm, the individual lines overlap and the resulting contour cannot be fit with additive or superposable Lorentzian or Voigt component lineshapes. This is a manifestation of collisional interference or line mixing where inelastic collisions redistribute intensity among the overlapping transitions. The three Q branches, which have radically different degrees of overlap due to a small vibrational dependence to the rotational constants, can be consistently fit with a modified collisional cross relaxation matrix using a hybrid power-exponential gap rate law taking into account the symmetry of the intermolecular potential and possible extraneous relaxations to states not involved in the Q branch transitions. Models used successfully in prior studies of N_2O and CO_2 predict too much line coupling for HCCH.

C. Hydrogen-bonded and van der Waals Complexes

1. Millimeter and submillimeter wave spectrum of $(HF)_2$

(W. J. Lafferty and R. D. Suenram)

A collaboration on the spectrum of the interesting HF dimer molecule with the sub-millimeter wave spectroscopy group at Gorky in the USSR is under way. Using earlier NIST microwave and IR data and Pade approximate fitting techniques, Krupnov and coworkers tentatively assigned a line series in the 180-380 GHz region to a previously unobserved high J R-branch K=3 series. Observation of the Q- and P- branches of this subband in the millimeter wave region here at NIST verified the assignment. Both the Gorky and NIST data have been combined to obtain an improved set of spectroscopic constants. An atlas of the a- and b-type microwave and far infrared transitions is being prepared.

2. Electric-Resonance Optothermal Spectroscopy of $(H_2O)_2$

(G.T. Fraser, R.D. Suenram, L.H. Coudert*, and F.J. Lovas)

The tunneling motions in $(H_2O)_2$ and $(D_2O)_2$ have been studied by microwave spectroscopy using an electric-resonance optothermal spectrometer (EROS) recently developed at NIST. The EROS spectrometer operates by monitoring the intensity of a state-selected molecular beam of $(H_2O)_2$ as a function of microwave frequency. The molecular beam is state selected using an electric field of quadrupole symmetry. Microwave-microwave double resonance experiments are used to guide and verify spectral assignments. For $(D_2O)_2$, pulsed-nozzle Fourier transform microwave measurements have also been made.

For the protonated species, the reported measurements extend previous results on the a-type K=0-0 and 1-1 bands for the $A_2^{\pm}$, $B_2^{\pm}$, and $E^{\pm}$ rotational-tunneling states and include the first observations of the c-type K=1-0 band for the $A_2^{\pm}$, $B_2^{\pm}$ and $E^{\pm}$ states and the a-type K=0-0 band for the $A_1^{\pm}$ states. For the $A_1^{\pm}$ states an interconversion tunneling splitting of 22.6 GHz is obtained, compared to the 19.5 GHz value found previously for the K=0 $A_2\pm$ and $B_2\pm$ states.

For the deuterated species, the tunneling splitting for the K=0 $A_2\pm/B_2\pm$ states is determined to be 1083 MHz, which is slightly lower than the

1172 MHz value found previously for the $A_1^\pm/B_1^\pm$ states. These splittings are also shown to have a large K dependence, being 1077 and 992 MHz for the K=1 levels of the $A_1\pm/B_1\pm$ and $A_2^\pm/B_2\pm$ states, respectively. The tunneling splittings indicate that the geared type pathway dominates the tunneling process. The B+C rotational constant is relatively insensitive to tunneling state, whereas the B-C rotational constant varies by nearly a factor of two between tunneling states. This indicates that corrections for tunneling effects need to be applied before using B-C in a structural analysis.

3. Infrared Molecular Beam Optothermal Spectroscopy of Complexes (G.T. Fraser and A.S. Pine)

a. Isomerization and Vibrational Predissociation of HF-HCl and HCl-HF

Microwave and infrared spectra of HF-HCl and HCl-HF have been obtained using the EROS spectrometer. The HF-HCl microwave measurements extend to $K_a=1$ the previous $K_a=0$ results of Janda, Steed, Novick, and Klemperer, allowing the determination of the K_a dependence and asymmetry of the Cl quadrupole coupling constant. For the metastable HCl-HF isomer no previous spectroscopic measurements have been reported. Here, microwave spectra are observed for the $K_a=0$ and 1 states and interpreted in terms of an L-shaped hydrogen-bonded structure for the complex, with a 3.235 Å center-of-mass separation between the HF and HCl subunits. The D_J distortion constant indicates that the harmonic stretching force constant for HCl-HF is ~35 % larger than that of HF-HCl. Infrared spectra of the K_a=0-0 and 1-0 subbands of the H-F stretching band for HF-HCl and of the K_a=0-0 subband of the H-F stretch for HCl-HF are also reported. The vibrational predissociation linewidths depend on vibration, K_a state, isotopic species, and isomer excited.

b. Vibrational Predissociation in the H-F Stretching Mode of HF-DF

The high-resolution infrared spectrum of the K=1-0 subband of the H-F stretching vibrational band of the hydrogen-bonded HF-DF complex has been recorded using the EROS spectrometer. The spectrum exhibits minor perturbations and vibrational predissociation linewidths of 23±2 MHz (FWHM) for comparison to the 11±1 MHz widths found for the corresponding mode of the homonuclear HF-HF dimer. This implies that tunneling is not responsible for the predissociation of the free-H stretch of HF-HF since tunneling is quenched in the mixed isotopic species.

c. Angular-Radial Coupling Effects in Ar-HCN

Microwave and infrared spectra of Ar-HCN have been obtained by means of the EROS spectrometer. The microwave measurements extend to higher J the previous results of Leopold *et al.* and Klots *et al.*, allowing the determination of higher-order centrifugal distortion constants for this quasilinear, highly non-rigid complex. A Padé approximant fit to the microwave data indicates a significant rotation-induced asymptotic increase in the zero-point center-of-mass separation between the Ar and the HCN, above that expected from pure radial distortion. This results from the large coupling between the angular and radial degrees in the intermolecular potential forcing the centrifugal alignment of the HCN. Infrared spectra are reported for the C-H stretching fundamental, ν_1, and the combination band $\nu_1+\nu_5{}^1$, where ν_5 is the van der Waals bending vibration. The band-origin difference between these two bands gives $\nu_5 = 7.8$ cm^{-1}, in rough agreement with the 10 cm^{-1} harmonic value predicted from the microwave-determined nuclear quadrupole coupling constant. The complexation-induced red shift of the C-H stretching vibration is 2.69 cm^{-1} and the vibrational predissociation linewidths, Γ, are < 10 MHz (FWHM). The vibrationally excited complex predissociates before striking the bolometer detector, implying that the predissociation lifetime, $\tau < 1$ ms.

4. Studies of van der Waals Complexes of Reacting Molecules

(J. Z. Gillies*, C. W. Gillies*, R. D. Suenram, and F. J. Lovas)

Several systems are under investigation with the pulsed-beam Fourier transform microwave spectrometer (FTMW), where the individual molecular species involved in forming the complex are very reactive towards one another under normal circumstances. The goal in these studies is to determine the structures of the reaction complexes which will help in understanding more about the mechanism of cycloaddition reactions. We have recently measured the rotational spectra and determined the structures of the ozone-ethylene and the ozone-acetylene complexes by sampling a flowing mixture of Ar/O_3 and Ar/hydrocarbon introduced into the pulsed nozzle through separate inlets near the nozzle orifice. These reactants are classical examples of the 1,3-dipolar cycloaddition reaction (Diels Alder type of reaction) in which the electrostatic positive ends of the dieneophile (ozone) react simultaneously with the diene (ethylene or acetylene) to form a five membered ring adduct. The structures of the complexes are similar to the final reaction product (1,2,3-trioxolane in the case of ethylene) with the terminal oxygen atoms directed toward the two carbon atoms. The C-O distance is ~3.3 Å in the ethylene complex compared to 1.417 Å in the compound. These studies show how the electrostatic properties of the individual compounds control the reaction pathway. It is expected that related species will be studied in the near future to further probe these reaction intermediates.

5. Van der Waals Complexes with Large Internal Tunneling Splittings

(F. J. Lovas, R. D. Suenram and K. Matsumura*)

Many of the van der Waals complexes and hydrogen bonded species that we have investigated with the FTMW spectrometer are very weakly bound and exhibit large rotation-inversion tunneling splittings in their rotational spectra. Examples of complexes investigated during the past year are: argon-formaldehyde, formaldehyde dimer, argon-water, water dimer, water-ozone, water-sulfur dioxide and H_2S-CO_2. The spectra of complexes that exhibit internal motions such as this are often difficult to interpret. However, collaborations with J. Hougen, L. Coudert and G. Fraser, who have developed new mathematical modeling concepts to describe the spectra for large internal motions, have been extremely successful. In addition to defining the tunneling paths and energies, the molecular structures and electric dipole moments have been determined for the complexes listed above.

6. Fourier Transform Spectroscopy of Laser Vaporized Refractory Materials

(R. D. Suenram, F. J. Lovas and K. Matsumura*)

A technique that has been used for several years in optical spectroscopy and mass spectrometry involves the use of a pulsed high power laser, typically a Nd:YAG or eximer laser, to vaporize non-volatile materials in the exit channel of a pulsed molecular beam valve. We have adapted this technique to Fourier transform microwave spectroscopy in an effort to probe a new class of molecular species that is difficult to study by other methods. Initial tests have been promising. We have used the technique to study SiC_2 which is produced from the laser vaporization of a silicon carbide rod. The 1_{01}-0_{00} rotational transition was easily observable with a single gas pulse. The less abundant isotopic species with ^{29}Si, ^{30}Si, and ^{13}C have been observed in natural abundance.

A set of experiments has also been carried out using some refractory metal oxides as laser target materials. Rotational spectra of YO, LaO, ZrO, and HfO have been observed and the electric dipole moments measured. Two species (YO and LaO) have $^2\Sigma$ ground electronic states, and their rotational spectra are split by an interaction with the earth's magnetic field. We have constructed a set of Helmholtz coils around the Fourier-transform spectrometer to reduce the earth's magnetic field to less than 20 mG in the resonance region. With these coils installed, other paramagnetic species can now also be studied. A number of nozzle modifications are being tried which should soon improve the signal-to-noise of the laser vaporization spectrometer for the study of van der Waals complexes of refractory materials.

D. FTIR Matrix Isolation Studies

(M. E. Jacox and W. E. Thompson*)

Studies of the codeposition of a small molecule (XY) contained in a large excess of neon with a beam of neon atoms excited in a microwave discharge have continued. Spectroscopic observations on these systems using the Bomem Fourier transform system have yielded much new information on the vibrational spectra of small molecular ions and cluster ions. In each system, extensive isotopic substitution is performed to establish product identifications. The first studies, for XY = CO_2 and O_2, led to the infrared identification of CO_2^+, CO_2^-, O_4^+, and O_4^-. The results of those studies have recently been published. When XY = N_2, the Σ_u^+ stretching fundamental of N_4^+ appears at 2237.6 cm^{-1}. For the noncentrosymmetrically substituted species (e.g., $^{14}N^{14}N^{15}N^{15}N^+$), infrared activation of ν_1 (Σ^+) is observed. When XY = CO, a weak absorption of CO^+ appears a few cm^{-1} from the band center for the gas-phase vibrational fundamental. Prominent absorptions have been assigned to $(CO)_2^+$ and $(CO)_2^-$, for which vibrational data have not previously been reported. When XY = N_2O, the two stretching fundamentals of ground-state N_2O^+ appear close to the previously reported gas-phase band centers. In addition, the

1200 cm^{-1} absorption of $N=NO_2^-$, previously identified in this laboratory in studies of the interaction of alkali metals with N_2O isolated in an argon matrix, is present. Other product absorptions are contributed by cis-$(NO)_2$ and possibly by N_2O^- and $(NO)_2^-$. When a $Ne:CO_2:O_2$ sample is codeposited with a beam of excited neon atoms, three new infrared absorptions, which are not characteristic of experiments on either a $Ne:CO_2$ or a $Ne:O_2$ sample. All three of these absorptions are associated with CO_2 vibrations. The relative photolytic stability of the new product and the pattern of isotopic shifts are consistent with its identification as $(O_2 \cdots OCO)^+$. Detailed analysis of the isotopic data is in progress. Experiments in which XY = NO have been initiated. Prominent absorptions of several different cluster ions contribute to the spectrum. Survey experiments for XY = H_2O have been extended to the OH stretching region, and a rather broad absorption near 3215 cm^{-1} has been tentatively assigned to the ν_3 fundamental of H_2O^+, for which the ν_2 absorption was previously detected in this system near 1403 cm^{-1}. During the coming year, the experiments on the NO and H_2O systems will be completed, and studies on a number of other molecules, including NO_2, C_2H_2, HCN, HCl, and the fluoromethanes, are planned.

E. Spectroscopic Theory

(J. Hougen, L. H. Coudert*, I. J. Kleiner* and W. Fawzy*)

Theoretical activity has continued to focus on the derivation, testing and application of effective rotational Hamiltonian operators for classes of molecular systems currently not discussed in the literature.

A final global fit of all known water dimer lines (173 transitions) using the formalism developed during the last three years has been successfully carried out, indicating that we now have some understanding of the four tunneling motions that occur in this complex. Attempts will now be made to apply this method to the ammonia dimer spectrum, which has been measured by Saykally's group in Berkeley. At present we know almost nothing about the tunneling motions in this complex, and even the type of bonding (hydrogen-bond or not) is still in question. In addition to these two dimers, the method has been successfully applied (by LHC) to a number of other complexes and stable molecules.

The formalism for rotational energy levels of open shell complexes, developed with W. Fawzy, has been applied successfully to the jet-cooled NO-HF infrared spectrum of Pine and Fraser. This spectrum is complicated by a large P-type doubling in the P = 1/2 state, which arises primarily from the interplay between spin-orbit interaction in the NO molecule and a Renner-Teller-like quenching of the Π orbital degeneracy of the NO molecule when the HF partner approaches.

Work has begun (with IJK) on testing the limits of applicability of various theoretical treatments for the spectra of molecules with internal rotation (methanol and acetaldehyde). Ultimately we hope to investigate vibration-rotation interactions leading to energy transfer from the high-frequency vibrations into highly excited quasicontinuum levels of the internal rotation motion, but this goal is still a long way off.

A final direction of study concerns the development of a formalism for the amino inversion motion in CH_3-NHD, the question here being how much the heavy deuterium atom "refuses to move" during the -NHD inversion tunneling. This work follows the successful descriptions of the v = 0 and $v_{torsion}$ = 1 tunneling-rotational levels in CH_3-NH_2.

III. MOLECULAR DYNAMICS GROUP

This group primarily performs 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 Surface Science Division staff (denoted by +++).

A. Condensed Phase Energy Transfer

(J. D. Beckerle+++, M. P. Casassa, R. R. Cavanagh+++, E. J. Heilweil, and J. C. Stephenson)

During the past year we continued using tunable ultrafast lasers to measure the vibrational energy relaxation times (T_1) for CO(v=1) groups bound to metal atoms.

Using a one color infrared bleaching pump/probe method, we determined T_1 for CO(v=1) chemisorbed on the surface of large (20-30 Å diameter) Pt particles. The very fast decay time (T_1 = 7 ± 1 ps) was found to be independent of temperature in the range $100 \le T \le 400$ K, and the same T_1 was measured for an isotopic mixture of $^{12}C^{16}O$ dilute (1:3) in $^{12}C^{18}O$. The lack of temperature dependence is consistent with a damping mechanism in which the 2090 cm^{-1} vibrational quantum decays by exciting an electron-hole (e/h) pair in the Pt, and is not consistent with decay to any available low frequency ($\nu < 500$ cm^{-1}) surface or substrate vibrational modes. Likewise, the lack of isotope dependence is consistent with relaxation by e/h pair formation, and argues, albeit inconclusively, against nearly resonant (dipole-dipole) transfer to other CO sites as the mechanism responsible for the observed bleaching decays.

Rather than continue energy transfer studies on these amorphous Pt particles, we began T_1 measurements for an ordered monolayer of CO on the surface of single crystal Pt(111). This necessitated construction of a new ultrahigh vacuum chamber especially designed for optical studies of metal surfaces using both FTIR for spectral studies (FWHM resolution ≤ 0.1 cm^{-1}) and tunable ultrafast lasers for time-resolved measurements. Our bandwidth studies of CO/Pt(111) as a function of temperature and coverage are in agreement with the most recent results from other laboratories (e.g. Bradshaw, Trenary). By the uncertainty principle, the IR absorption bandwidth (6 cm^{-1}) sets a limit $T_1 \ge 0.8$ ps for CO or Pt(111) at room temperature. We have seen transient infrared bleaching signals induced by an ultrafast infrared pump pulse for CO(v=1)/Pt(111), and we expect soon to have a time-resolved measurement of T_1 to compare to the bandwidths.

These initial experiments involve CO/Pt(111) because it is the best studied adsorbate/metal system. However, many other interesting surface species can be studied with our apparatus, such as NO and N_2; polyatomics like CH_3O (methoxy), HCO_2 (formate), CCH_3 (vinylidine), and PF_3; or CO co-absorbed with electron doners like potassium. All the preceding adsorbates form ordered adlayers on various transition metal crystal faces, and have large infrared absorptions ($\Delta R/R>1\%$) which facilitate our infrared pump/probe experiments. We hope that future studies will determine the dependence of vibrational energy transfer rates on parameters like surface coverage, electron density, temperature, bonding site, adsorbate/substrate distance, bond dipole moment, etc.

Complementing the CO(v=1)/Pt measurements, we have studied vibrational energy transfer involving the high frequency CO(v=1) stretching modes of metal carbonyl molecules in solution. We have used a new broadband IR probe method to obtain the transient IR absorption spectrum over the entire CO stretching region, and hence to identify pathways for vibrational energy flow in these molecules.

The broadband infrared (BBIR) probing apparatus generates IR in the 2000 cm^{-1} region by taking the difference frequency in a non-linear crystal ($LiIO_3$) between a fixed frequency ps visible pulse (i.e. 532 nm) and a broadband tunable ps dye laser pulse. The BBIR probe pulse goes through the sample at a computer-controlled delay time after the pump pulse and records the transient IR spectral changes in absorption. The BBIR pulse containing transient spectral information is then upconverted in a second $LiIO_3$ crystal by sum frequency generation with the 532 nm pulse. The resultant blue (~480 nm) ps pulse is sent through a spectrograph and dispersed on a multichannel detector (i.e. an OMA III). In this way the entire IR absorption spectrum in the CO-stretch region is recorded on every laser shot with a time resolution limited by the duration of the BBIR probe pulse and spectral resolution limited by the spectrograph dispersion and detector pixel spacing.

The new BBIR studies have revealed important information about vibrational relaxation in these metal carbonyl molecules. For the molecules we have studied carefully, if one of the CO stretching modes is pumped, the vibrational excitation flows rapidly to the other high frequency CO stretch modes in the molecule. For instance, in $Rh(CO)_2(C_5H_7O_2)$ there are CO stretch modes at $\nu_1 = 2084$ cm^{-1} and $\nu_2 = 2015$ cm^{-1}. If ν_1 is pumped, population flow into ν_2 is evidenced by transient features at 2000 cm^{-1} ($\nu_2 \rightarrow 2\nu_2$) and 2059 cm^{-1} ($\nu_2 \rightarrow \nu_2 + \nu_1$). Absorptions at both those frequencies appear in a time short compared to the 18 ps pulses used in these experiments, suggesting that $\nu_1 \rightarrow \nu_2$ transfer occurs in a time ≤ 10 ps. These coupled CO stretching modes then relax together, by multiquantum transfer to lower frequency modes, on the much longer timescale which we previously reported.

During the next few months we will use BBIR pulses of much shorter duration to completely time-resolve the initial vibrational energy transfer in these molecules. Also we expect to begin IR pump/BBIR probe studies of hydrogen bonded OH stretching modes of simple alcohol dimers in solution.

This research was partially funded by AFOSR.

B. Overtone Photodissociation of HN_3

(M.P. Casassa, B.R.Foy+, D.S.King, and J.C. Stephenson)

Vibrational overtone excitation of molecules enables highly state-specific studies of unimolecular decomposition. In our experiments, picosecond or high-resolution nanosecond laser pulses initiate unimolecular decomposition of hydrazoic acid, HN_3, by exciting high NH stretching overtone (ν_1) and combination levels. In the collision-free environment of a molecular beam or in a low pressure gas cell, the following reactions are observed:

$$\begin{aligned} HN_3(X\ {}^1A') &\longrightarrow HN(X\ {}^3\Sigma^-) + N_2(X) \quad \Delta H = 15\text{kcal/mol}, \quad E_a \approx 36\text{kcal/mol}, \\ &\longrightarrow HN(a\ {}^1\Delta) + N_2(X) \quad \Delta H = 51\text{kcal/mol}. \end{aligned}$$

The NH fragments are detected by laser-induced fluorescence of the $A^3\Pi$-$X^3\Sigma^-$ or $c^1\Pi$-$a^1\Delta$ transitions using a frequency-doubled dye laser. During the past year we measured the overtone photodissociation spectra of the $5\nu_1$ and $6\nu_1$ levels at resolution sufficient to resolve widths of individual rovibrational transitions, and we performed time-resolved experiments on $5\nu_1$, $6\nu_1$ and four combination bands to determine the unimolecular decomposition rate as a function of vibrational energy and mode excited. These temporal and spectral data complement our measurements of detailed product state distributions, and together this information provides an unprecedented detailed view of unimolecular decomposition.

High-resolution overtone photodissociation spectra reveal the nature of the initially excited vibrational motion. Spectra of the $5\nu_1$ and $6\nu_1$ bands are obtained by scanning the frequency of the overtone-pump laser near 15,120 cm^{-1} and 17,670 cm^{-1}, and monitoring fluorescence excited by a probe laser tuned to a NH fragment transition ($A^3\Pi$-$X^3\Sigma^-$, $R_1(1)$ line near 336 nm). The spectra exhibit P,R-branch structure characteristic of parallel bands of a near-prolate top, but the (J,K=0) transitions appear as multiplets of features, and the patterns of the multiplets vary erratically with J. These sets of transitions can only arise by anharmonic (Fermi) mixing of the ($n\nu_1$,J,K=0) rovibrational levels of HN_3 with other rovibrational states of the molecule.

The $6\nu_1$ spectrum exhibits more components than $5\nu_1$, reflecting the increase in the density of nearly isoenergetic states with increasing vibrational energy. Also, the spectral extent of the Fermi-mixed components is larger for $6\nu_1$ than for $5\nu_1$, indicating an increase in the coupling matrix elements between the vibrational states. A deperturbation analysis shows the matrix elements are in the range 0.010-0.065 cm^{-1} for $5\nu_1$, and up to 0.1 cm^{-1} for $6\nu_1$. In both levels, the density of features in the spectra is comparable to the calculated total density of HN_3 vibrational states (ρ_{vib} = 7 and 13 states/cm^{-1} for $5\nu_1$ and $6\nu_4$, respectively). This suggests that the NH stretching overtones couple to any neighboring states that fall within the coupling strength of $\approx 0.1\ cm^{-1}$, regardless of the type of motion involved.

Spectra recorded with a spectral bandwidth of $0.007\ cm^{-1}$, obtained using a pulse-amplified single-mode dye laser, show the individual rovibrational lines in the $5\nu_1$ spectrum are Doppler broadened (160MHz FWHM in the 8K molecular beam), while the $6\nu_1$ lines show widths in excess of the Doppler width. Best-fit Voigt profiles give Lorentzian widths ranging from 150 to 270 MHz for different lines in the $6\nu_1$ spectrum. Based on comparison to the dissociation rate measured in real time, we attribute these widths to homogeneous broadening due to dissociation.

Picosecond and nanosecond lasers were used to measure product appearance rates in time-resolved experiments. Figure 1 shows data obtained for $5\nu_1$ and $6\nu_1$ and four intermediate combination bands. The modes are designated in the figure using their zero-order labels. Lifetimes decrease monotonically with energy from $\approx$210ns for $5\nu_1$ to $\approx$1ns for $6\nu_1$. There is no marked deviation from this trend, even though the initial vibrational motions are notionally quite different. For example, $5\nu_1+2\nu_4$ includes two quanta in the internal NN stretching mode (i.e., the reaction coordinate) and might be expected to dissociate more rapidly. An explanation for the lack of mode specificity in lifetimes is suggested by the mode-mixing observed in the $5\nu_1$ and $6\nu_1$ spectra: the actual motions excited are mixtures of zero-order states, and not simply the distinct motions suggested by the zero-order labels.

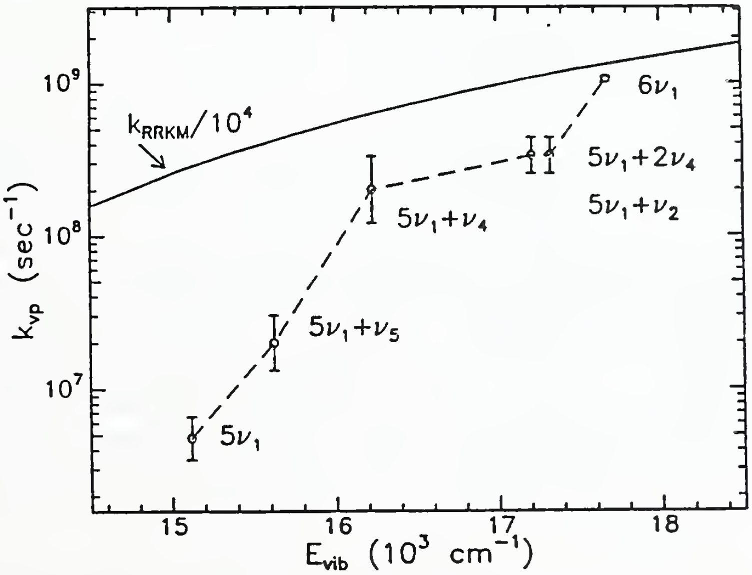

Figure 1. Unimolecular decomposition rates for overtone-excited HN_3.

Lifetimes shorter than 10 ns were measured in picosecond experiments and are actually band-averaged lifetimes, since the spectral width of picosecond pulses (limited by the uncertainty principle) subtends the multiple components in the overtone spectra. For the long-lived modes, nanosecond lasers were used, enabling measurement of lifetimes for individual Fermi resonance components of particular (J,K) levels. In these circumstances, mode-specific effects are observed, showing that lifetimes do depend upon the specific vibrational trajectory initiated. For example, lifetimes measured within the $5\nu_1$ band vary by a factor of two. Similar variation in lifetimes among the $6\nu_1$ components is deduced from the variation in the $6\nu_1$ linewidths.

Figure 1 indicates that a 200-fold increase in the vibrational predissociation rate occurs for a 17% increase in vibrational energy. Statistical theory predicts a less dramatic increase in the rate with energy and ρ_{vib}: the RRKM calculation shown in the figure gives only a factor of 4 increase at these energies. The spin-forbidden nature of the reaction at these energies is reflected in the 10^4 ratio of calculated (assuming spin-allowed) and observed rates. Ab initio calculations by M. Alexander indicate that the large increase of rate with energy arises because the activation barrier actually lies slightly above the $5\nu_1$ level, and levels near $5\nu_1$ dissociate by tunneling through the potential energy barrier.

In the future, we will measure spectra, lifetimes, and product states associated with excitations in the region of the $7\nu_1$ level, which is above the threshold for dissociation via the spin-allowed channel. Analogous experiments on molecules such as CH_3OOH, with spatially distinct groups of ν_{XH} states, and CH_2N_2 are also planned.

This work was partially funded by AFOSR.

C. Carrier-driven Surface Reactions

(S. A. Buntin++, R. R. Cavanagh*, D. S. King, and L. J. Richter+++)

State-resolved diagnostics of NO desorbed from Pt(111) following laser irradiation of the surface have demonstrated that hot, photogenerated carriers can initiate selected surface reactions. Those experiments used nanosecond duration, pulsed YAG and tunable dye lasers and were performed in an ultra-high vacuum chamber. Determinations of the desorption dynamics versus incident YAG laser fluence and wavelength were used to distinguish carrier-driven processes from thermal processes. We have recently directed our exploration of laser-induced, carrier-mediated surface reactions to include the reaction/desorption of NO from Si(111). In semiconductors, as opposed to metals, both the photogenerated carriers and excited surface species are expected to have significantly longer lifetimes; therefore, the detailed dynamics of optically driven surface reactions on Si may be significantly different from those observed on Pt.

Full characterization of the energy partitioning in the desorbed NO is achieved using laser-induced fluorescence. The kinetic energy distributions of NO molecules desorbed in a specific [electronic (Ω), rotational (J), and vibrational (v)] quantum state are measured using an optically-detected time-of-flight (TOF) technique by varying the time delay between the firing of the desorption and probe lasers. Velocity-integrated state distributions are derived from the TOF spectra for a selection of states (Ω,J,v). Complete measurements are performed at various surface coverages and desorption-laser fluences and wavelengths.

A Si(111) surface saturated with NO at a temperature of 100 K (multilayer adsorption does not occur at this temperature) and irradiated by 355 nm ($E_{h\nu}$=3.5 eV) photons at fluences which induce negligible surface temperature changes (Δ T < 1 K) that yields desorbed NO with very high kinetic energies. The mean kinetic energy increases from 800 to 2000 K with increasing rotational energy in the NO species being probed. These results are independent of the product vibrational state. The rotational population distributions of the desorbed NO were well described by a Boltzmann distribution, characterized by a "rotational temperature" of about 600 K. Surprisingly, almost half of the desorbed NO molecules were in vibrationally excited states. Relative populations v=0:1:2 of 1.0:0.65:0.14 were obtained. The desorption quantum yield is estimated to be 10^{-2} per absorbed photon. These dynamical results are sensitive to initial surface coverage and excitation laser wavelength, but are independent of desorption-laser fluence.

Comparison of the dynamics for carrier-mediated desorption of NO from Pt(111) versus Si(111) shows both similarities and differences. Both substrates produce desorbed NO with comparable mean kinetic energies that are dependent on rotational, but not vibrational, state, and both produce desorbed NO with significant amounts of vibrational excitation. These dynamical trends might then be taken to be signatures of carrier-mediated desorption. In the surface-harpooning model developed in collaboration with J. W. Gadzuk for the carrier-mediated desorption of NO from Pt(111), the lifetime of the high-energy ionic intermediate is seen to strongly influence both the yield and the extent of vibrational excitation. The enhanced yield and extent of vibrational excitation from Si(111) versus Pt(111) are in qualitative agreement with this expectation. Experimental work on this system will continue in order to obtain a better understanding of the microscopic details of carrier driven processes on semiconductors.

As a prototype in the exploration of molecule-surface dynamics, NO has been extensively studied, primarily because of the ease with which this species may be detected in a state-specific manner. However, the extension of results for NO to the development of general trends in surface dynamics is complicated by the fact that NO is an open shell species. Because of the extensive number of both theoretical and experimental surface science studies involving CO (closed shell ground state) we have directed our efforts toward the implementation of the hardware necessary to detect CO with rovibrational state selectivity. Laser-induced fluorescence detection requires the generation of vacuum ultraviolet radiation (VUV) in the region 140 to 155 nm. For dynamical studies of the desorption of CO from surfaces, VUV intensities must be sufficient to provide for the detection of molecular densities on the order to 10^8/cc. Our approach, given its high conversion efficiency, is to generate the necessary probe wavelengths by two-photon resonance enhanced four-wave sum frequency mixing in Mg vapor. The necessary facilities (i.e., a second dye laser, heat pipe, detectors, etc.) are now in place and being optimized. Future experiments will explore the dynamics of CO desorption initiated by thermal excitation of the substrate, by excitation of hot carriers, and by direct photoexcitation of metal carbonyl adsorbates.

This work was supported in part of the U.S. Department of Energy, Office of Basic Energy Sciences.

IV. QUANTUM CHEMISTRY GROUP

The Quantum Chemistry Group has expanded the scattering program with the recent hire of R. Heather. This effort is enhanced by active guest researcher collaborations, strong coupling to experimental programs in slow atom spectroscopy at NIST, the University of Maryland, and in France, and by many theoretical collaborations throughout the world. The electronic structure program also maintains an active collaborative program with NIST's Center for Advanced Research in Biotechnology (CARB) and other groups to permit a range of spectroscopic and biochemical applications.

A. Scattering Theory and Molecular Spectroscopy

1. Molecular Photodissociation and Predissociation

We are actively involved in several collaborations in which a close coupling analysis of molecular photodissociation processes is necessary. These studies use standard time independent close coupling methods and offer an opportunity to apply new time dependent methods.

a. Generalized MCQDT Methods
(F. H. Mies, P. S. Julienne, and R. Dubs+)

We have developed numerical methods for calculating a half collision matrix. These will prove useful in interpreting the dynamics of nonadiabatic processes in both photodissociation and full collision problems. This matrix, derived from the generalized multichannel quantum defect theory (MCQDT) of the close coupled wavefunction, is expected to have applications in developing a variety of approximations. We will make application to interpreting photodissociation experiments on K_2 and NaK.

We are also working with M. Raoult, University of Paris-Sud, to incorporate a generalized MCQDT analysis of closed channels into our close-coupled scattering codes. This allows a rigorous analysis of non-adiabatic effects and departures from the Born-Oppenheimer approximations in both predissociating and stable bound states of molecules.

b. Analysis of Molecular Predissociation
(P. S. Julienne)

In a collaboration with F. Rostas of the Observatory of Paris, we are studying predissociations and strong perturbations in the extreme ultraviolet spectrum of CO. These are due to a crossing of the $^1\Sigma^+$ states of the ns Rydberg series by the D $^1\Sigma^+$ valence state. We have constructed a model of this crossing to account for observed vibrational and rotational perturbations and predissociation widths.

The predissociation line shapes of the Schumann-Runge bands of O_2 have been and still are the object of numerous experimental studies. These line shapes are difficult to measure due to the complex triplet fine structure of these bands. In conjunction with L. Vahala of Old Dominion University close coupling and MCQDT models are being developed to interpret the role of triplet fine structure in the predissociation line shapes of the Schumann-Runge bands of O_2.

In a collaboration with H. Hotop, University of Kaiserslautern and S. Peyerimhoff, University of Bonn an ab initio model was constructed to account for the strong predissociations observed in the A $^1\Sigma^+$ state of HBr^+ in the photoelectron spectrum of HBr. The predissociation widths are comparable to the vibrational spacing, so a close coupling analysis is necessary. The model requires treating the coupling of the A state with 5 different predissociation channels through spin-orbit coupling.

c. Multiphoton Photodissociation of H_2^+
(F. H. Mies and A. Giusti*)

We have used our time-independent half collision codes to calculate the multiphoton photodissociation rate and product kinetic energy distribution of H_2^+ in an intense laser field of 10^{+13}watts/cm^2 or more. At these intensities our calculations predict above threshold dissociation (ATD), in which additional quanta of photon energy appear as evenly spaced peaks in the kinetic energy spectrum of the atomic fragments. These results are valid for laser pulse lengths that exceed the dissociation time.

d. Time Dependent Study of Molecular Photodissociation
(R. Heather and F. H. Mies)

A new project has been started to integrate the time-dependent Schroedinger equation for a photodissociating molecule subject to an intense short-time laser pulse. Excellent agreement has been obtained with the time-independent calculations in the long pulse limit. Preliminary results predict quite significant effects on the momentum distribution in the short-pulse limit which may be amendable to experimental confirmations.

2. Collisions of Ultracold Atoms

Ultracold (T<1mK) atom traps developed at NIST and elsewhere offer a number of new opportunities in atomic and molecular physics, including studies of fundamental physics, high precision spectroscopy, and improved time and frequency standards. It is important to understand collisions in such traps, since (1) collisions introduce heating processes which limit the density and lifetime of an atom trap and (2) ultracold collisions involve novel effects not normally encountered.

a. Threshold Behavior of Ultracold Collisions
(P. S. Julienne, F. Mies, and R. Dubs+)

We have used generalized MCQDT to investigate the quantum threshold behavior of ultracold collisions. We have developed analytic and numerical treatments of various types of threshold behavior. The onset of threshold behavior depends strongly on the atomic mass and long range interaction potential. Ground state collisions in light traps will generally be in the quantum threshold regime which is not described semiclassically. We use the low temperature Penning ionization of two ^3S He atoms as an example of threshold behavior.

b. Spontaneous Emission in Ultracold Collisions
(P. S. Julienne)

We have studied the role of spontaneous emission in ultracold excited state collisions. This process has a dramatic effect on effective collision rates, and can not be treated by normal scattering theory. We have developed criteria for the onset of such effects as temperature is decreased from normal to ultracold. Experiments by W. Phillips' group at NIST and J. Weiner's group at the University of Maryland are investigating our predicted effects.

c. Ultracold Collisions in a Magnetic Field
(P. S. Julienne and F. H. Mies)

In a collaboration with C. Williams, Northwestern University we are developing numerical close coupling methods for treating collisions in a magnetic field, where Zeeman splittings of hyperfine sublevels can be large compared to kT. Initial applications will be to ground state H atoms, and we plan to develop codes for treating Na and Cs atoms.

B. Electronic Structure

1. Alkali Cluster Binding to Group III-V Semi-conductor Surfaces
(M. Krauss and W. J. Stevens (CARB))

The dominant binding interaction for quasi-linear clusters of Cs atoms to the (110) surface of GaAs is calculated to be van der Waals (VDW) like with only weak charge transfer from Cs to surface. Quasi-linear clusters of bound alkali atoms are calculated to have polarizabilities that increase non-linearly with the number of atoms in the cluster (see Fig. 2); since the VDW interaction is proportional to the polarizability, the binding per Cs atom increases with the length of the cluster.

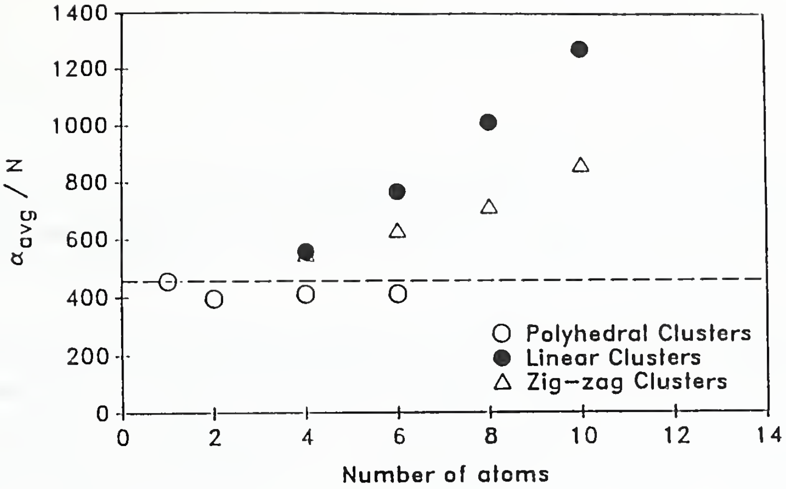

Figure 2. Computed polarizabilities of quasi-linear clusters of bound alkali atoms.

Hyperpolarizabilities of the alkali cluster are non-linear with the length of the cluster; non-linear optical transitions in the semiconductor can then be enhanced by the large alkali cluster hyperpolarizability or can induce such transitions in the alkali cluster.

Calculations planned for other alkali-semiconductor surfaces and ligand- and reaction fields will be used to simulate electronic surface field and dielectric effects.

2. Biochemical Applications

(M. Krauss, W. J. Stevens (CARB), D. Garmer (CARB), H. Basch*)

The spectroscopy and transition state behavior of the active site of the enzyme, carbonic anhydrase, is now being investigated as a function of the metal at the active site; environmental effects in the protein will be investigated with the reaction field code. The main effort in the coming year will be devoted to metalloenzyme studies now that a version of the reaction field code is completed. The need to study a variety of metals prompts us to complete construction of compact effective potentials (CEP) for elements from K to Rn.

Comparative electronic structure calculations of the P-O and V-O bonds suggest that the five-coordinate vanadate complex when bound to the active site of ribonuclease is <u>not</u> a transition state analogue because of the great disparity in the electronic structure and the binding of hydrogen to oxygen. Transition state analogue proposals in the literature will be examined to see if a study of the electronic structure would support the purely geometric considerations that are normally applied. Borate tetrahedral complexes will be considered for the protease enzymes.

Systematic studies of the vibrational frequencies of Mg, Ca, Cd, and Na cations bound to increasing numbers of water ligands show the relatively small effects on the geometry and frequencies as the number of ligands increases.

3. Spectroscopic Applications

Assignment of the electronic spectra of the $PtA_4{}^+$ ($A = NH_3$, PH_3) complex by ab initio calculation of the excitation energies compares well with experiment. This study shows that Co spectra in proteins may be examined for environmental effects.

Dipole moments, polarizabilities, and electronic structure were analyzed for the following systems: nucleic acid bases, heteronuclear rare gas diatomic molecules, hydrogen-bonded structures of H_2O and H_2S, HfO (data of interest to various experimental and theoretical projects in the Division and CARB).

Spectroscopic constants and energy curves were calculated to large distances for Cs_2 ground and excited states to illustrate accuracy obtainable with effective potential calculations for alkali molecules. This study evolved from the study of clusters on surfaces since the gas-phase properties are needed for comparison. The larger gas-phase clusters will be examined at low priority.

V. PUBLICATIONS

(a) Publications of Past Year

Beckerle, J. D., Casassa, M. P., Cavanagh, R. R., Heilweil, E. J., and Stephenson, J. C., "Time Resolved Studies of Vibrational Relaxation Dynamics of CO(v=1) on Metal Particle Surfaces," J. Chem. Phys. 90, 4619-4620 (1989).

Burgess, D., Jr., Cavanagh, R. R., and King, D. S., "NO/NH_3 Coadsorption on Pt(111): Kinetic and Dynamical Effects in Rotational Accommodation," Surface Science, 214, 358-376 (1989).

Burkholder, J. B., Howard, C. J., Escribano, R., and Maki, A. G., "Spectroscopic Constants for the ν_9 Infrared Band of HNO_3," J. Mol. Spectrosc. 131, 195-200 (1988).

Coudert, L. H. and Hougen, J. T., "Tunneling Splittings in the Water Dimer: Further Development of the Theory," J. Mol. Spectrosc. 130, 86-119 (1988).

Coudert, L. H., Hougen, J. T., and Suenram, R. D., "Effect of Tunneling Motions on the Quadrupole Hyperfine Structure of Hydrazine," J. Mol. Spectrosc. 135, 314-333 (1989).

Fawzy, W. M. and Hougen, J. T., "Rotational Energy Levels and Line Intensities for $^{2S+1}\Lambda$ - $^{2S+1}\Lambda$ and $^{2S+1}(\Lambda \pm 1)$ - $^{2S+1}\Lambda$ Transitions in a Diatomic Molecule van der Waals Bonded to a Closed Shell Partner," J. Mol. Spectrosc. 137, 154-165 (1989).

Foy, B. R., Casassa, M. P., Stephenson, J. C., and King, D. S., "Dissociation Lifetimes and Level Mixing in Overtone-excited HN_3 ($\tilde{X}^1A'$)," J. Chem. Phys. 90, 7037-7045 (1989).

Fraser, G. T., Pine, A. S., Suenram, R. D., Dayton, D. C., and Miller, R. E., "Infrared and Microwave Spectra of OCO-HF and SCO-HF," J. Chem. Phys. 90, 1330-1336 (1989).

Fraser, G. T., "Vibrational Exchange upon Interconversion Tunneling in $(HF)_2$ and $(HCCH)_2$," J. Chem. Phys. 90, 2097-2108 (1989).

Fraser, G. T., Suenram, R. D., and Coudert, L. H., "Microwave Electric-Resonance Optothermal Spectroscopy of $(H_2O)_2$," J. Chem. Phys. 90, 6077-6085 (1989).

Fraser, G. T. and Pine, A. S., "Vibrational Predissociation of the H-F Stretch of HF-DF," J. Chem. Phys. 91, 633-636 (1989).

Fraser, G. T. and Pine, A. S., "Microwave and Infrared Electric-Resonance Optothermal Spectroscopy of HF-HCl and HCl-HF," J. Chem. Phys. 91, 637-645 (1989).

Fraser, G. T., Suenram, R. D., Coudert, L. H., and Frye, R. S., "Electric-Resonance Optothermal Spectrum of $(H_2O)_2$: Microwave Spectrum of the K=1-0 Subband for the $E_2^{\pm}$ States," J. Mol. Spectrosc. 137, 244-247 (1989).

Fraser, G. T., Suenram, R. D., and Lovas, F. J., "Electric-Dipole Moments of H_2O-Formamide and CH_3OH-Formamide," J. Mol. Struct. 189, 165-172 (1988).

Fraser, G. T., Suenram, R. D., Lovas, F. J., Pine, A. S., Hougen, J. T., Lafferty, W. J., and Muenter, J. S., "Infrared and Microwave Investigations of Interconversion Tunneling in the Acetylene Dimer," J. Chem. Phys. 89, 6028-6045 (1988).

Gillies, J. Z., Gillies, C. W., Suenram, R. D., and Lovas, F. J., "The Ozonolysis of Ethylene. Microwave Spectrum, Molecular Structure and Dipole Moment of Ethylene Primary Ozonide (1,2,3-Trioxolane)," J. Am. Chem. Soc. 110, 7991-7999 (1988).

Gillies, J. Z., Gillies, C. W., Suenram, R. D., Lovas, F. J., and Stahl, W., "The Microwave Spectrum and Molecular Structure of the Ethylene-Ozone van der Waals Complex," J. Am. Chem. Soc. 111, 3073-3074 (1989).

Gould, P. L., Lett, P. D., Julienne, P. S., Phillips, W. D., Thorsheim, H. R., and Weiner, J., "Observation of Associative Ionization of Ultracold Laser-trapped Sodium Atoms," Phys. Rev. Lett. 60, 788-791 (1988).

Heilweil, E. J., Stephenson, J. C., and Cavanagh, R. R., "Measurements of CO(v=1) Population Lifetimes: Metal-Carbonyl Cluster Compounds Supported on SiO_2," J. Phys. Chem. 92, 6099-6103 (1988).

Heilweil, E. J., Cavanagh, R. R., and Stephenson, J. C., "Picosecond Study of the Population Lifetime of CO(v=1) on SiO_2-supported Rhodium Particles," J. Chem. Phys. 89, 5342-5343 (1988).

Heilweil, E. J., Cavanagh, R. R., and Stephenson, J. C., "Vibrational Relaxation Measurements of Carbon Monoxide on Metal Clusters," in Ultrafast Phenomena VI, T. Yajima, K. Yoshihara, C. B. Harris, and S. Shionoy, eds. (Springer-Verlag Pub., Berlin, (1988)), pp. 447-450.

Heilweil, E. J., "Ultrashort Pulse Multichannel Infrared Spectroscopy Using Broadband Frequency Conversion in $LiIO_3$," Optics Letters, 14, (11), 551-553 (1989).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Picosecond Studies of Vibrational Energy Transfer in Surface Adsorbates," Ann. Rev. Phys. Chem. 40, 143-171 (1989).

Hoke, M. L., Clough, S. A., Lafferty, W. J., and W. B. Olson, "Line Coupling in Oxygen and Carbon Dioxide," Proc. of the International Radiation Symposium, Lille, France, December 1988.

Jacox, M. E., "The Stabilization and Spectroscopy of Free Radicals and Reactive Molecules in Inert Matrices," in Chemistry and Physics of Matrix Isolated Species, L. Andrews and M. Moskovits, ed. (North-Holland; Amsterdam, 1989), pp. 74-105.

Jacox, M. E. and Thompson, W. E., "The Vibrational Spectra of Molecular Ions Isolated in Solid Neon. I. CO_2^+ and CO_2^-," J. Chem. Phys. 91, 1410-1416 (1989).

Jacox, M. E. and Thompson, W. E., "The Production and Spectroscopy of Molecular Ions Isolated in Solid Neon," Res. Chem. Intermed. 12, 33-56 (1989).

Jewell, P. R., Hollis, J. M., Lovas, F. J., and Snyder, L. E., "Millimeter- and Submillimeter-wave Surveys of Orion A Emission Lines in the Ranges: 200.7-202.3 GHz, 203.7-205.3 GHz, and 330-360 GHz," Astrophys. J. Suppl. 70, 833-864 (1989).

Julienne, P. S. and Frommhold, L., "Roundtable Discussion on Laser-induced Collisions and Collision-induced Spectra," in Spectral Line Shapes, Vol. 5, ed. by J. Szudy (Ossolineum, Warsaw, 1989) p. 800-806.

King, D. S. and Cavanagh, R. R., "Molecular Desorption from Solid Surfaces: Laser Diagnostics and Chemical Dynamics," in Molecular Surface Interactions, K. Lawley, ed., Advances in Chemical Physics (J. Wiley and Sons, Ltd., Chichester 1989) p. 45-89.

Krauss, M. and Guillot, "Dipole Moments of Rare Gas Interactions," Chem. Phys. Lett. 158, 142-144 (1989).

Krauss, M. and Stevens, W. J., "A Theoretical Model of Metal Binding Sites in Proteins," Computer-Assisted Modeling of Receptor-Ligand Interactions: Theoretical Aspects and Applications in Drug Design, in Progr. Clin. Biology. Res. 289, 95-107 (1989).

Leung, H. O., Marshall, M. D., Suenram, R. D., and Lovas, F. J., "Microwave Spectrum and Molecular Structure of the N_2-H_2O Complex," J. Chem. Phys. 90, 700-712 (1989).

Lovas, F. J. and Suenram, R. D., "Microwave Spectral Tables III, Hydrocarbons, CH to $C_{10}H_{10}$," J. Phys. Chem. Ref. Data, 18, (1988).

Maki, A. G. and Olson, Wm. B., "Infrared Spectrum of the ν_6, ν_7, and ν_8 Bands of HNO_3," J. Mol. Spectrosc. 133, 171-181 (1989).

Meerts, W. L., Ozier, I., and Hougen, J. T., "Influence of an AC Stark Effect on Multiphoton Transitions," J. Chem. Phys. 90, 4681-4688 (1989).

Ohashi, N., Takagi, K., Hougen, J. T., Olson, Wm. B., and Lafferty, W. J., "Far Infrared Spectrum of Methyl Amine. Assignment and Analysis of the First Torsional State," J. Mol. Spectrosc. 132, 242-260 (1988).

Ohashi, N., Tsunekawa, S., Takagi, K., and Hougen, J. T., "Microwave Spectrum of Methyl Amine. Assignment and Analysis of the First Torsional State," J. Mol. Spectrosc. 137, 33-46 (1989).

Peterson, K. I., Suenram, R. D., and Lovas, F. J., "The Structure of the CO_2-CO_2-H_2O van der Waals Complex Determined by Microwave Spectroscopy," J. Chem. Phys. 90, 5964-5970 (1989).

Pine, A. S. and Pliva, J. M., "Doppler-Limited Spectra of the C-H Bending Overtone of Fluoroform," J. Mol. Spectrosc. 130, 431-444 (1988).

Pine, A. S., Fraser, G. T., and Pliva, J. M., "Molecular Beam Spectrum of the Highly Perturbed C-H Stretching Region of Fluoroform," J. Chem. Phys. 89, 2720-2729 (1988).

Pine, A. S. and Fraser, G. T., "Vibrational, Rotational, and Tunneling Dependence of Vibrational Predissociation in the HF Dimer," J. Chem. Phys. 89, 6636-6643 (1988).

Pine, A. S., "Photoacoustic Measurement of Differential Broadening of the Λ Doublets in NO($X^2\Pi_{½}$, v=2-0) by Ar," J. Chem. Phys. 91, 2002-2009 (1989).

Richter, L. J., Buntin, S. A., Cavanagh, R. R., and King, D. S., "Non-Boltzmann Rotational and Inverted Spin-orbit State Distributions for Laser-induced Desorption of NO from Pt(111)," J. Chem. Phys. 89, 5344-5345 (1988).

Schneider, M., Maki, A. G., Vanek, M. D., and Wells, J. S., "Heterodyne Measurements on OCS near 1372 cm^{-1}," J. Mol. Spectrosc. 134, 349-353 (1989).

Suenram, R. D., Lovas, F. J., and Matsumura, K., "Laboratory Measurement of the 1_{01}-0_{00} Transition and Electric Dipole Moment of SiC_2," Astrophys. J. Letters 342, L103-105 (1989).

Suenram, R. D., Lovas, F. J., Fraser, G. T., and Marfey, P. S., "Microwave Spectrum ^{14}N Quadrupole Coupling Constants of Carbazole," J. Mol. Struct. 190, 135-141 (1988).

Suenram, R. D., Fraser, G. T., Lovas, F. J., Gillies, J. Z., and Gillies, C. W., "Microwave Spectrum, Structure and Dipole Moment of the Ar-Formamide van der Waals Complex," J. Chem. Phys. 89, 6141-6146 (1988).

Vanek, M. D., Schneider, M., Wells, J. S., and Maki, A. G., "Heterodyne Measurements on N_2O near 1635 cm^{-1}," J. Mol. Spectrosc. 134, 154-158 (1989).

Wells, J. S., Schneider, M., and Maki, A. G., "Calibration Tables Covering the 1460 to 1550 cm^{-1} Region from Heterodyne Frequency Measurements on the ν_3 Bands of $^{12}CS_2$ and $^{13}CS_2$," J. Mol. Spectrosc. 132, 422-428 (1988).

b) Publications in Progress

Basch, H., Garmer, D., Jasien, P. G., Krauss, M., and Stevens, W. J., "Electric Properties of Nucleic Acid Bases," Chem. Phys. Lett. (in press).

Buntin, S. A., Richter, L. J., King, D. S., and Cavanagh, R. R., "Laser-Induced Desorption: State Resolved Evidence for Optically Driven Surface Reaction," J. Chem. Phys. (in press).

Coudert, L. H. and Hougen, J. T., "Analysis of the Microwave and Far Infrared Spectrum of the Water Dimer," J. Mol. Spectrosc. (submitted).

Foy, B. R., Casassa, M. P., Stephenson, J. C., and King, D. S, "Overtone-excited $HN_3(\tilde{X}^1A')$: Anharmonic Resonance, Homogeneous Linewidths, and Dissociation Rates," J. Chem. Phys. (submitted).

Foy, B. R., Casassa, M. P., Stephenson, J. C., and King, D. S., "Vibrational Predissociation Dynamics of Overtone-Excited HN_3," Proceedings of ILS-IV (American Physical Society, 1989) (in press).

Fraser, G. T. and Pine, A. S., "Infrared and Microwave Study of Angular-Radial Coupling Effects in Ar-HCN," J. Chem. Phys. (in press).

Gadzuk, J. W., Buntin, S. A., Richter, L. J., King, D. S., and Cavanagh, R. R., "Optically Driven, Hot-carrier Induced Desorption," J. Chem. Phys. (in press).

Giusti-Suzor, A., He, X., Atabek, O., and Mies, F. H., "Above Threshold Dissociation of H_2^+ in Intense Laser Fields," Phys. Rev. Letts. (submitted).

Gillies, C. W., Rickus, L., Gillies, J. Z., Justnes, H., Suenram, R. D., Lovas, F. J., and Guiseppe, T. D., "Microwave Spectrum and Molecular Conformation of Methoxy Difluorophosphinoxide," J. Mol. Structure (submitted).

Gillies, J. Z., Gillies, C. W., Suenram, R. D., Lovas, F. J., Schmidt, T., and Cremer, D., "The Microwave Spectrum, Structure and Electric Dipole Moment of the Ozone-water Complex," J. Chem. Phys. (submitted).

Haag, Uijt de, Spooren, R., Ebben, M., Meerts, L., and Hougen, J. T., "Internal Rotation in 1,4- Dimethylnaphthalene Studied by High Resolution Laser Spectroscopy," Mol. Phys. (in press).

Hollis, J. M., Jewell, P. R., and Lovas, F. J., "A Search for Methylene in the Orion Nebula," Astrophys. J. Lett. (in press).

Jacox, M. E. and Thompson, W. E., "The Production and Spectroscopy of Small Polyatomic Molecular Ions Isolated in Solid Neon," High Temp. Sci. (in press).

Julienne, P. S. and Mies, F. H., "Collisions of Ultracold Trapped Atoms," J. Opt. Soc. Am. B., (in press).

Julienne, P. S., "Theory of Ultracold Atomic Collisions in Optical Traps," Electronic and Atomic Collisions, ed. by A. Dalgarno, R. S. Freund, M. S. Lubell, and T. B. Lucatorto, (North Holland, Amsterdam, 1990) (in press).

Krauss, M. and Stevens, W. J., "Analysis of Protein Metal Binding Selectivity in a Cluster Model," J. Am. Chem. Soc. (in press).

Krauss, M. and Stevens, W. J., "Polarizabilities of Alkali Clusters," Chem. Phys. Lett. (submitted).

Lovas, F. J., Suenram, R. D., Coudert, L. H., Blake, T., Grant, K. J., and Novick, S. E., "The Torsional-Rotational Spectrum and Structure of the Formaldehyde Dimer," J. Chem. Phys. (submitted).

Maki, A. G., "Infrared Spectrum of Thallium Chloride at 450°C," J. Mol. Spectrosc. 137, (in press).

Maki, A. G., "Infrared Spectrum of the 1205 cm^{-1} Band of HNO_3," J. Mol. Spectrosc. 136, (in press).

Matsumura K., Lovas, F. J., and Suenram, R. D., "The Microwave Spectrum and Structure of the H_2O-SO_2 Complex," J. Chem. Phys. (submitted).

McCarthy, S. L., Hinde, R. J., and Krauss, M., "The Binding of cis-Pt(11)-diammines to Duplex DNA," Biopolymers (in press).

McCarthy, S. L., Hinde, R. J., and Krauss, M., "The Binding of Substituted Pt-diammines to Duplex DNA," Biopolymers (in press).

McCarthy, S. L., Miller, K. J., and Krauss, M., "The Binding of cis-Pt(11)-DAC and Its Derivatives to Duplex DNA," J. Med. Chem. (submitted).

Meijer, G., Heinze, J., Meerts, W. L., Meulen, J. J., and Hougen, J. T., "High-Resolution Spectroscopy on the $A^1B_1(0,6,0) \leftarrow X^1A_1(0,0,0)$ Transition in $SiCl_2$," Chem. Phys. Lett. (in press).

Ortigoso, J., Escribano, R., and Maki, A. G., "The ν_2 IR Bands of SO_3," J. Mol. Spectrosc. (submitted).

Suenram, R. D., Lovas, F. J., Fraser, G. T., Gillies, J. Z., Gillies, C. W., and Onda, M., "Microwave Spectrum, Structure, and Electric Dipole Moment of Ar-CH_3OH," J. Mol. Spectrosc. (in press).

Suenram, R. D., Fraser, G. T., and Lovas, F. J., "Microwave Spectrum of $(D_2O)_2$," J. Mol. Spectrosc. (in press).

Thompson, W. E. and Jacox, M. E., "The Vibrational Spectra of Molecular Ions Isolated in Solid Neon. II. O_4^+ and O_4^-," J. Chem. Phys. 91, (1989).

Vanek, M. D., Jennings, D. A., Wells, J. S., and Maki, A. G., "Frequency Measurements of High-J Rotational Transitions of OCS and N_2O," J. Mol. Spectrosc. (in press).

Wofford, B. A., Ram, R. S., Quinonez, A., Bevan, J. W., Olson, W. B., and Lafferty, W. J., "Rovibrational Analysis of the $\nu_7{}^1$ Intermolecular Hydrogen Bonded Bending Vibration in HCN•••HF Using Far Infrared Fourier Transform Spectroscopy," Chem. Phys. Lett. (in press).

VI. INVITED TALKS

Casassa, M. P., "Time and State Resolved Studies of the Overtone-Pumped Photodissociation of HN_3 ($\tilde{X}^1A'$)," 1989 Time-resolved Vibrational Spectroscopy Conference, Princeton, NJ, June 1989.

Casassa, M. P., "Time and State Resolved Studies of the Overtone-Pumped Photodissociation of HN_3 ($\tilde{X}^1A'$)," 1989 High Energy Density Materials Conference, New Orleans, LA, March 1989.

Fraser, G. T., "Vibrational Exchange upon Interconversion Tunneling in Homogenous Dimers," 198th International ACS Meeting, Miami, FL, September 1989.

Heilweil, E. J., "Population Relaxation of CO-stretching Vibrations for Carbon Monoxide on Metal Clusters," 174th Meeting of the Electrochemical Society, Symposium on "Photonics," Chicago, IL, October 1988.

Heilweil, E. J., "Picosecond Studies of Vibrational Energy Relaxation for Molecules in Solution and on Surfaces," Optical Sciences and Chemistry joint symposium, Naval Research Laboratory, Washington, D.C., November 1988.

Heilweil, E. J., "Picosecond Studies of CO(v=1) Vibrational Relaxation for Carbon Monoxide on Metal Clusters," NIST Staff Research Seminar, Research Adivsory Committee, NIST, February 1989.

Heilweil, E. J., "Picosecond Studies of CO(v=1) Vibrational Relaxation for Carbon Monoxide on Metal Clusters," Physical and Analytical Joint Seminar, University of Delaware, DE, April 1989.

Heilweil, E. J., "Picosecond Vibrational Energy Transfer Studies of Surface Absorbates," Overview Lecture, Time Resolved Vibrational Spectroscopy IV International Conference, Princeton, NJ, June 1989.

Heilweil, E. J., "Vibrational Energy Transfer Processes Studied by Ultrashort Pulsed Infrared Spectroscopy," 198th International ACS Meeting, Miami, FL, September 1989.

Hougen, J. T., "A Group Theoretical Approach to Certain Multi-Dimensional Tunneling Problems," Institute for Molecular Science, Okazaki, Japan, December 1988.

Hougen, J. T., "High-Resolution Gas-Phase Spectroscopic Studies of Tunneling Processes in Small Molecules," Rensselaer Polytechnic Institute, Chemistry Department Seminar, Troy, NY, December 1988.

Hougen, J. T., "Rotational Energy Levels and Line Intensities for Open-Shell Diatomic Molecules van der Waals Bonded to a Closed-shell Partner," All-Belgium High-Resolution Spectroscopy Mini-Meeting, Brussels, April 1989.

Jacox, M. E., "Vibrational and Electronic Spectra of Combustion Intermediates Trapped in Solid Argon," Department of Chemistry and Physics Seminar, Texas Christian University, Fort Worth, TX, October 1988.

Jacox, M. E., "Spectroscopy of Reaction Intermediates in Nitramine Decomposition and Combustion. Progress and Plans," ONR Workshop on Energetic Materials, Combustion Research Facility, Sandia National Laboratories, Livermore, CA, December 1988.

Jacox, M. E., "The Production and Spectroscopy of Molecular Ions Isolated in Solid Neon," U.S. Air Force Astronautics Laboratory, Edwards Air Force Base, CA, January 1989.

Jacox, M. E., "The Production and Spectroscopy of Small Polyatomic Molecular Ions Isolated in Solid Neon," Department of Chemistry, University of Arizona, Tucson, AZ, May 1989.

Jacox, M. E., "The Production and Spectroscopy of Small Polyatomic Molecular Ions Isolated in Solid Neon," Department of Chemistry, Arizona State University, Tempe, AZ, May 1989.

Julienne, P. S., "The Strange World of Ultracold Atomic Collisions," Physics Colloquium, University of Connecticut, Storr, CT, October 1988.

Julienne, P. S., "The Strange World of Ultracold Atomic Collisions," Physics Colloquium, Old Dominion University, Norfolk, VA, November 1988.

Julienne, P. S., "The Strange World of Ultracold Atomic Collisions," Physics Colloquium, New York University, NY, November 1988.

Julienne, P. S., "Laser Modification of Ultracold Collision Processes," Conference on Quantum Electronics and Laser Science, Baltimore, MD, April 1989.

Julienne, P. S., "Theory of Ultrafast Atomic Collisions in Optical Traps," 15th International Conference on the Physics of Electron and Atomic Collisions, New York, NY, July 1989.

Julienne, P. S., "Collisions of Ultracold Trapped Atoms," 5th Interdisciplinary Laser Science Conference, Stanford University, Palo Alto, CA, August 1989.

King, D. S., "Dynamics of Highly Vibrationally Excited Molecules," XVIII Informal Photochemistry Meeting, Santa Monica, CA, January 1989.

Lovas, F. J., "Laboratory Microwave Studies of Refractory Materials: SiC_2, YO, LaO, ZrO, and HfO," Max-Plank-Institut für Radioastronomie, Bonn, Germany, September 1989.

Lovas, F. J., "Pulsed-beam Fourier Transform Microwave Spectroscopy - Studies of Weakly Bound Complexes," Eleventh Colloquium on High Resolution Molecular Spectroscopy, Giessen, Germany, September 1989.

Lovas, F. J., "Pulsed-beam Fourier Transform Microwave Spectroscopy at NIST," Institut für Physikalische Chemie, Universität Kiel, Kiel, Germany, September 1989.

Stephenson, J. C., "Laser Studies of Molecular Dynamics," Argonne National Laboratory, July 1989.

Stephenson, J. C., "State Specific Reaction Dynamics of Highly Vibrational Excited HN_3 (V,J,K)," Argonne National Laboratory, July 1989.

Stephenson, J. C., "Ultrafast Laser Studies of Vibrational Relaxation of Molecules on Surfaces," Gordon Conference on Molecular Energy Transfer, Boston, MA, July 1989.

Suenram, R. D., "Mechanistic Studies of the Ethylene Ozone Reaction," Virginia Polytechnic Institute, Department of Chemistry, Blacksburg, VA, October 1988.

Suenram, R. D., "Rotational Spectroscopy of Some Refractory Metal Oxides using Laser Vaporized Samples," Kansas State University, Department of Chemistry Seminar, Manhattan, KS, April 1989.

Suenram, R. D., "A Coupled Laser Vaporization Source-Pulsed Fabry Perot Cavity Microwave Spectrometer: Initial Tests," 198th International ACS Meeting, Miami, FL, September 1989.

VII. MOLECULAR PHYSICS DIVISION SEMINARS

Angel, S., Department of Chemistry, University of Colorado, Boulder, CO, "Picosecond Absorption Spectroscopy of Intermolecular Electron Transfer in Solution," January 1989.

Dixit, S. N., Lawrence Livermore National Laboratory, Livermore, CA, "High Intensity Effects in Stimulated Rotational Raman Scattering," May 1989.

Dixon, R., University of Bristol, School of Chemistry, Bristol, England, "Dissociation Dynamics of NH_3 and H_2O_2," October 1988.

Dubs, R. L., Molecular Spectroscopy Division Seminar, NIST, "Circular Dichrosim in Photoelectron Angular Distributions: A New Probe of Alignment in Free and Adsorbed Molecules," January 1989.

Fawzy, W. M., Brookhaven National Laboratory, Upton, NY, "Electronic and Vibrational Spectroscopy of Open Shell Complexes," July 1989.

Glownia, J., IBM Research Division, T. J. Watson Research Center, Yorktown Heights, NY, "Femtosecond Flash Photolysis," December 1988.

Goovaerts, E., Physics Department, University of Antwerpen, Antwerpen, Belgium, "Intrinsic and Impurity Induced Dephasing of Raman-Active J=2 Rotons in Parahydrogen Crystals," August 1989.

Hansen, P. A., Department of Chemistry, University of Pennsylvania, Philadelphia, PA, "Picosecond Infrared Transient Absorption Spectroscopy," February 1989.

Heather, R., University of California at Santa Barbara, Santa Barbara, CA, "Time-dependent Theory of Photodissociation: Raman and Femtosecond Transition State Spectroscopy," December 1988.

Ho, C., Department of Chemistry, University of Pennsylvania, Philadelphia, PA, "Spectroscopy and Relaxation Dynamics of the Second Excited Singlet State of Aromatic Molecules in the Condensed Phase," January 1989.

Jones, D., University of Massachusetts at Amherst, Amherst, MA, "Theory of Associative Ionization and Laser-induced Excitation Transfer Collisions," December 1988.

Kasinski, J., Department of Chemistry, University of Rochester, Rochester, NY, "Ultrafast Dynamics of Fundamental Processes on Semiconductor Surfaces," January 1989.

Kimel'feld, Y., Institute for Spectroscopy, USSR Academy of Sciences, Troitzk, Moscow, USSR, "Molecular Interaction in Liquefied Rare Gases," December 1988.

Miller, J. C., Chemical Physics Section, Oak Ridge National Laboratory, Oak Ridge, TN, "Nanosecond and Picosecond Multiphoton Ionization of Weakly Bound Molecules," March 1989.

Mølmer, K., Ecole Normale Superieure, Paris, France, "Quantum and Semiclassical Motion of Ultracold Atoms in Laser Fields," August 1989.

Page, R., IBM Almaden Research Center, "Spectroscopy in a Sputtering Discharge: Dicopper LIF Spectra and Transition Metal IP's," May 1989.

Polyansky, O. L., USSR Academy of Sciences, Institute of Applied Physics, Gorky, USSR, "Application of One Dimensional Approximation of Effective Hamiltonian to Quasilinear Molecules and Complexes," June 1989.

Steimle, T., Arizona State University, Tempe, AZ, "High Resolution Optical Spectroscopy of Transition Metal Oxides," September 1989.

Zare, R. N., Chemistry Department, Stanford University, Stanford, CA, "The H + D_2 Reaction," November 1988.

Zygelman, B., Harvard, Smithsonian Center for Astrophysics, Cambridge, MA, "Radiative Emission Induced in Slow Atomic Collisions," November 1988.

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This report summarizes the technical activities of the NIST Molecular Physics Division during the Fiscal Year 1989. The activities span experimental and theoretical research in high resolution molecular spectroscopy, quantum chemistry and molecular dynamics, and include the development of frequency standards, critically evaluated spectral data, applications of spectroscopy to important scientific and technological problems, and the advancement of spectroscopic measurement methods and techniques. A listing is given of publications and talks by the Division staff.

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