NBSIR 86-3313

Technical Activities 1985
Molecular Spectroscopy Division

A. Weber, Chief

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

December 1985

Issued January 1986

Prepared for:
U.S. DEPARTMENT OF COMMERCE
nal Bureau of Standards
ersburg, MD 20899

NBSIR 86-3313

TECHNICAL ACTIVITIES 1985
MOLECULAR SPECTROSCOPY DIVISION

A. Weber, Chief

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

December 1985

Issued January 1986

Prepared for:
U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Gaithersburg, MD 20899

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

ABSTRACT

This report summarizes the technical activities of the NBS Molecular Spectroscopy Division during the Fiscal Year 1985. The activities span experimental and theoretical research in high resolution molecular spectroscopy, quantum chemistry and laser photochemistry, 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 NBS Molecular Spectroscopy Division for the period of October 1, 1984 to September 30, 1985. The report was prepared as part of the Annual Report of the Center for Chemical Physics within the National Measurement Laboratory of NBS. The Molecular Spectroscopy Division is organized into three working groups comprised of permanent staff, post-doctoral fellows, guest workers, and support personnel. An organizational chart of the Division is given at the end of this Forword.

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, Laser Photochemistry, and Quantum Chemistry Groups. Each group report gives project objectives, details of results obtained during the past year, and plans for future work. A mini-table of contents precedes each group report to afford a quick overview of the group's activities.

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.

This report was prepared during the period July-August, 1985. While anticipating some of the accomplishments that resulted from the work done during the remainder of the reporting period, the report clearly can not do

justice to the full range of activities and accomplishments that actually did take place. Some of these will be presented in the report for the following year.

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, Chief, Molecular Spectroscopy Division, Physics Building, B268, National Bureau of Standards, Gaithersburg, MD 20899.

Staff of the Molecular Spectroscopy Division

A. Weber, Chief

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

Laser Photochemistry

Stephenson, J. C., Group Leader
Elwell, L. B.
Jacox, M. E.
King, D. S.
Casassa, M. P. (P.D.)
Heilweil, E. J.
Mantell, D. A. (P.D.)
Perry, J. W. (P.D.)
Woodward, A. M. (P.D.)
Mialocq, J. C. (G.W.)
Bodaness, R. (G.W.)
Cavanagh, R. R.*
Burgess, D. (P.D.)*

Quantum Chemistry

Krauss, M., Group Leader
Julienne, P. S.
Mies, F. H.
Stevens, W. J.
Jasien, P. (P.D.)
Basch, H. (G.W.)
Lengsfield, B. H. (G.W.)
Konowalow, D. (G.W.)

High Resolution Spectroscopy

Maki, A. G., Group Leader
Hougen, J. T.
Lafferty, W. J.
Lovas, F. J.
Olson, W. B.
Pine, A. S.
Rotter, G. L.
Suenram, R. D.
Weber, A.
Thompson, G. A. (P.D.)

Bevan, J. W. (G.W.)
Hollis, J. M. (G.W.)
Howard, B. J. (G.W.)
Jennings, D. E. (G.W.)
Lovejoy, R. W. (G.W.)
Mills, I. M. (G.W.)
Ohashi, N. (G.W.)
Sattler, J. P. (G.W.)
Wofford, B. A. (G.W.)

P. D. - Post Doc
G. W. - Guest Worker
* - Surface Science Division

TABLE OF CONTENTS

MOLECULAR SPECTROSCOPY DIVISION

A. Weber, Chief

SUMMARY OF ACTIVITIES

Fiscal Year 1985

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 energy transfer thrust has been 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 workers. During the past year we have had thirteen guest workers and seven postdoctoral 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 workers, their permanent affiliations, and their activities is given in Section 8 of this report.

C. Division Programs

With the technological advances of micro- and main frame computers and the development of tunable dye and diode lasers that have taken place during the last eight years, the fields of experimental molecular spectroscopy and theoretical quantum chemistry have grown rapidly.

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 must be 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. The soundness of 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 isotope separation and fusion, laser chemistry, and combustion diagnostics are a few of the many important high-technology areas that depend on modern spectroscopic techniques.

In order to meet the calibration and standards requirements for the design and application of tunable infrared lasers and Fourier transform instrumentation over the next decade, several frequency standards activities are pursued in collaboration with several groups from within and outside NBS. A project on spectral frequency standards is undertaken jointly by scientists from the Time and Frequency Division of NBS/Boulder and members of the HRS group. Details about our Calibration Standards work are given in Section 2.B.

There has always been a need for accurate intensity parameters for molecular transitions. Recently these needs have been emphasized and the requirements for accuracy enhanced in connection with the determination and monitoring of trace atmospheric species. Accordingly we are now engaged in the determination of accurate transition moments, line strenghts, and line broadening parameters of several molecular species which are believed to play an important role in the chemistry of the earth's atmosphere (see Section 2.C)

We continue to be involved in the spectroscopy of the environmental and space sciences. Our work is directed toward the broadening of the data base upon which spectroscopic measurements of trace atmospheric constituents by means of ground based, balloon and satellite borne instruments are performed and evaluated. This, as well as similar efforts of interest to various branches of NASA and other user groups, is part of our continuing involvement in problems of national concern. Details about these and other activities may be found in Section 2.C.

Our Division has significant other agency contracts with Air Force Office of Scientific Research (AFOSR), Department of Energy (DOE), National Aeronautics and Space Administration (NASA), Chemical Manufacturers Association (CMA), and the National Foundation for Cancer Research that help these agencies fulfill their missions. Details are discussed in the group reports. These efforts along with the consultations, talks, publications, and collaborative activities show our strong coupling with industry, other government agencies, and the research community.

During the past year efforts of the LPC group have been redirected and have acquired a stronger focus in the quantum-state specific studies of molecular dynamics, especially in the role played by energy transfer in the spectroscopy and kinetics of molecules in the condensed phase. Investigations of energy transfer from vibrationally excited bonds in liquids and solids, as well as in molecules bound to solid surfaces are described in Section 3.B. As an outgrowth of the work done in previous years on infrared multiphoton dissociation experiments, new work has been started on the dynamics of van der Waals complexes, especially on vibrational predissociation (see Section 3.D). These experiments, performed in the time domain, measure directly the vibrational lifetimes and supplement the work done in the frequency domain in which lifetimes are inferred from spectral line widths (see Section 2.D as well as earlier descriptions in the FY'83 and '84 Annual Reports).

Work was also carried forward in Matrix isolation spectroscopy (Section 3.E) and the desorption of molecules from surfaces (Section 3.C). Thermal desorption of molecules chemisorbed on well characterized surfaces were studied with a dedicated facility incorporating several techniques for surface sensitive analysis, a computer controlled data acquisition system and a laser probe system with sub-Doppler resolution capability. Since thermal desorption takes place slow enough to be modelled as an equilibrium process, new work has been started on fast desorption brought about by rapid heating of the surface by non-resonant laser radiation.

The field of Quantum Chemistry has in recent years experienced significant new developments which extend the range of reliable and useful calculations to complex polyatomic systems. A new program to attack the problems of the stabilities, conformations, spectroscopy and reactivity of complex molecules, clusters, ions, radicals, and transition states, among others, was successfully conducted for the third year 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 has been significantly enhanced through the acquisition of an IBM-4381 superminicomputer which forms the core of the newly formed Molecular Structure and Modeling Facility of the Molecular Spectroscopy Division. Details of the activities of the QC Group are given in the group report.

In the Annual Report for 1982 we described the results of our initial work on the spectroscopy of molecular complexes in the gas phase. This initial work, on the rotation-vibration spectrum of the hydrogen-bonded HF-dimer has been expanded since that time to include the study of a variety of hydrogen-bonded and van der Waals complexes by all three groups of the Division. Thus, detailed investigations are underway with new instrumentation of microwave and infrared high resolution spectra (see the reports by the High Resolution Group in Section 2.D). The measurements for these investigations are made in the frequency domain and knowledge about the lifetimes of excited states is had only by inference from the widths of the spectral lines. Direct information about lifetimes and, especially, pre-dissociation rates is obtained from measurements made in the time domain; these are performed in the Laser Photochemistry Group and are reported in Section 3.D. These experimental efforts are often done in conjunction with work done in the Quantum Chemistry Group (see report 4.B.2). The study of weak chemical interaction as exemplified by the hydrogen bonding and van der Waals forces is of considerable interest for the present and the forseeable future (see the Pimentel Report "Opportunities in Chemistry", National Academy Press, Washington D. C., 1985) and our Division is expected to fully participate in this field during the coming years.

The research described in the following report was performed in a cooperative manner between the permanent staff of the Division, NBS/NRC postdoctoral research associates, and guest-scientists from the U.S. and abroad. Close collaboration also exists with members of the Surface Science Division of the Center for Chemical Physics in areas of picosecond spectroscopy, spectroscopic studies of surface desorption processes, and energy transfer.

2. High Resolution Spectroscopy Group

J. W. Bevan, J. T. Hougen, B. J. Howard, D. E. Jennings,
W. J. Lafferty, R. W. Lovejoy, F. J. Lovas, A. G. Maki, I. M. Mills,
N. Ohashi, W. B. Olson, A. S. Pine, G. Rotter
R. D. Suenram, G. A. Thompson, A. Weber, and B. A. Wofford

A. Introduction

B. Calibration and Data Center Activities

1. Tying the Lower Vibrational Levels of N_2O to the Cesium Frequency Standard
2. Infrared Calibration Atlas
3. Revised Recommended Rest Frequency List
4. Microwave Spectral Tables
5. Supplement to Structural Data Tables for Polyatomic Molecules
6. Review of SO_2

C. Spectroscopy for Environmental Studies

1. High Resolution Spectrum of the ν_2 and ν_3 Bands of HOl
2. Measurement of the ν_3 and ν_4 Bands of Nitric Acid (HNO_3)
3. New Intensity and Frequency Measurements on $C\ell O$
4. Self-Broadening in the Fundamental Bands of HF and $HC\ell$
5. Analysis of the Spectrum of H_2O_2

D. Spectroscopy of Hydrogen-Bonded and van der Waals Complexes

1. Hydrogen-Bond Energies of the HF and $HC\ell$ Dimers
2. Rotational Predissociation and Libration in the Infrared Spectrum of Ar-$HC\ell$
3. Study of Hydrogen-Bonded Complexes in the Gas Phase Using Fourier Transform Spectroscopy
4. Pulsed Beam Fabry-Perot Cavity Fourier Transform Microwave Spectrometer
5. Microwave Study of the Ar...Acrylonitrile van der Waals Complex
6. Microwave Study of the Kr...OCS van der Waals Complex
7. A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer

E. General Spectroscopy and Theory

1. Efficient Sampling Systems for the Fourier Transform Spectrometer
2. Diode Laser Measurements on Unstable Diatomic Molecular Species
3. Fourier Transform Raman Spectroscopy of H_2 and D_2 in Flames
4. Infrared Spectrum of Cyanogen
5. Fourier Transform IR Spectra of Monodeuterosilane
6. Far Infrared Spectrum of the Torsional Band of Hydrazine
7. The Torsional-Wagging-Tunneling Problem and the Torsional-Wagging-Rotational Problem in Hydrazine

8. The Use of Extended Permutation-Inversion Groups for Constructing Hyperfine Hamiltonians for Symmetric-Top High-Barrier Internal Rotor Molecules Like H_3C-SiH_3
9. Improved Least Squares Determination of Potential Energy Surfaces from Spectroscopic Data
10. The Proper Choice of the Lagrangian for a Relativistic Particle in External Fields
11. A Note on the Uniform Asymptotic Expansion of Integrals with Coalescing End Point and Saddle Points
12. Generalized Stirling Approximation to N!
13. Accurate Emission Spectra from Planar Strong Field Wigglers with Arbitrary Field Variation
14. Dynamical Symmetries and Equivalent Lagrangians for One-Dimensional Systems
15. On the Relationship of Normal Modes to Local Modes

F. Future Plans

A. Introduction

The work of this 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 novel molecular species, particularly floppy molecules.

The major activity of the Molecular Spectra Data Center, supported by the Office of Scientific Reference Data (OSRD) is to provide evaluated data on molecular rotational spectra in the microwave region and to develop 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.

Molecular radioastronomy continues to demand accurate laboratory microwave data and spectroscopic expertise and the measurement, critical evaluation, and dissemination of microwave data of astrophysical interest is being continued. Our collaboration with radio-astronomers provides the contacts and experience necessary to insure that these evaluations and compilations are both practical and useful.

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 the Chemical Manufacturers Association. These efforts will continue to play an important role in our work 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 group 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.

The work conducted during the past year has been aided through the efforts of a number of guest-scientists from the U.S. and abroad. Moreover, sustained collaboration with non-NBS groups serves to disseminate the results of our work in the quickest and most far reaching way to the user community. Such collaboration also benefits our work through access to data and facilities not presently available at NBS. Particularly noteworthy among the non-NBS institutions with which beneficial collaborations have occurred during the past year are: The University of Oulu, Oulu, Finland, The University of Illinois, The University of Alberta, Texas A&M University, Lehigh University, Oxford University, Oxford, England, The University of Reading, Reading, England, The National Research Council of Canada, The Institute of Molecular Science, Okazaki, Japan, Kanazawa University, Kanazawa, Japan, The Harry Diamond Laboratories of the U.S. Army, The NASA-Greenbelt, NASA-Langley NASA-Goddard, and NASA-Ames Laboratories, and The National Solar Observatory at Kitt Peak, AZ.

In the following the group's activities are described according to the three broad topics of calibration and Data Center activities, environmental problems, and spectroscopy of weakly bound molecular complexes. In addition to these programmatic activities there were others of a more general and varied nature, including several studies in the field of mathematical physics by one of our guest workers. These are described in the fourth section under General Spectroscopy and Theory.

B. Calibration and Data Center Activities

We collect under this heading the work of the group connected most closely with the core mission of NBS, namely the production and dissemination of compilations of accurately measured frequencies or wavenumbers for use as secondary standards, of compilations of critically evaluated molecular constants for use in other disciplines, or occasionally of spectral fitting programs, for use in reducing data in other laboratories. 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 in both the infrared and microwave spectral regions.

1. Tying the Lower Vibrational Levels of N_2O to the Cesium Frequency Standard

(A. G. Maki and J. W. Wells)

Our continuing collaborative effort with Dr. J. W. Wells (NBS Boulder) this past year has seen some new frequency measurements that were the key to tying all the lower vibrational energy levels of N_2O to the cesium frequency standard. These levels previously had been measured using wavelength measurement techniques, but now we have independent frequency measurements of these levels. One of the most satisfying aspects of this work was the incorporation of the very accurately measured N_2O laser frequencies.

The new measurements that were made in Boulder involved the 00°1-00°0 and 01'1-01'0 transitions of N_2O which were measured against a CO laser local oscillator in the 1257 to 1340 cm^{-1} region. The CO frequencies were in turn measured with respect to combinations of CO_2 laser frequencies. Since the well measured N_2O laser frequencies involved the 10°0-00°1 transition, combining these measurements gave accurate frequency values for the 10°0-00°0 transitions between 2135 and 2268 cm^{-1} (see Fig 2.1).

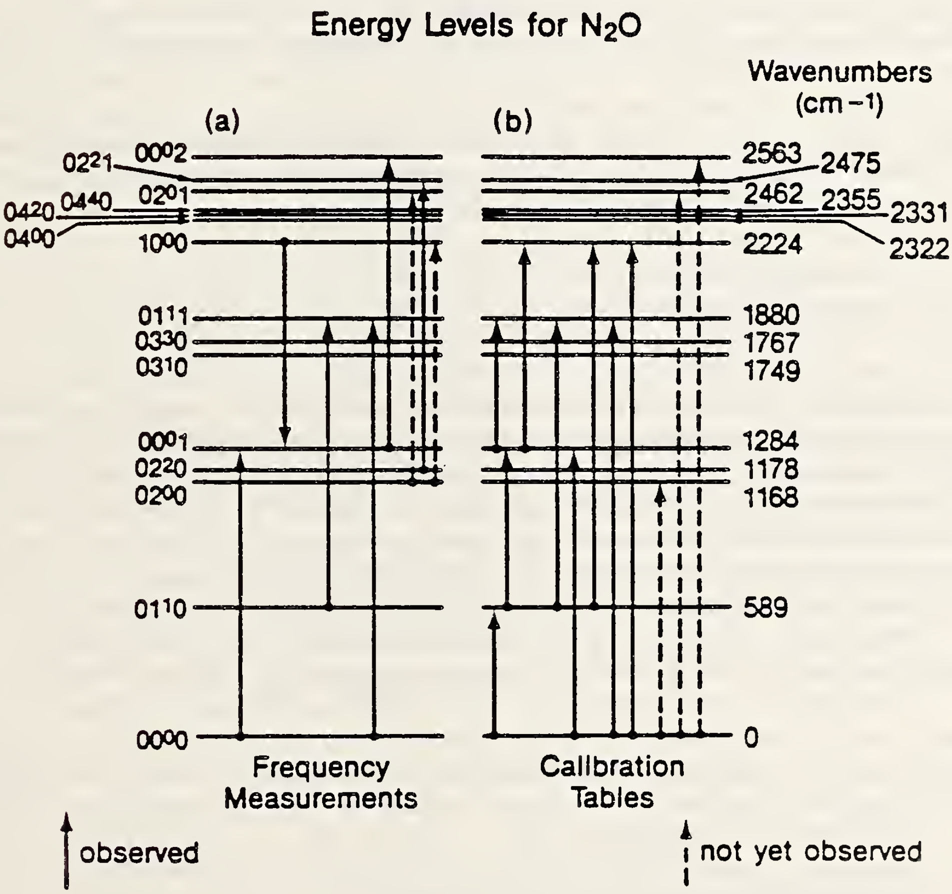


Figure 2.1. Energy level diagram that illustrates on the left (a) the frequency measurements that have been made on the lower levels of N_2O (solid arrows), or that we hope to make (dashed arrows). On the right (b) are the resulting calibration tables that can be prepared based on the frequency measurements.

Also, combining the new 01'1-0110 measurements with earlier ones on the 01'1-00°0 transitions gave us good frequency values for the 01^{1}0-00°0 transitions near 590 cm^{-1}. These new frequency measurements have been combined with older frequency measurements and with other microwave and infrared data that determined some of the rotational constants for the various states to obtain the best term values for the lower vibrational states of N_2O, all related to the cesium frequency standard. These term values are being used to prepare the infrared calibration atlas for N_2O described in the next section.

In the coming year we expect to be able to measure some of the weaker hot band lines in the 1285 cm^{-1} band of N_2O to obtain term values that will provide frequency calibration in the 2000-3000 cm^{-1} region. Our long range goals also include the measurement of hot bands accompanying the laser transitions near 940 cm^{-1} and the frequency measurement of some lines due to the 10°0-02°0 transitions near 1060 cm^{-1}. Finally, with a little bit of luck it may be possible to obtain a diode with enough power in a single mode to make a few saturated absorption measurements on the 1285 cm^{-1} band of N_2O. That would give an order of magnitude improvement in the accuracy of the frequency measurements.

2. Infrared Calibration Atlas

(A. G. Maki)

During the past four or five years we have been developing infrared spectral frequency tables for calibrating tunable IR laser spectrometers. We have worked with several groups in obtaining highly accurate heterodyne and Fourier transform spectra on many bands of the OCS and N_2O molecules which will form the basis of two reviews. Much of the manuscript and tables for the OCS review were completed previously. The new results on the ν_2 band will be added to the existing tables to complete this review. During the past year further heterodyne measurements on N_2O bands up to 2200 cm^{-1} have been obtained (see preceeding section) and allow calibration tables to be produced in the regions of 520 cm^{-1}, 930 cm^{-1}, 1300 cm^{-1}, 1880 cm^{-1}, and 2200 cm^{-1} with each covering a range of 90-150 cm^{-1}. Some additional measurements needed for calibration near 2700 cm^{-1} are being sought to complete the analysis and produce a set of tables which will replace the previous publication on N_2O in the Journal of Chemical and Physical Reference Data. This work is supported by the OSRD.

3. Revised Recommended Rest Frequency List

(F. J. Lovas)

In May 1985 the manuscript entitled "Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions - 1984 Revision" was submitted to J. Phys. Chem. Ref. Data by F. J. Lovas. This is a complete revision and update of a 1979 publication in Astrophys. J. Supplement by F. J. Lovas, L. E. Snyder, and D. R. Johnson. The reported astronomical observations of new species and new rotational transitions of previously identified molecules has more than tripled the number of lines reported in the first publication.

Preprint copies of this manuscript have been distributed to the nearly 300 astronomers and spectroscopists on our mailing list with the request that they examine it for oversights or errors. A number of useful responses have already been received. In fact among the responses was a preprint of a survey of Orion A between 247 GHz and 263 GHz which contains more than 200 new transitions which were added to the table. We have also filled a request for a magnetic tape copy of the data file to be used on the new British - Dutch 15-metre submillimeter wave telescope being constructed on Mauna Kea, Hawaii. The most pleasing aspect of the responses has been the interest of the astronomy community in the accuracy of the reported information as well as providing new observations to keep it as up-to-date as possible. The manuscript has been submitted to J. Phys. Chem. Ref. Data and the major tables of data have been converted via a magnetic tape to the Bedford system used by OSRD. This work is supported by the OSRD.

4. Microwave Spectral Tables
(R. D. Suenram and F. J. Lovas)

We continue to carry out the general literature search for all published (and unpublished) microwave spectra for this project. Evaluation and coding new data continues on the diatomic and triatomic species to keep the computer files from the earlier publications current.

Work on the third publication of the Microwave Spectral Table series "Hydrocarbons" is progressing. The spectral fittings of all the normal symmetric top and asymmetric top species are complete. The corresponding data files of the measured and predicted spectra have been produced and all isotopic and vibrational species have been coded. The analysis of the species with internal rotation remains to be accomplished since the programs for these analyses were not fully implemented on the Univac. Since we have moved all programs and data files to NBS's new Cyber computer, implementation of these programs on the Cyber is in progress. This work is supported by the OSRD.

5. Supplement to Structural Data Tables for Polyatomic Molecules
(W. J. Lafferty)

Ten years ago members of the Molecular Spectroscopy Division collaborated with spectroscopists from Japan, Germany and England to produce a set of structural tables of polyatomic molecules. All structures obtained for gas phase molecules by electron diffraction and infrared, Raman, electronic, and microwave spectroscopy were included. The tables were published by Landolt-Börnstein in their New Series (Group II, Volume 8).

This year we have updated these tables. The literature has been searched from 1974 to the beginning of 1985. All new structures as well as structures whose parameters have been significantly improved have been included in the tables. The entry for each molecule includes the structural parameter as well as a schematic drawing of its structure. This supplement will once again be published by Landolt-Börnstein. This work is supported by the OSRD.

6. Review of SO_2
(F. J. Lovas)

After several years in the process, the publication of a review on the spectrum of SO_2 is forthcoming in J. Phys. Chem. Ref. Data Vol. 14 (1985). This is part 22 of the series "Microwave Spectra of Molecules of Astrophysical Interest." This work is supported by the OSRD.

C. Spectroscopy for Environmental Studies

Many small molecules play a significant role in the chemistry of the earth's atmosphere. As such, they are of significant interest to agencies like NASA, DOD and the CMA (Chemical Manufacturers' Association). The interest of the latter 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 not on band analyses per se, but rather 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. High Resolution Spectrum of the ν_2 and ν_3 Bands of $HOC\ell$
(W. J. Lafferty and W. B. Olson)

Our interest in the spectrum of $HOC\ell$ has been motivated by very practical reasons. $C\ell$ atoms produced from the photolysis of freons in the upper atmosphere react with stratospheric O_3 via the routes:

$$C\ell + O_3 = C\ell O + O_2$$

and

$$C\ell O + O = C\ell + O_2$$

There are a great number of competing reactions in the stratosphere, and the extent of the damage done by the freons is at this point still controversial. $HOC\ell$ can be produced from $C\ell O$ by the reaction

$$C\ell O + HO_2 = HOC\ell + O_2$$

which, if the $HOC\ell$ formed is sufficiently stable, serves to withdraw $C\ell$ atoms from the chain reaction.

The stability of $HOC\ell$ in the upper atmosphere is still somewhat uncertain. A number of laboratory studies have been carried out on these and other reactions, but it appears that the most practical way in which to get a handle on the role played by HOCℓ in stopping or slowing the ozone destroying chain reactions is to directly observe this species in the stratosphere and directly monitor its concentration.

A number of unsuccessful attempts to detect HOCℓ with both ground based and balloon spectrometers have been made. One of the problems of detection of this molecule arises from that fact that even in the atmospheric windows, the HOCℓ absorption bands are overlapped by the lines of very minor stratospheric constituents which have about the same intensities expected from the lines of HOCℓ.

In order to positively identify the lines arising from the HOCℓ spectrum, it is necessary to have very precisely known line frequencies since only a few lines of a band may fall in a clear spot in the spectrum. We, therefore, with the partial support of the Chemical Manufacturers Association, have recorded and assigned the two lowest frequency bands of HOCℓ with the NBS BOMEM FTS spectrometer with a resolution of 0.004 cm^{-1}. Careful attention has been given to frequency calibration; fortunately, both bands fall in regions where there are very well measured calibration lines. The ν_2 band centered at about 1220 cm^{-1}, was calibrated against N_2O while the ν_3 band was calibrated against CO_2 absorption lines. The absolute frequency calibration of the BOMEM spectrometer was found to be surprisingly good. Corrections of only a few ten thousands of a cm^{-1} were found to be necessary. We conservatively estimate that the absolute precision is better than +/- 0.0005 cm^{-1}; the relative precision is somewhat better, and is on the order of 0.00002 cm^{-1}.

Both ν_2, the bending vibration, and ν_3, the Cℓ-O stretching mode, are a-type bands. Figure 2.2 shows a much compressed scan over the ν_2 band.

The assignment is complicated by the presence of two chlorine isotopes, but line assignment presented no difficulties; a very complete assignment has been accomplished for both bands of both isotopic species. The observed lines have been fit using a Watson Hamiltonian, and the standard deviation of the fittings for all the bands was 0.0002 cm^{-1}.

Currently relative line intensities are being measured for both bands in order to determine the magnitude of the Herman-Wallis effect on the intensities. When this is completed, line intensities will be computed, and a band atlas including line frequencies and line strengths at several temperatures will be produced. This work is supported by CMA.

2. Measurements on the ν_3 and ν_4 Bands of Nitric Acid (HNO_3)
(A. G. Maki)

The ν_3 and ν_4 bands of nitric acid were investigated in collaboration with Prof. A. Fayt of the University of Louvain - la Neuve, Belgium. We have used the NBS BOMEM interferometric spectrometer to measure the

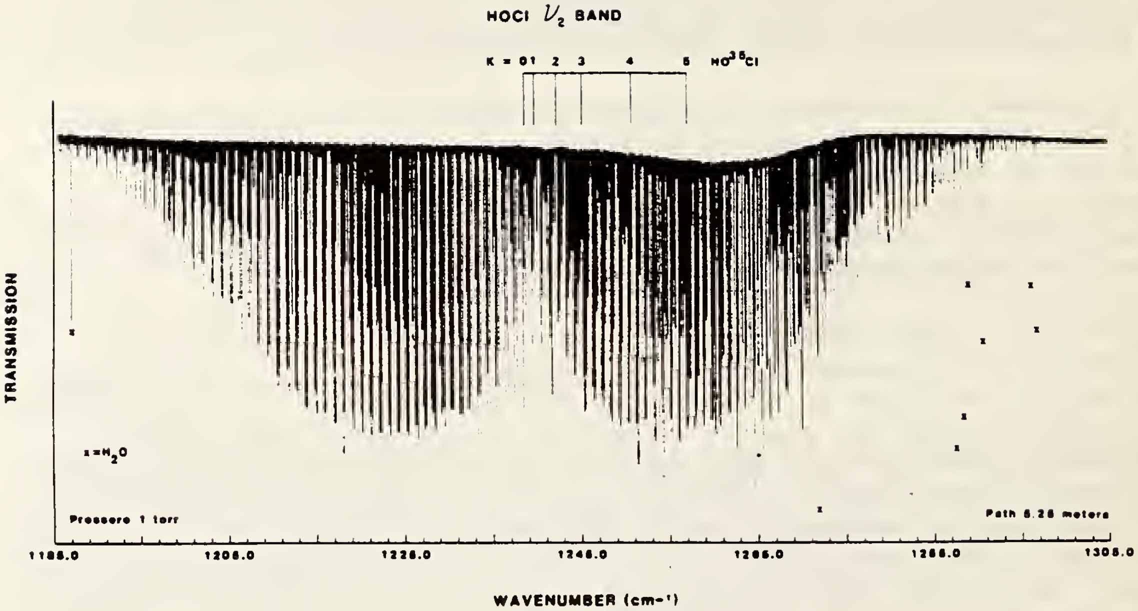


Figure 2.2 The ν_2 band of HOCℓ recorded under full instrumental resolution of 0.004 cm^{-1}. The sub-band centers of the major isotopic species are labelled at the top.

spectrum of nitric acid (HNO_3) in the 1250 to 1360 cm^{-1} region which includes the ν_4 band at 1303 cm^{-1} and the ν_3 band at 1326 cm^{-1}. In collaboration with Dr. Andre Fayt transitions for both of these bands have been assigned and fit to appropriate asymmetric rotor constants.

These bands are used by certain laboratories for atmospheric measurements since they fall in a spectral region where the atmosphere is relatively transparent. It is important that the rotational line structure of these bands be understood so that modeling calculations can be used to simulate atmospheric spectra both to interpret the atmospheric distribution of nitric acid, and also to cancel out the nitric acid features when searching for underlying transitions due to other atmospheric species, such as chlorine nitrate.

To supplement the BOMEM spectrum we have also measured diode laser spectra for several small spectral regions in order to resolve some of the more tightly clustered features such as the ν_4 Q-branch. Figure 2.3 shows an example of the diode laser spectrum of ν_4. Although only the K_c=0,1 transitions are labelled many other features seen in the figure have been identified and assigned.

Thus far the spectra have been fit with a standard deviation of about 0.002cm^{-1}. It is not clear if the fit could be improved by including some interactions with nearby bands. In the coming year we hope to obtain some laser diode spectra of the ν_3 band of HNO_3 in order to see if some of the

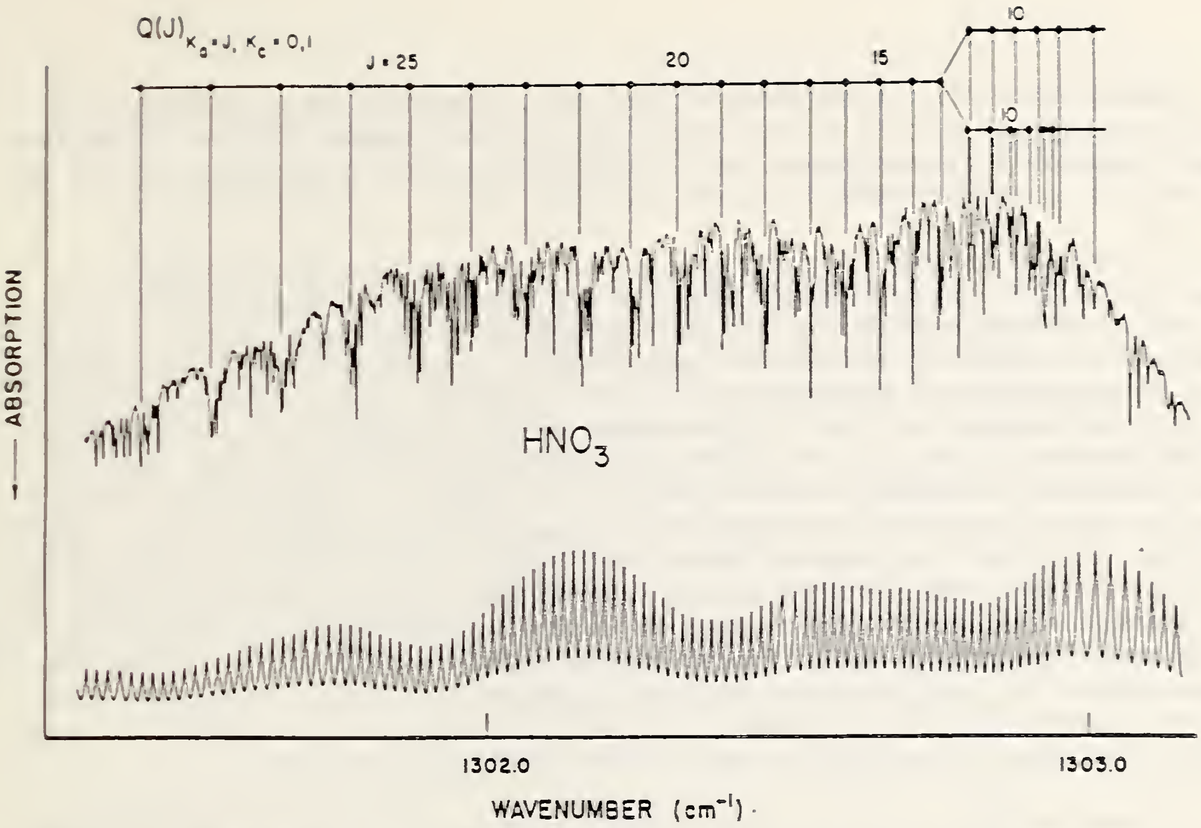


Figure 2.3. Diode laser spectrum of the ν_4 Q-branch for nitric acid (HNO_3). The lower trace is the fringe pattern from a solid germanium étalon; FSR = 0.016cm^{-1}.

more obvious deviations are artifacts due to incompletely resolved clusters of lines. It appears, however, that there should be a weak $\Delta k=2$ interaction between ν_3 and ν_4 similar to what we have found between ν_5 and $2\nu_9$. This work is supported by NASA.

3. New Intensity and Frequency Measurements on ClO
(A. G. Maki, and G. A. Thompson)

Chlorine monoxide (ClO) is one of the reactive intermediates involved in the chlorine cycle in the atmospheric chemistry that governs the concentration of ozone in the upper atmosphere. Much interest centers on measurements of the concentration of ClO in the atmosphere and a number of techniques have been used to try to measure the concentration of ClO in the atmosphere.

At the present time microwave techniques seem to have been most successful in determining the concentration of ClO in the upper atmosphere but there is an apparent disagreement between the ground based microwave measurements[1,2] and the ground-based infrared measurements.[3] In particular, the ground-based measurements of Mumma _et al_.[3] failed to detect any ClO although the expected column density was expected to give a detectable signal. Since it has been suggested that errors in either the frequencies or the intensities of the ClO lines might contribute to the non-observation of ClO in the Mumma et al. experiments, we have undertaken an independent remeasurement of the intensities and frequencies of the ClO spectrum in the infrared.

Accurate intensity measurements are not easy to make on stable molecules and are even more difficult for unstable molecules since it is normally necessary to know how many molecules are present in the absorption path. The microwave measurements do not have this problem since the microwave absorption intensity is proportional to the square of the dipole moment and the dipole moment can be measured quite accurately from the Stark effect. The several measurements that have been made of the infrared intensity indicate that it is relatively weak and for that reason Dr. Chackerian (NASA/Ames) has suggested the possibility that the Herman-Wallis effect, which relates the infrared band intensity to the ratio of the intensity of R-branch transitions to the intensity of the P-branch transitions, can be used to determine the transition moment (infrared intensity) without measuring the ClO concentration. Since the measurement of the ClO concentration is quite difficult, we believe that such a technique that by-passes that one difficult and controversial step merits further investigation and we have began such a study.

What we plan to do is measure the intensity ratio of P- and R-branch transitions that arise from the same energy levels (in order to eliminate any temperature dependence). For maximum accuracy these measurements must be made under identical operating conditions for both the R-line and the P-line. We plan to switch back and forth between measurements of the R-line intensity and the P-line intensity several times in order to verify that the operating conditions are indeed identical. This work is supported by NASA.

Table 2.1 gives an example of the intensity ratio expected for the different band intensities suggested by various other papers.

Table 2.1. R- and P- Branch Intensity Ratio Calculated for ClO for Different band Intensities.

Band Intensity (cm^{-2} atm^{-1})	32.0	11.8	5.0
Intensity Ratio R(16.5)/P(16.5)	1.243	1.334	1.469

Finally, this project also includes a re-measurement and re-analysis of the infrared frequencies of the ClO absorption lines in order to improve the reliability of the calculated infrared spectrum of ClO.

(1) A. Parish, R. L. DeZafra, P. M. Solomon, J. W. Barrett, and E. R. Carlson, Science 211, 1158 (1981).

(2) P. M. Solomon, R. deZafra, A. Parish, and J. W. Barrett, Science 224, 1210 (1984).

(3) M. J. Mumma, J. D. Rogers, T. Kostiak, D. Deming, J. J. Hillman, and D. Zipoy, Science 221, 268 (1983).

4. Self-Broadening in the Fundamental Bands of HF and HCl

(A. S. Pine and A. Fried (CAC))

In collaboration with Dr. A. Fried of the Center for Analytic Chemistry, the self-broadened lineshapes have been measured for the fundamental bands of HF and HCl with the high-resolution tunable difference-frequency laser spectrometer in the Molecular Spectroscopy Division. This is a continuation of a project to improve the data base on the spectral band parameters (intensities, self- and N_2- and air-broadened lineshapes and shifts) in support of the NASA Upper Atmospheric Research Program (Project HALOE) to monitor ozone depletion caused by reaction with halogen-containing molecules. Using the narrow-linewidth (~1 MHZ) linear-scan-controlled tunable laser system, we observed spectral lineshapes free of instrumental distortion that exhibited deviations from the usual Voigt profile due to collisional (Dicke) narrowing. In Figure 2.4 we show an example of the P(7) line of HF at 50.5 Torr least-squares fit by a Voigt function and by the "soft" and "hard" collisional narrowing models which yield much reduced obs.-calc. residuals. The self-broadening coefficients and shifts for the $v=1\leftarrow0$ transitions of HF and HCl are displayed in Figure 2.5. No significant differences were found for the two chlorine isotopes in the natural abundance sample. Particular care was taken in sample handling for these reactive, readily polymerizable, gases to ensure accuracy, linearity and reproducibility in the pressure and broadening measurements. This work is supported by NASA.

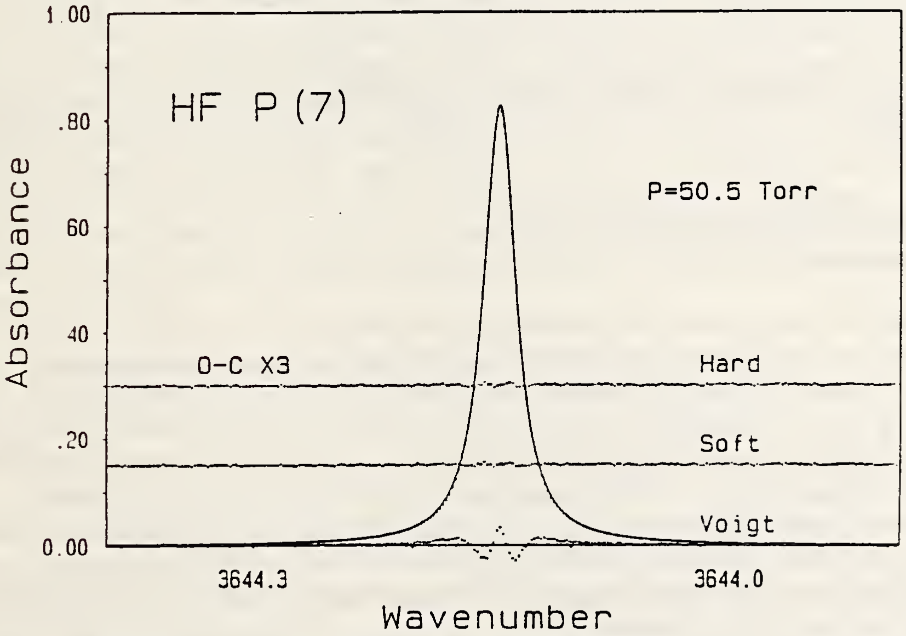


Fig. 2.4. Self-broadened lineshape of the P(7) line of HF compared to various collisional models.

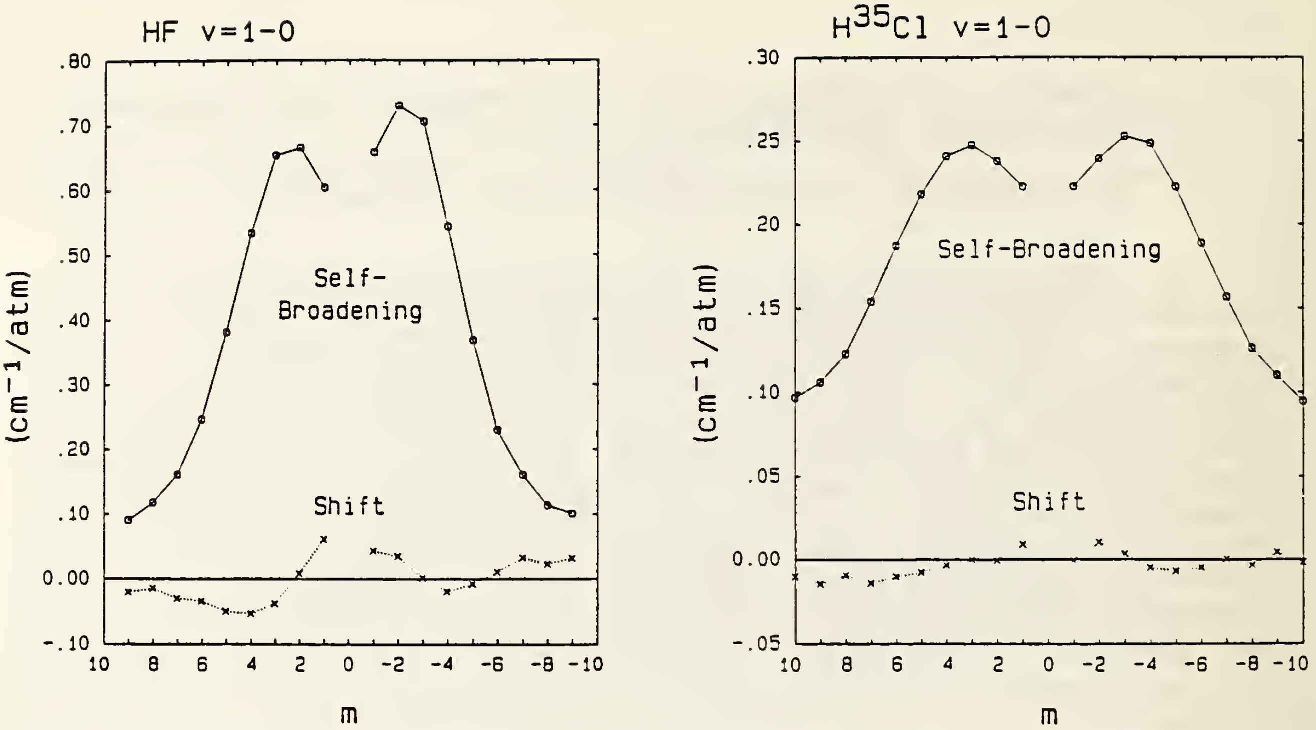


Fig. 2.5. Self-broadening coefficients and shifts for HF and HCl at T=295K.

5. Analysis of the Spectrum of H_2O_2

(W. B. Olson)

The pooling of our data for hydrogen peroxide with those of Prof. Robert Hunt of Florida State University has led to some reassignments of the absorption lines in the OH stretching region of the spectra, and to a direct determination of energy differences between ground state rotational levels and the levels perturbing them, up to J = 25 on the most perturbed levels (ground state K = 8). The previous limit was J = 15. These reassignments were made possible by a clarification of the group theory, and enumeration of the types of perturbations possible in hydrogen peroxide, provided by the permutation-inversion group theory treatment of hydrogen peroxide by J. T. Hougen.[1]

In addition to extending assignments, it has been possible, using Hougen's symmetry treatment, to introduce some reforms in terminology and notation for hydrogen peroxide energy levels and transitions which we feel will greatly simplify the understanding of hydrogen peroxide, and greatly facilitate verbal and written communication. The basis of the new terminology is a two valued overall symmetry level (U for ungerade and G for gerade), for the two torsional substates for a given principal torsional quantum number, rather than the old four valued numerical τ label.

Selection rules for transitions had been worked out in terms of the τ labels, but these had no direct connection with overall symmetries, and this led to considerable confusion as to the source of perturbations when these were evident. A preliminary account of this work has been given in a report to NASA.

A coupled asymetric rotor program for simultaneous fitting of combination differences in the ground state (0G) and perturbing first excited torsional state (1G) was expected to be available in Sept. 1984, but was delayed, and is now expected to available in Sept. 1985. Fitting of our data with this program should lead finally to a definitive set of ground state rotational constants for H_2O_2. This work is supported by NASA.

(1) J. T. Hougen, Can. J. Phys. 62 1392-1402 (1984).

D. 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 about 25% of the group's total effort. In addition to studies using a difference frequency laser spectrometer in the 3 micron region, this year brings forth studies using the BOMEM Fourier transform spectrometer in both the mid- and far-infrared, studies using the new pulsed Fourier transform microwave spectrometer (Flygare type), as well as theoretical studies. 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. Hydrogen Bond Energies of the HF and HCl Dimers

(A. S. Pine and B. J. Howard)

The dissociation energies of the hydrogen-bonded complexes, $(HF)_2$ and $(HCl)_2$, have been obtained from high-resolution measurements of absolute infrared line strengths at a single temperature and pressure under the assumption of minimally-perturbed local-mode behavior of the outer hydrogen stretch. The measurements were made with a difference-frequency laser system on low pressure (P~1-2 Torr) gas samples cooled to near the condensation point (T~219 K for HF, T~127 K for HCl) in a long path (L~64-80 m) White cell. The observed absolute intensity pattern of the ${}^rQ_0$ subbranch of the outer or "free H" stretching band, ν_1, of $(HF)_2$ is shown in Figure 2.6 along with a simulated trace based on the usual Hönl-London and Boltzmann factors for the J assignments and tunneling splittings obtained in our previous work. The transition lineshapes in the simulated trace are Voigt profiles obtained by convolving the calculated Doppler distribution with a pressure-broadened Lorentzian of half-width = 34 MHz. The agreement between the observed and calculated spectra is excellent as can be seen in the subtracted residuals trace of the bottom of Figure 2.6 which exhibits only the ${}^rR_0$ lines and some hot band structure not included in the model.

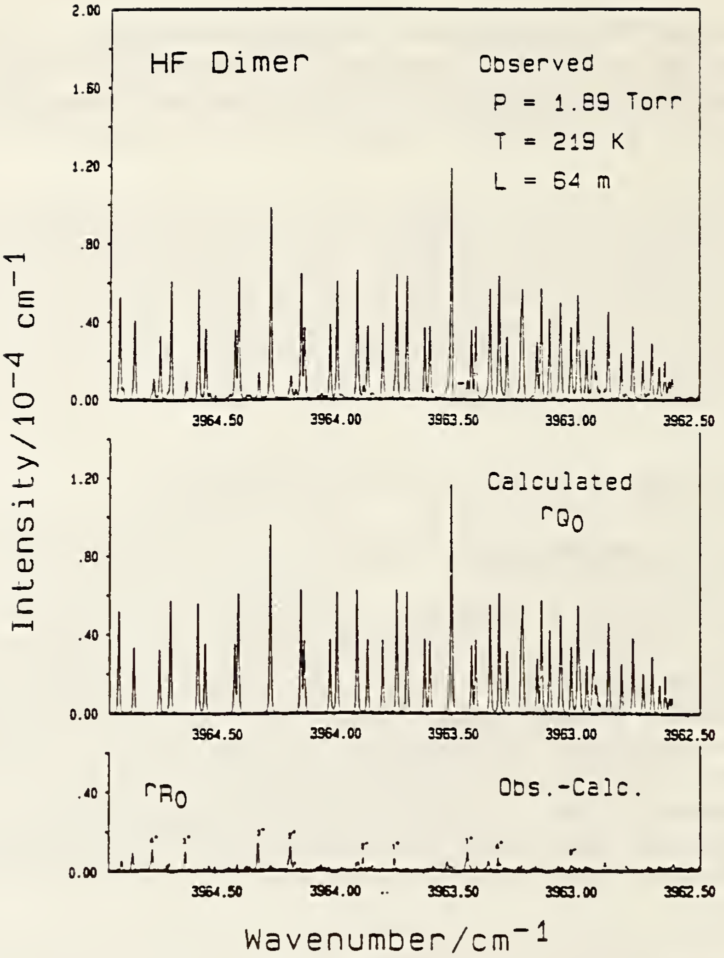


Fig. 2.6. Observed, calculated and residual spectra of the ^rQ_o subbranch of the ν_1 band of the HF dimer.

The spectral intensities can be related to the dimer concentration n_D, and partition function, Q_D, and the transition moment, $\langle\mu_1\rangle_b$, for the band component measured using standard formulae. In turn, n_D and Q_D can be expressed in terms of the monomer concentration, n_M, and partition function, Q_M, and the zero-point dissociation energy, D_o, under thermal equilibrium by

$$K_{eq} = n_D/(n_M)^2 = (Q_D/Q_M^2)\, e^{Do/kT} \quad .$$

Since n_M is measured from the pressure assuming negligible polymerization and Q_M can be calculated trivially for a diatomic molecule, the only unknowns in the problem are D_o and the transition moment for the dimer. Recent ab initio calculations have shown that the bond transition moment for the outer hydrogen is only ~10% enhanced over that of the monomer, which is known quite accurately from our recent measurements of the absolute intensities of the monomers. Thus we need only to project the value of this moment onto the b-axis of the dimer to relate it to the $\langle\mu_1\rangle_b$ observed.

We obtain zero-point dissociation energies for the HF and HCl dimers of D_0 = 1038 (+43,-34) cm^{-1} and 431(±22) cm^{-1} respectively. Estimates of the zero-point energies of the low frequency intermolecular vibrations enable us to obtain the well depths and the equilibrium dissociation energies, D_e = 1595 (+103,-94)cm^{-1} for $(HF)_2$ and 794 (± 86) cm^{-1} for $(HCl)_2$ for comparison to *ab initio* and model calculations for these complexes.

2. Rotational Predissociation and Libration in the Infrared Spectrum of Ar-HCl

(B. J. Howard and A. S. Pine)

Fully-resolved rotational structure in the high-frequency vibrational region of the Ar-HCl van der Waals complex has been recorded under thermal equilibrium conditions at T=127 K with a tunable difference-frequency laser. Both the fundamental H-Cl stretch and its combination with the low-frequency large-amplitude bend (libration) have been observed with comparable intensities. The fundamental H-Cl stretch gives rise to a parallel-type band in the null gap of HCl as shown in Figure 2.7. The assigned Ar-HCl spectrum is indicated in the calculated trace below the

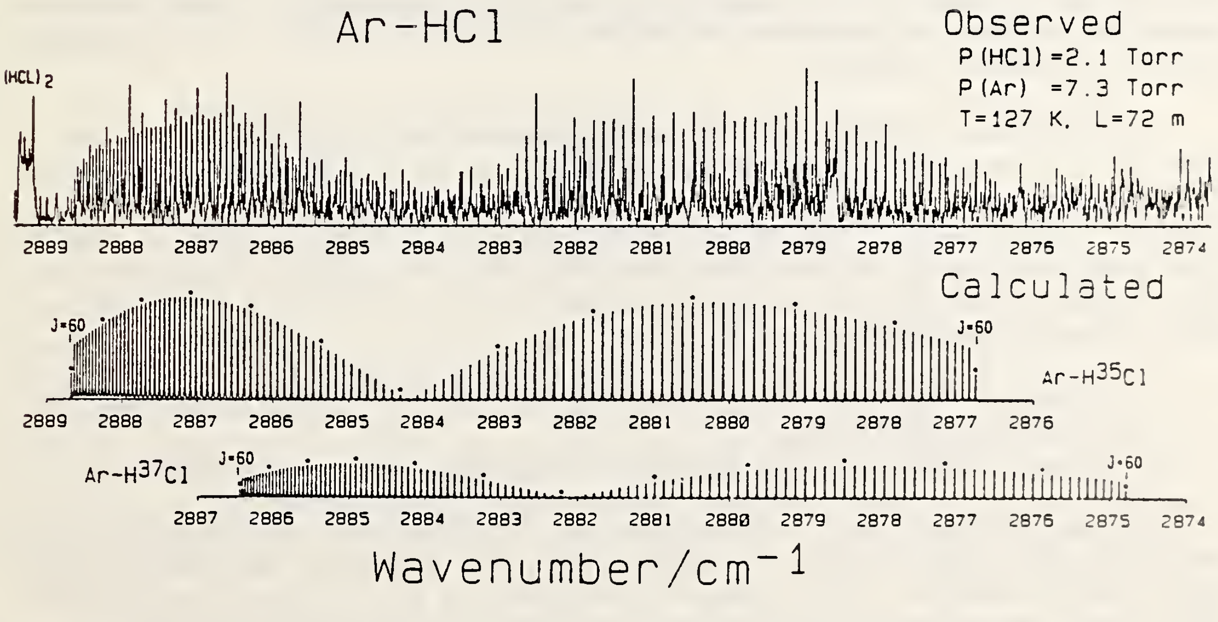


Fig. 2.7. Observed and calculated spectra of the ν_1 fundamental H-Cl stretching band of Ar-HCl.

observed spectrum which is unavoidably contaminated by HCl dimer structure (known from previous work) and hot bands. Both Cl isotopes contribute in their natural abundance. The abrupt cutoff of the spectrum at J = 60 arises from rotational predissociation as the rotational energy exceeds the binding energy and may tunnel through the top of the centrifugal barrier. The rotational eigenvalues and predissociation have been modeled with a one-dimensional radial potential of the Maitland-Smith form to give a zero-point dissociation energy of D_0=114.7 (±1.0) cm^{-1} and a van der Waals stretching frequency of ν_3 = 31.3 (±1.0)cm^{-1}. These values are in good agreement with empirical models based on precise microwave measurements near the minimum in the potential well, but disagree seriously with prior estimates based on the temperature dependence of the low resolution infrared spectrum. The rotational constants in the ground and excited H-Cl stretch vibrations yield a measure of the extension of the center-of-mass separation due to the motion of the proton. The red shift of the Ar-HCl spectrum from the isolated HCl monomer implies a stronger van der Waals attraction upon excitation of the H-Cl stretch.

The combination band of the H-Cl stretch, ν_1, with the van der Waals band, ν_2, is shown in Figure 2.8. It is a perpendicular-type band (Π-Σ) of anomalously high intensity transferred from the fundamental stretch by the strong modulation due to the wide librational motion. The blue shift from the fundamental band is about 34 cm^{-1} corresponding to the frequency of the bending mode. The rotational constants yield the extreme shortening of the van der Waals bond length upon bending the molecule, and they give the ℓ-doubling constant $q_1 = B_Q - B_R = +34.2$ (± 0.2) MHz arising from Coriolis perturbations from nearby states with Σ-symmetry. These measurements should lead to improved estimates of the anisotropy of the potential and its dynamical behavior.

We have also obtained preliminary assignments of hot bands arising from ν_3, the van der Waals stretching mode, in the fundamental band region of Ar-HCl. This gives us further information about the intermolecular potential and about interactions between the low frequency modes. Spectra have also been recorded for other rare gas (Ne, Kr, Xe)-HCl complexes to obtain the trends of the van der Waals potential with regard to atomic mass and polarizability.

3. Study of Hydrogen-bonded complexes in the Gas Phase Using Fourier Transform Spectroscopy

(B. A. Wofford, J. W. Bevan, W. B. Olson, and W. J. Lafferty)

During the past year, we have had a very fruitful collaboration with Professor John Bevan and B. A. Woffard from the Chemistry Department of Texas A&M University. From designs developed by W. B. Olson (see Section 3.1), Prof. Bevan and his co-workers have built a long-path absorption cell which can be cooled to ca. -100° C. At low temperatures, the hydrogen-bonded complexes are present at higher concentrations. The long absorption path (up to 64 meters) serves to enhance the instrumental

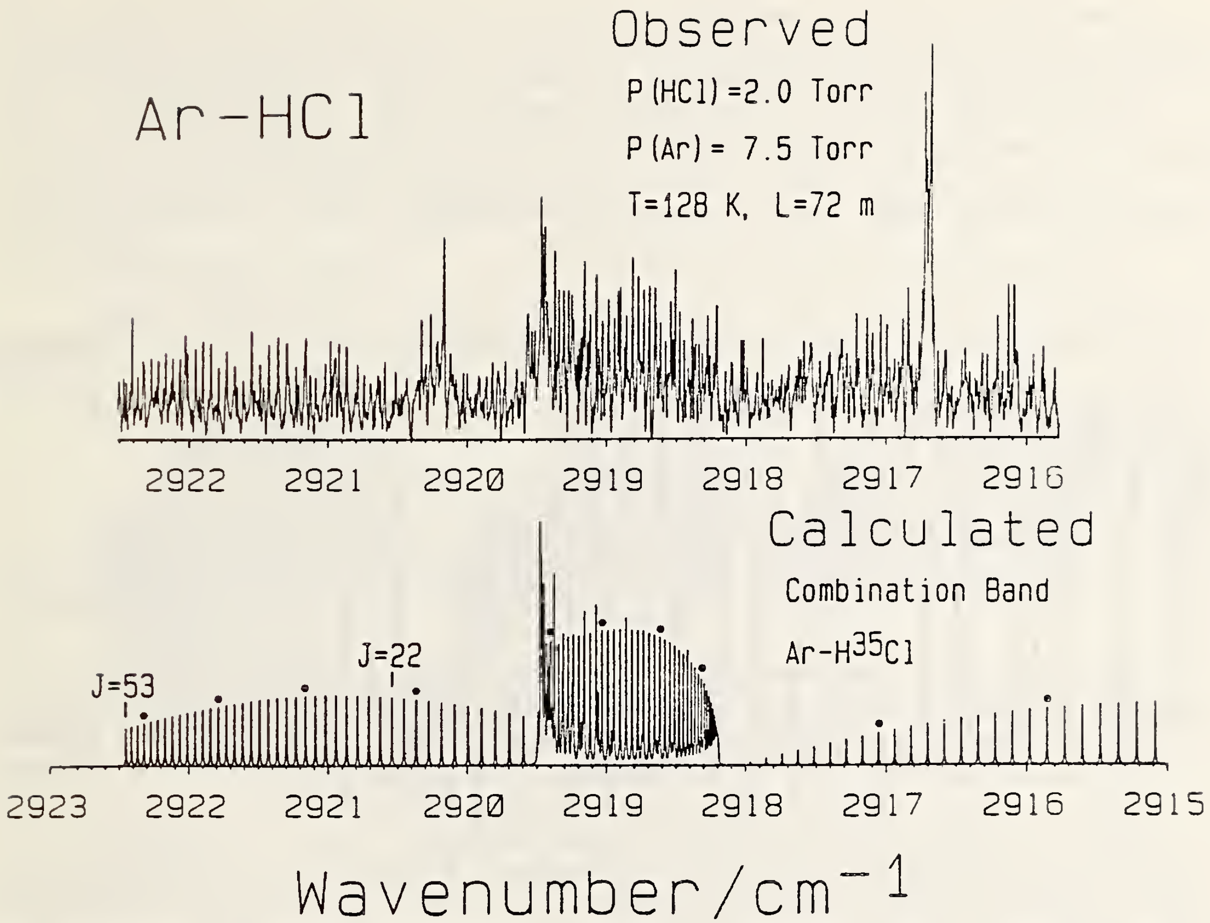


Fig. 2.8. Observed and calculated spectra of the $\nu_1+\nu_2$ stretch-bend combination band of Ar-HCl.

sensitivity. This cell has been coupled into the NBS BOMEM spectrometer and used to study a number of rotation-vibration bands of several hydrogen-bonded complexes including HCN···HF, HCN··HCN, and HCN···HCl. At this point the work on the HCN-HF complex is most complete. Five of the absorption bands of this complex have been observed, and many of the individual line transitions assigned. These bands arise from the C-H stretching fundamental and its overtone, the CN stretching vibration, the internal HCN bending vibration, as well as the bending vibration in which one end of the complex twists with respect to the other end. The latter vibration is unique to the hydrogen-bonded complex, and is not overlapped by lines from either HCN or HF. The Q-branch of this band is shown in Figure 2.9.

The dissociation energy for these weakly bound complexes is, of course, rather low; e.g., for HCN···HF, D_0 is about 1600 cm^{-1}. Thus many of the molecular vibrations lie above the dissociation limit, and high resolution spectroscopy, in addition to providing information on the energy levels of hydrogen-bonded molecules, allows one to approximate the life time of molecules in energy levels above this limit. The width of a

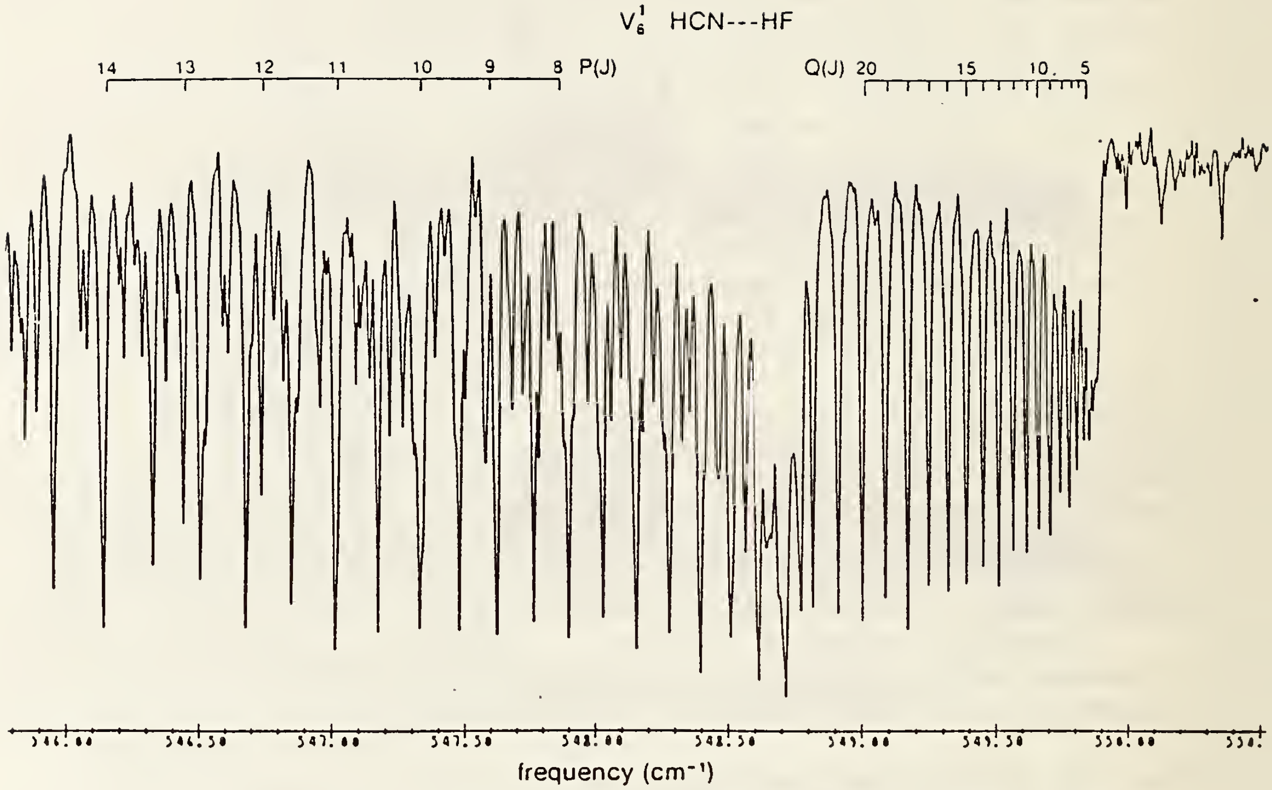


Fig. 2.9 A Q-branch of the high-frequency bending vibration, $\nu_6{}^1$, of the hydrogen bonded complex HCN•••HF recorded at a temperature of -50°C. Despite the unusually high stability of this complex, a path length of 64 meters was required to obtain the spectrum with a reasonable signal-to-noise level. This vibration is unique to the hydrogen-bonded complex and there is no overlapping from lines of the parent species.

ro-vibrational line is inversely proportional to the lifetime of the molecule in the upper state of the transition. The lines of several bands of the HCN•••HF molecule were found to be considerably broader than the instrumental resolution, and, therefore, lifetimes of several vibrational states could be estimated. For example, the lines of the C-H stretching vibration at 3310 cm^{-1} were not broadened and one can estimate that the molecular lifetime of this state is at least 10^{-8} sec. The overtone of this vibration at 6517 cm^{-1} is slightly broadened, and the lifetime of this level is on the order of 2.4 ns. The CN group is directly involved in the hydrogen bond, and the lines of the CN stretching vibration at 2121 cm^{-1} are very broad. The lifetime of molecules in this state is about 2.56 ns. Not surprisingly the lower frequency bands, which have vibrational frequencies below D_0, have sharp lines, and only an upper limit estimate of the lifetimes can be made for the upper states of these vibrations.

These studies will shortly be extended to the far infrared region to study the rest of the vibrational transitions unique to the complex.

4. Pulsed Beam Fabry-Perot Cavity Fourier Transform Microwave Spectrometer

(R. D. Suenram and F. J. Lovas)

The construction of a pulsed beam Fabry-Perot cavity Fourier transform microwave spectrometer was briefly described in last year's annual report.

The major emphasis of our efforts in the past year have involved testing the new spectrometer with a number of previously observed hydrogen bonded species and van der Waals complexes to obtain experience in the operation of the instrument and optimization of the detected signals.

Two areas in which the instrument excels are high sensitivity and high resolution. In order to assess the sensitivity a 2% mixture of OCS in argon was prepared and the 1-0 transition of the various isotopes of OCS studied in natural abundance. Figure 2.10 shows the 1-0 transition of

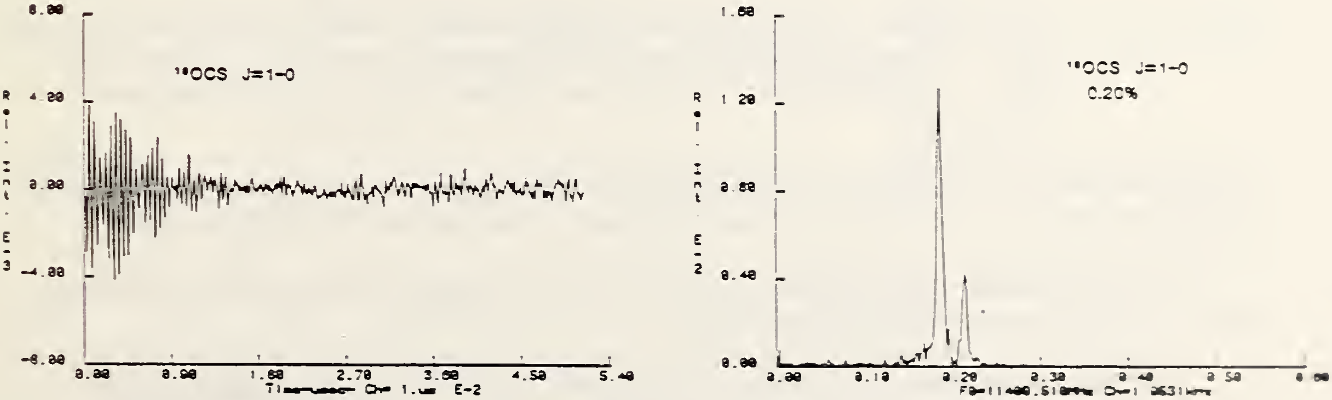


Fig. 2.10. Rotational spectrum of the J=1-0 transition of ^{18}OCS. Left: time domain spectrum obtained with 500 nozzle pulses. Right: frequency domain spectrum; Fourier transform of spectrum shown on the left. The signals were observed with a 2% mixture of OCS in argon.

^{18}OCS which occurs in 0.21% natural abundance. The trace is a summation of signals for 500 nozzle pulses but this signal is easily observable on a single pulse. The weakest signal observable was that of ^{18}OC^{34}S which occurs in 0.0086% natural abundance. This signal was observed with a summation of 2500 pulses. The ^{18}OCS signal, which is observable on a single pulse, corresponds to approximately 10^{13} molecules per pulse. Several improvements of the instrument are planned for the next year which should easily increase the sensitivity by an order of magnitude.

The high resolution aspect is shown in Figure 2.11 where the 1-0 transition of $(H_2O)_2$ is shown. The four individual peaks arise from the spin-spin hyperfine interaction associated with the H nuclei. The splittings are on the order of 16-20KHz. We have found that with certain nozzle/pressure configurations we can obtain line widths on the order of 8-12kHz (FWHM).

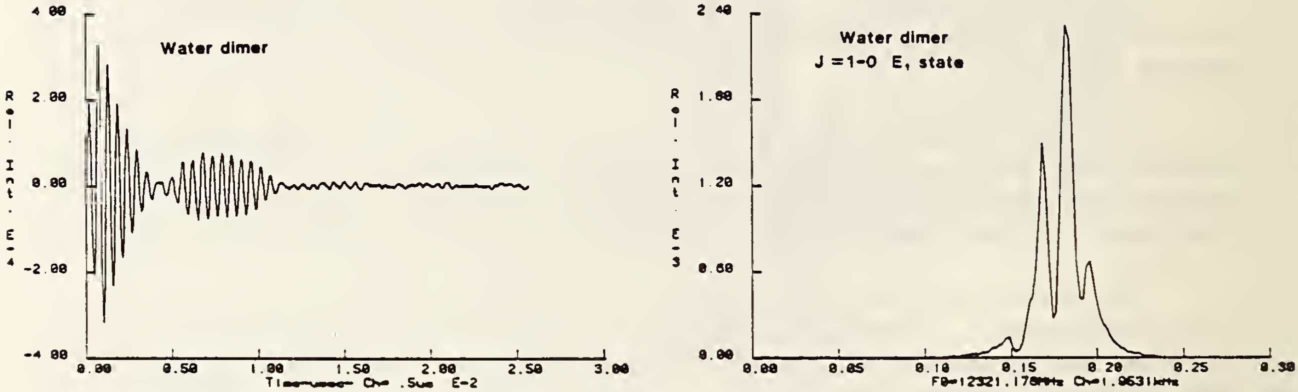


Fig. 2.11. Time domain (left) and frequency domain (right) spectrum of the J=1-0, E-state transition of the water dimer at ν = 12321.0 MHz. The frequency splittings (right side) are approximately 16-20 kHz.

The following two reports (D.5 and D.6) describe new results obtained for Ar···acrylonitrile and Kr···OCS.

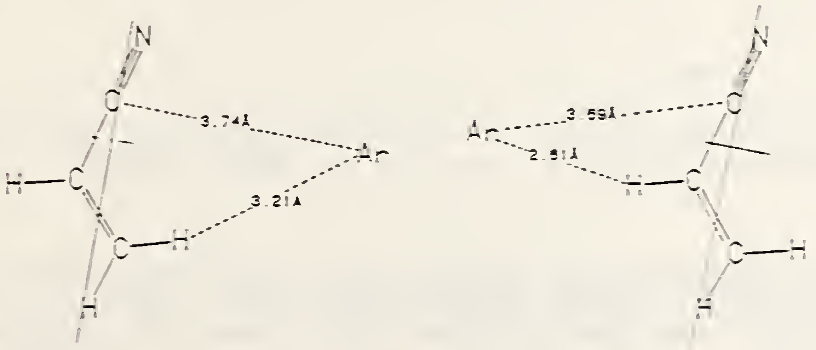
5. Microwave Study of the Ar...Acrylonitrile van der Waals Complex

(F. J. Lovas and R. D. Suenram)

The van der Waals complex of argon with acrylonitrile (Ar...CH_2CHCN) has been observed with the pulsed beam instrument. This particular complex was chosen as the first new molecular species for the new instrument for a variety of reasons. First the dipole moment is large so the spectra should be quite intense. Second, the ^{14}N nucleus provides characteristic quadrupole splittings which should be predictable and thus useful for the assignments of the transitions. Third, the species is large enough so that the transition density is fairly high (a strong transition every 100 MHz or so) which should enable several transitions to be found without a great deal of searching. Last, there are a variety of sites where the Ar could bind to acrylonitrile. It will be extremely interesting to see which conformation is the dominant one.

Two discrete sets of rotational transitions have been observed. For one set, the energy levels lie approximately 0.5 - 1.0 cm^{-1} higher in energy than the other set. More than thirty transitions have been observed and fitted for the low energy (ground state) and over twenty transitions have been measured and fitted for the higher energy (vibrational) state. Each of these transitions is split by the nuclear quadrupole interaction associated with the ^{14}N nucleus.

From a rotational analysis of the transitions, and analysis of the nuclear quadrupole hyperfine structure, the molecule appears to favor one of the two possible structures shown in Figure 2.12. Further work with deuterium isotope labeling will have to be done in order to discriminate which is the true structure. Our intuitive feeling is that the "inside" structure is probably the correct one, since the "outside" structure requires an Ar...H distance that is shorter than for the normal van der Waals radii of the atoms. In either case, the Ar atom lies at an angle of approximately 40° with respect to the plane of the acrylonitrile subunit.



Ar "inside" Ar "outside"

Fig. 2.12. Favored structures for the argon-acrylonitrile van der Waals complex.

6. Mirowave Study of the Kr...OCS van der Waals Complex
(F. J. Lovas and R. D. Suenram)

During Dr. B. J. Howard's visit at NBS the possibility was discussed of looking for the microwave spectrum of neon and krypton bonded to carbonyl sulfide. Work in the infrared region in his laboratory at Oxford

University had provided approximate values for the rotational constants of both Ne...OCS and Kr...OCS in the ground state and v=1 of the CO stretching vibration. Accurate values for the rotational constants of these species in the ground state, obtained by microwave spectroscopy, could be used in the analysis of the infrared spectra to obtain very precise values for the upper state constants.

Some time was spent searching for Ne...OCS but no transitions were found. Transitions of Kr...OCS on the other hand were readily observed. Subsequent microwave-infrared double resonance work on Ne...OCS in Oxford indicated that the preliminary rotational constants were much more uncertain than originally thought; as a result, we never searched the proper region to detect a transition of Ne...OCS.

For Kr...OCS transitions for four isotopes (^{84}Kr, 57%; ^{86}Kr, 17%; ^{82}Kr, 11%; and ^{83}Kr, 11%) have been observed and analyzed. The structure of the complex is planar and T-shaped, similar to Ar...OCS (see Fig 2.13). One note of interest is that nuclear hyperfine structure has been observed on ^{83}Kr...OCS transitions (see Figure 2.14). The ^{83}Kr atom has a nuclear spin of 9/2 and thus, a nuclear electric quadrupole moment. Although the electron orbitals of the atom are spherically symmetric, these are distorted in the van der Waals complex and cause hyperfine interactions. Analysis of this hyperfine structure should enable us to study the distortion of the spherical symmetry upon complexation.

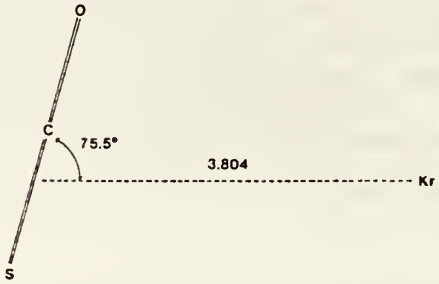


Fig. 2.13. Structure of the Kr...OCS van der Waals complex

Quite recently we have incorporated a set of Stark plates into the spectrometer for dipole moment measurments. These were placed ~25 cm apart, so that the cavity Q would not be changed appreciably, and provide $\Delta M_J = \pm 1$ selection rules. Analysis is in progress on the Stark effect of Kr···OCS. Figure 2.15 shows three Stark components of the 3_{12}-2_{02} transition.

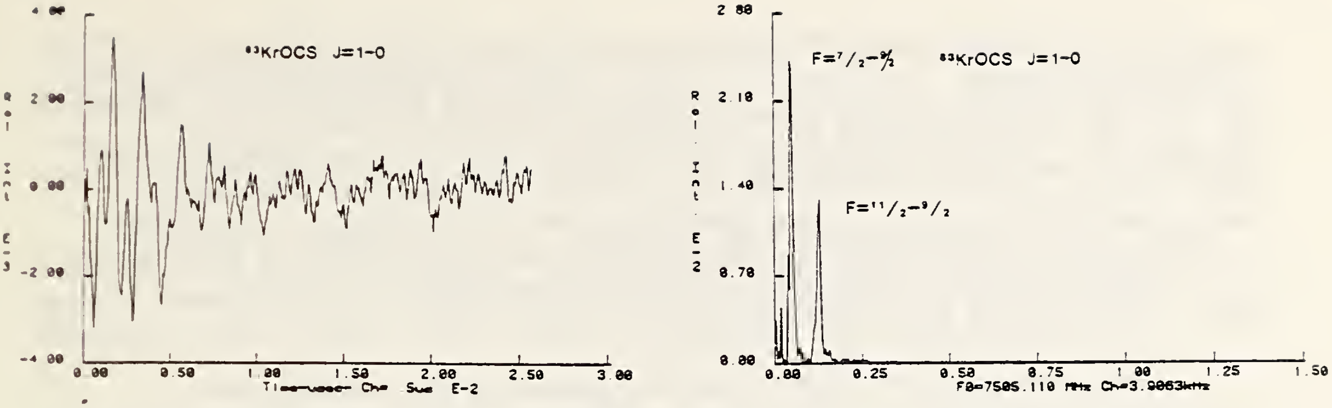


Fig. 2.14. Time domain (left) and frequency domain (right) spectrum of the J=1-0 rotational transition in ^{83}Kr...OCS at 7505.11 MHz. The $\Delta F=0$ transition is not shown in the figure; it was found at 7504.6 MHz.

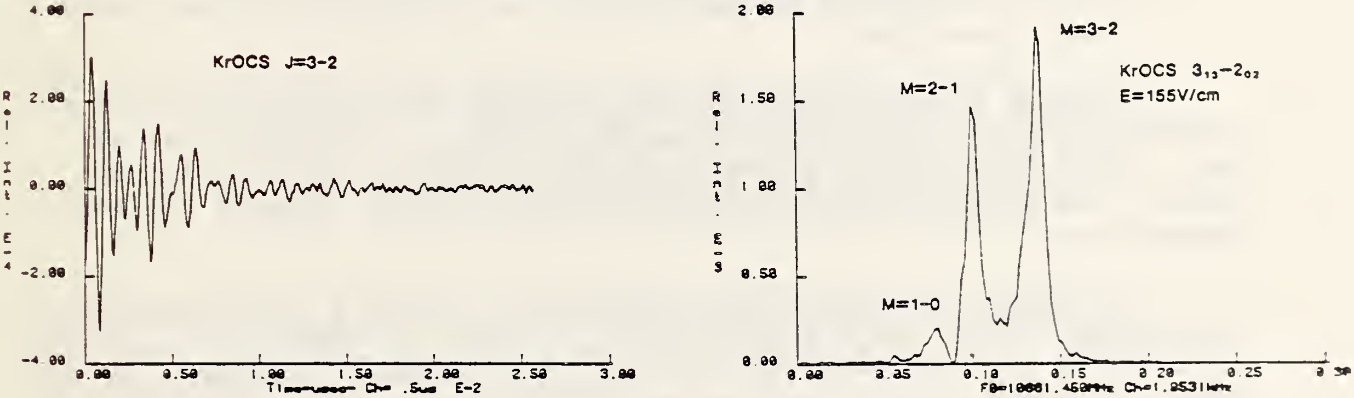


Fig. 2.15. Time domain (left) and frequency domain (right) Stark spectrum of the J=3-2 line of Kr..OCS obtained with a field of 155V/cm.

7. A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer

(J. T. Hougen)

When more than one large amplitude vibrational motion is present in a molecule, it is often not possible to define a global internal-axis-method (IAM) coordinate system and set of basis functions. In the present work, a method is presented for extending the IAM treatment to tunneling problems in such cases, using as an illustration a model for the water dimer with three large amplitude vibrational coordinates. The method involves the construction of two different sets of local IAM-like coordinate systems. The first of these contains n coordinate systems, one for the small neighborhood surrounding each of the n equilibrium frameworks. The second contains on the order of $n^2/2$ coordinate systems, one for each feasible tunneling path between each pair of frameworks. Basis functions written in the second set of local IAM-like coordinates are used to determine the complex phase factors associated in this method with tunneling matrix elements of the phenomenological rotational Hamiltonian in the high barrier limit.

These phase factors govern the way in which the various real tunneling frequencies in the molecule constructively and/or destructively interfere in the Hamiltonian matrix elements and final energy expressions. Various mathematical approximations are involved in using the local IAM-like basis sets to obtain matrix elements; the full extent of the adverse effects of these approximations will not be known until an attempt to fit experimental data is carried out.

E. General Spectroscopy and Theory

1. Efficient Sampling Systems for the Fourier Transform Spectrometer (Wm. Bruce Olson)

A transfer optics system has been designed, and constructed for the coolable White cell made from our design by Prof. J. Bevan at Texas A&M Univ. Prof. Bevan also had made an evacuable chamber for the transfer optics. The utility of this system for use in the far infrared has been demonstrated.

A preliminary optical design using a single concave mirror has also been worked out for the transfer optics to couple the BOMEM FTIR spectrometer to an existing heat pipe for use in the far infrared. An important feature of this and the previous system is that a single concave mirror is used to accomplish two objectives. An image of the input aperture of the FTIR is placed at the entrance of the cell, and an image of the beamsplitter is placed on, and exactly fills, a back mirror of the White cell, or exactly fills the exit aperture of the heat pipe. Under these conditions a simple thin window, but no field lens is required at the input of the sample cell, in order to pass the maximum possible signal radiation, and the problem of a suitable optical material for a field lens is eliminated.

2. Diode Laser Measurements on Unstable Diatomic Molecular Species (A. G. Maki, G. A. Thompson, and A. Weber)

In an effort to study molecular species that are unstable in the gas phase under ordinary conditions, we have used a high temperature technique to measure the infrared spectrum of GeO, LiI, and LiD in the gas phase. These are the first resolved gas phase infrared measurements to be made of these species although the electronic and microwave spectra have been studied in the gas phase. The extent of the measurements is indicated in

Figure 2.16. which gives the range of vibrational and rotational levels covered by these measurements for $^{74}Ge^{16}O$ and $^{7}Li^{127}I$. All five isotopic germanium species of GeO have been measured in natural abundance as can be seen in Figure 2.17 which shows a portion of the measured spectrum. So far only the most abundant isotopic species of LiI and LiD have been observed.

To analyze measurements of this sort we have developed a non-linear least-squares fitting program to determine a set of Dunham potential coefficients that define the lower part of the potential well for the molecules under study. Most other workers use such measurements to determine directly a set of ro-vibrational constants that ignores the underlying concept of a potential well and therefore may be in conflict with any reasonable potential function.

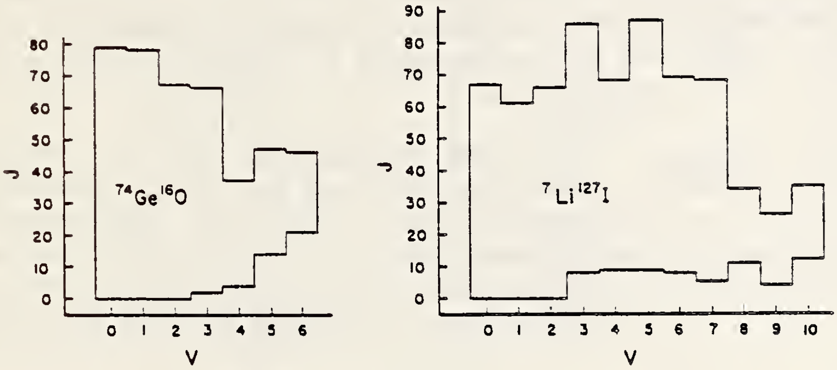


Fig. 2.16. Extent of data base for rotation-vibrational bands of GeO (left) and LiI (right) determined from infrared diode laser spectra. In these displays the vibrational states are depicted in strips one unit wide, and centered about the integral value of the vibrational quantum number v.

We believe that a more useful analysis uses the data to determine the potential function and then uses the potential function to determine a consistent set of ro-vibrational constants.

The problem with using ro-vibrational constants for calculations that represent an extrapolation outside the range of observations is that the constants are usually determined without restraining them to a physically meaningful model. Our way of determining the ro-vibrational constants gives them greater reliability for calculating levels and transitions outside the range of measurements because the underlying concept of a potential function restrains many of the higher order ro-vibrational constants to physically realistic values.

In the case of GeO all five measured isotopic species have been fit to a single potential function which can be used to calculate the observed transitions with an rms deviation of 17 MHz which we believe represents the accuracy of the measurements.

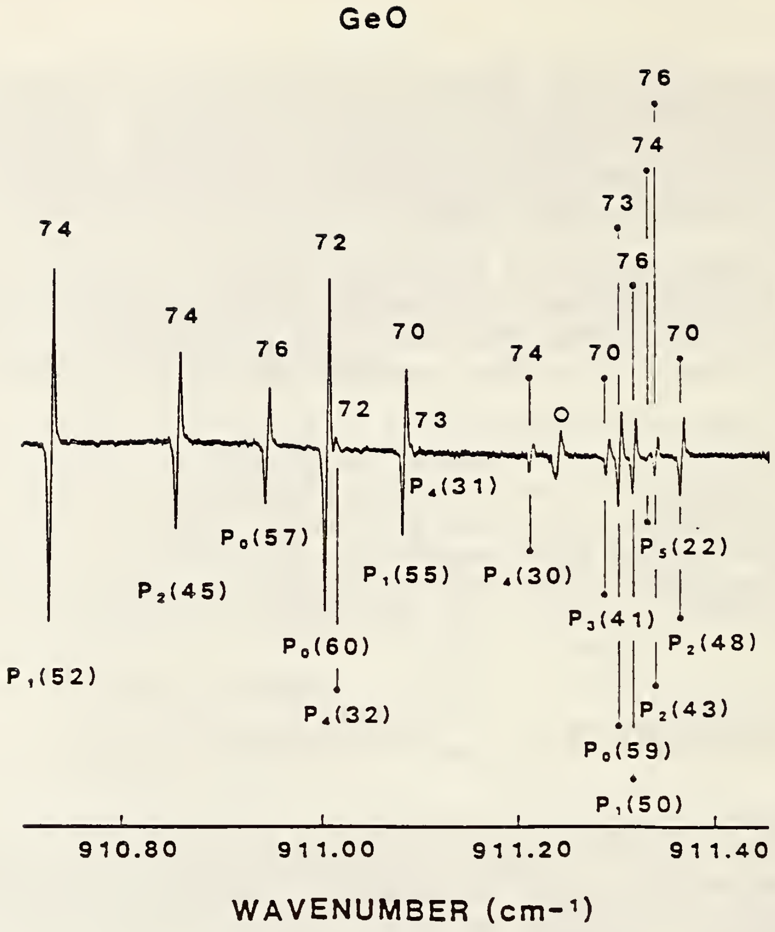


Fig. 2.17 Portion of the infrared diode laser absorption spectrum of GeO. Numbers in the top part identify the Ge-isotope. The assignments of the individual rotation-vibrations are given in the lower half; the subscripts label the vibrational state. The line marked with an open circle is due to an impurity.

The work on LiD is not yet finished. In the coming year we expect to also observe the spectrum of ^{6}LiD.

We have also been measuring transition frequencies and relative intensities for ClO. Since those measurements are of interest for atmospheric studies, they are described in section C on studies related to atmospheric chemistry.

3. Fourier Transform Raman Spectroscopy of H_2 and D_2 in Flames
(A. Weber and D. A. Jennings)

The successful demonstration of the use of a Fourier transform spectrometer to record Raman spectra of gases under high resolution was reported in last year's Annual Report. Together with Dr. J. W. Brault of the National Solar Observatory located at Kitt Peak, AZ, work on the high temperature spectra of H_2 and D_2 has been done with the 1-meter FTS instrument of the McMath Solar telescope at Kitt Peak.

Laboratory spectra of high rotational transitions in H_2 are important in astrophysics because they may be observable in hot stellar and interstellar sources, and have already been seen in quadrupole emission from the Orion molecular cloud.[1] The Orion emission lines are characteristic of an ~2000K rotational temperature. Infrared spectra of H_2 and D_2 at high temperatures are difficult to obtain in the laboratory because path lenghts of hundreds of meters are necessary to observe the quadrupole absorption. Vibration-rotation coefficients obtained from room temperature spectra cannot be extrapolated to the high-J lines observed in Orion to within the accuracies of the astronomical measurements.

Prompted by these considerations, we have recorded Raman spectra of high temperature molecular hydrogen and deuterium using a Fourier transform spectrometer. A diffusion flame source burning H_2 or D_2 in air was placed at the focal point of a multi-pass mirror system.[2] Figure 2.18 shows the pure rotation spectrum of D_2 obtained in this manner; the room temperature spectrum is shown for comparison.

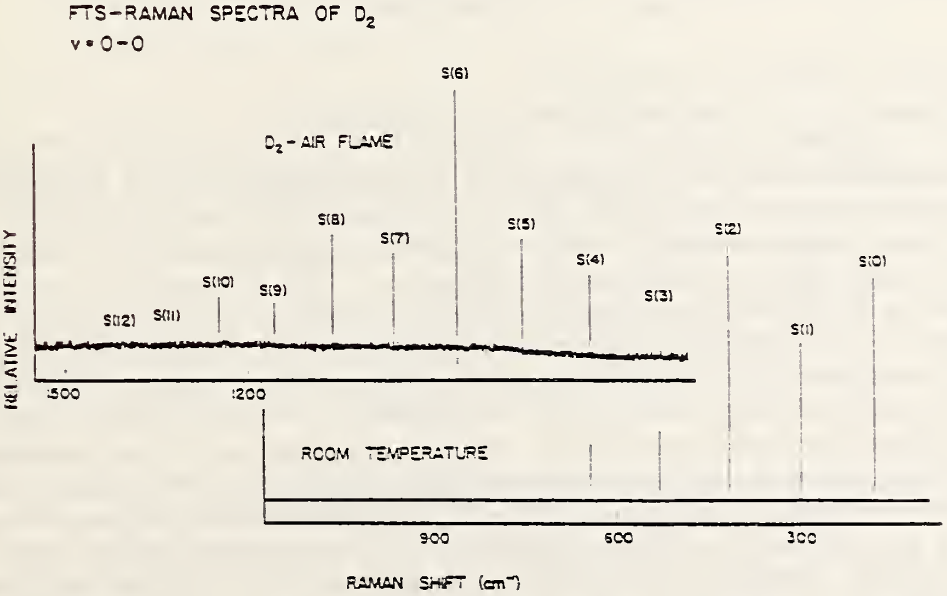


Fig. 2.18. Pure Rotational Raman Spectra of D_2 for a diffusion flame in air (top) and a stagnant gas at room temperature (bottom).

As expected the higher temperature spectrum (flame) shifts the intensity distribution toward higher J-values, with S(12) being the highest transition observed. The noisy and varying background in the high temperture spectrum is caused by the flame itself. Similar observations were made on H_2 for which both the v=0-0 and v=1-0 spectra were recorded to S(7) (v=0-0) and Q(5) (v=1-0) in the flame spectra. The data bases for the v=0-0 and v=1-0 transition of H_2 and D_2 have been extended through the inclusion of the Raman flame data. Improved ground state constants for D_2 are listed in Table 2.2.

Table 2.2 Ground State Parameters of D_2 (cm^{-1})

Constant	Flame + Room Temp.	Room Temp. Only
B_o	29.91371(44)	29.91439(40)
D_o	0.011527(22)	0.011599(19)
H_o	$6.84(40)\times10^{-6}$	$9.10(24)\times10^{-6}$
L_o	$-1.11(29)\times10^{-8}$	---
M_o	$3.09(69)\times10^{-11}$	---
ΔE_m	$\Delta E_6(J)$	$\Delta E_4(J)$

(1) R. F. Knacke and E. T. Young, Ap. J. (Letters) 249, L65 (1981).
(2) R. W. Hill, A. J. Mulac; and C. E. Hackett, Appl. Opt. 16, 2004 (1977).

4. Infrared Spectrum of Cyanogen
(A. Weber, W. J. Lafferty, and W. B. Olson)

Previous work on the high resolution infrared spectrum on C_2H_2 was described in last year's Annual Report. In that work the ν_3 and ν_5^1 fundamental bands were recorded with the BOMED DA3.002 Fourier transform spectrometer using only a 20cm absorption path. The ν_3 band was recorded at a pressure of 5 torr which caused noticable pressure broadening of the lines. In the present work a White cell (maximum path length 20 m) was employed to re-record the ν_3 band system, as well as to obtain spectra of the $\nu_1+\nu_5^1$, $\nu_3+\nu_4^1$, $\nu_1-\nu_5^1$, and $\nu_2-\nu_5^1$ combination and difference bands at an apodized resolution of 0.004 cm^{-1}. Because of the low lying fundamentals ν_4^1 and ν_5^1 these bands are accompanied by numerous hot bands which complicate the assignment process, but which yield precise values for the energy levels of the lower states. Figure 2.19 shows the region of the ν_3 band using a path length of 2.25m and a gas pressure of 1.51 torr. The OCS is present as an impurity in the gas sample. The $\nu_1-\nu_5^1$ band plus its hot bands is now present with a good signal to noise ratio. In the previous spectra only its Q-branch was visible, with very poor signal to noise. Similarily the ν_3 and $\nu_3+\nu_5^1-\nu_5^1$ bands of the isotopic species $^{13}C^{12}CN_2$, present in natural abundance, are observed in the present spectra. Extensive structure was observed in the $\nu_1+\nu_5^1$ and $\nu_3+\nu_4^1$ combination bands. The $\nu_1+\nu_5^1$ band contains an heretofore unreported perturbation. The $\nu_2-\nu_5^1$ band system near 610cm^{-1} was recorded for the first time under high resolution. This band is weak and, owing to the use

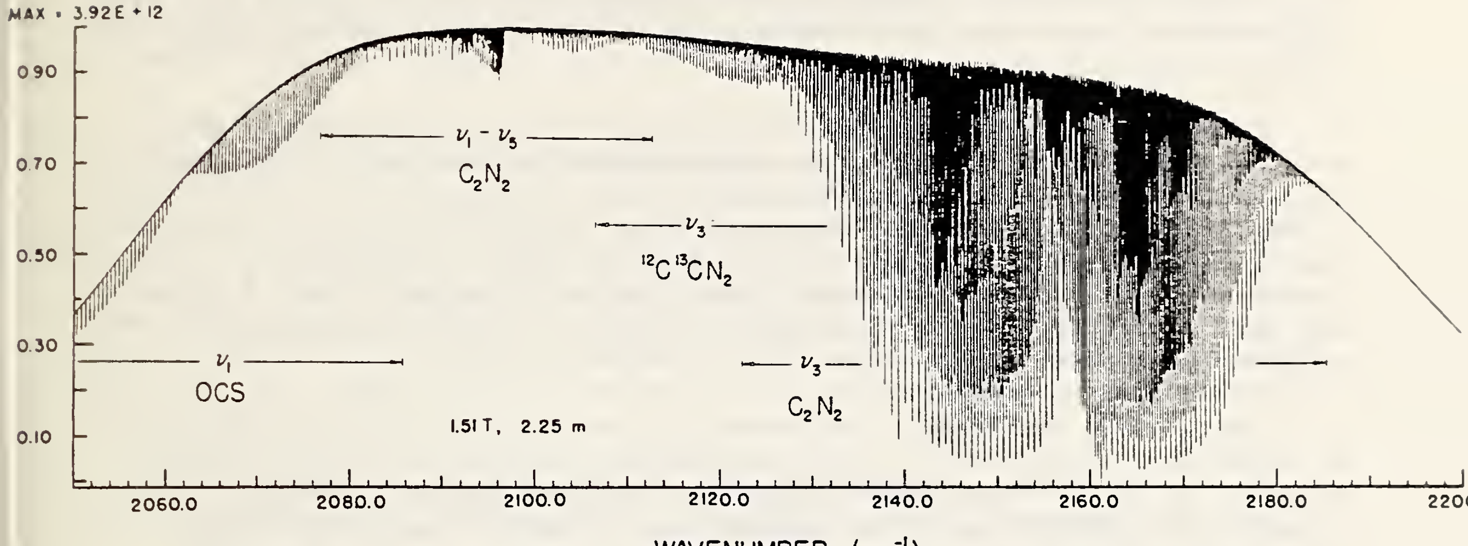


Fig. 2.19 Region of the ν_3-band of C_2N_2 recorded with the BOMEM DA3.002 Fourier transofrm spectrometer at a (opodized) resolution of 0.004 cm^{-1}. The spectrum is the result of 64 scans taken one a time of 5 h. 20 m.

of the less sensitive HgCdTe detector, a rather high pressure of 39.9 torr was necessary for its observation. The analyses of the various bands are well under way though the perturbation in the $\nu_1+\nu_5$ band remainds to be identified. The upper state of the $\nu_3+\nu_4^{\pm 1}+\nu_5^{\mp 1}-\nu_5^{1}$ band is split into a Σ_g^+ and a Σ_g^- component, both of which have been identified. This is only the second known case (the other being C_2H_2) in which a $\Sigma_g^- - \Pi_u$ transition has been observed and identified. Besides improved values for the constants of the ν_3, $\nu_1+\nu_5^1$ and $\nu_3+\nu_4^1$ band systems new results have been obtained for the $\nu_2-\nu_5^1$ system as well as for the ground state of $^{13}C^{12}CN_2$. The extensive data base of the combination and difference bands has also enabled us to obtain more accurate values for the frequencies of the ν_1 and ν_2 fundamentals. These fundamentals are of species Σ_g^+ and are thus only observable in the Raman spectrum. The present results are: $\nu_1=2330.4847(5)$ and $\nu_2=845.5965(15)$cm^{-1}. They are more accurate than the Raman results and will serve in the determination of a more accurate force field of cyanogen.

5. Fourier Transform IR Spectra of Monodeuterosilane

(Wm. B. Olson and R. W. Lovejoy)

Assignments in the vibrational bands ν_6, ν_3, ν_5, ν_2 and $2\nu_6$ have been greatly extended since last years report. Identification of perturbation allowed transitions with high values of the K quantum number in ν_3 and ν_5 has enabled for the first time a direct experimental determination of D_o^K and a smaller error (by a factor of 150) than that of our previous determiantion[1] of A_o.

We were unaware at the time of last year's report that another group of workers in Europe had taken the same spectra and had nearly completed the assignments. This group is headed by Prof. H. Bürger, Universität-Gesamthochschule, Wuppertal, West Germany. Since that group had access to computer software for fitting the three bending fundamentals, we (by agreement with Prof. Burger) abandoned work on these and have concentrated on the analysis of the ν_2 and $2\nu_6$ parallel and perpendicular bands.

The extreme weakness of the perpendicular component of $2\nu_6$ leads to no observable transitions in this band except those whose intensities are obtained by perturbations with ν_2 and the parallel component of $2\nu_6$. Several perturbations are observed, and about twenty transitions of $2\nu_6$ have ben assigned, but we do not yet have enough data for a reasonably good analysis, and the slow assignment and checking process is still in progress.

(1) Olson, W. B., and Lovejoy, R. W., J. Mol. Spectrosc. <u>66</u>, 314-330 (1977).

6. Far Infrared Spectrum of the Torsional Band of Hydrazine (N. Ohashi, W. J. Lafferty, and W. B. Olson)

Hydrazine has two large amplitude motions, an NH_2 wagging vibration (similar to the umbrella motion in NH_3), and the torsional vibration. Only recently have theoretical methods become available to treat the observed spectra[1], and they have been successfully used to fit the pure rotational microwave spectrum. While the ground state has large splittings arising from the inversion motion, torsional splittings in the ground state are quite small.

We have studied the torsional vibration of N_2H_4 where the torsional splitting contributions will be much larger than in the ground state spectrum in order to further test the theory, as well as to attempt to determine the barrier to internal rotation. The center of this band is at 376 cm^{-1}. It is a b-type band, and since the A rotational constant of the molecule is large, it covers a large portion of the spectrum from about 300 cm^{-1} to 450 cm^{-1}. The spectrum was recorded with the NBS BOMEM FTS spectrometer at a resolution of about 0.01 cm^{-1}.

Although the spectrum is somewhat complex due to the fact that each rovibrational transition is split into either four or six components (depending upon whether the lower state K of the transition is even or odd), and also because of overlapping by "hot band" transitions, we have been able to make a very satisfactory line assignment with the aid of combination differences calculated from ground state constants obtained in a recent microwave study.[2]

The assigned transitions were combined with the observed microwave data and fit using Hougen's Hamiltonian.[1] The inversion and torsional splittings of both the ground and torsional states were obtained. As expected, the torsional splitting in the vibrational state (1824 Mhz) was found to be many-fold larger than the torsional splitting in the ground state (5.8 MHz). However, a surprisingly large vibrational change in the inversion splitting was found. This splitting was determined to be 7976 MHz in the torsional state as compared to a splitting in the ground state of 16040 MHz. The height of the barrier to internal rotation was estimated to be 2100 ± 50 cm^{-1}.

(1) J. T. Hougen, J. Mol. Spectrosc. 89, 296 (1981).
(2) S. Tsunekawa, T. Kojima and J. T. Hougen, J. Mol. Spectrosc. 95, 133 (1982).

7. The Torsional-Wagging Tunneling Problem and the Torsional-Wagging-Rotational Problem in Hydrazine
(N. Ohashi and J. T. Hougen)

Results derived previously for the rotational levels of the eight-framework and three-large-amplitude vibrational problem in N_2H_4, using a tunneling formalism based on a treatment of the vibration-rotation problem as a whole, were rederived in a much simpler fashion, using a tunneling formalism based on separate treatment of the vibrational and rotational problems. The present formalism is thus much more akin to the usual vibration-rotation formalism, and the origins of the various contributions to the vibration-rotation energy levels can be understood relatively easily. It is convenient here, as earlier, to make extensive use of permutation-inversion and extended-group (double-group) ideas, but it is necessary in the present treatment to consider tunneling between 16 minima in molecular coordinate space, i.e. between a number of minima which is twice the number of nonsuperimposible molecular frameworks that can actually be constructed for N_2H_4.

8. The Use of Extended Permutation-Inversion Groups for Constructing Hyperfine Hamiltonians for Symmetric-Top High-Barrier Internal Rotor Molecules like H_3C-SiH_3
(J. T. Hougen)

The m-fold extended group $G_{18}^{(m)}$, corresponding to the permutation-inversion group G_{18} for molecules like H_3C-SiH_3, has been obtained. In this extended group, m is the smallest integer for which mρ is also an "integer," where ρ is the usual ratio of the moment of inertia of the top about the rotational A axis to the moment of inertia of the molecule about the A axis. The extended group has 18m elements, divided into (9m+3)/2 or (9m+6)/2 classes, for odd and even values of m, respectively. Using this extended group, it is possible to assign definite symmetry species in an internal-axis-method (IAM) treatment to laboratory-fixed, molecule-fixed, top-fixed and frame-fixed projections of vector operators like the rotational angular momentum and the nuclear spin angular momenta. Thus, it is possible to express the spin-rotation and spin-spin contributions to the hyperfine interaction operator in terms of rotational angular momentum components, nuclear spin angular momentum components, and functions of the torsional angle, all of which have known symmetry species and selection rules in the IAM basis set. Using a hyperfine Hamiltonian constructed from these considerations, it is possible to understand the large variations in magnitude of some observed hyperfine couplings in recent molecular beam studies of symmetric top internal rotor molecules.

9. Improved Least Squares Determination of Potential Energy Surfaces from Spectroscopic Data

(C. Leubner and J. T. Hougen)

The value of a knowledge of potential energy surfaces for the understanding of the overall properties and behavior of a molecule can hardly be overestimated. With the exception of the simplest molecules, it can safely be stated that currently it is the observed spectrum that contains the most complete - albeit indirect - information on the molecular force field. As a consequence, much effort has been expended on the retrieval of potential energy surfaces from spectroscopic data.

Vidal and coworkers have shown in a number of applications that such a program - termed "Inverted Perturbation Approach (IPA)" and reviewed in (1) - can indeed be carried quite far in the diatomic case, where a number of problems are absent that become crucial in the polyatomic case. These qualitative differences preclude a straightforward, similarly successful, generalization of the IPA to the determination of potential energy surfaces. However, the main ingredients of the IPA have been used by the workers in the field of polyatomic molecules with more moderate results. Chen et al. (2) recently showed that none of the surfaces determined by these methods for the water molecule agrees with the observations to within spectroscopic accuracy.

However, it is possible to identify three promising areas for the improvement of the conventional approach. First of all, the variational character of the IPA can be combined with the necessarily variational calculation of the eigenvalues of the Schroedinger equation for a polyatomic molecule to give a very compactly formulated optimization problem, the solution of which would, in principle, immediately give the optimum potential energy surface corresponding to the measured energy eigenvalues in a least squares sense.

Secondly, this optimization problem involves as a crucial step a sufficiently accurate determination of the ro-vibrational eigenvalues of the Hamiltonian of the molecule under study. Chen and coworkers (2) have reported encouraging results with the conventional expansion of the eigenstates in products of "rotationless vibrational" wavefunctions and symmetric top functions. Alternatively, one could invoke so-called "distributed Gaussian bases", as recently introduced into the nuclear molecular problem by Hamilton and Light (3), which, after all, have proved superior to all other basis sets in the electronic molecular problem, where they are now exclusively used.

Thirdly, one requires a sufficiently flexible representation of the potential energy surface. As an improvement over the conventional Taylor series expansion in suitably chosen coordinates around the equilibrium point of the surface, we propose to supplement this by a Spline approximation (4) that adequately incorporates the full symmetry of the problem. The parameters of this Spline approximation are then to be optimized in a least squares sense with respect to the observed spectrum.

An investigation that focuses on these three areas of improvement is currently under way in collaboration with M. Wolfsberg of the Department of Chemistry, University of California, Irvine, CA.

(1) C. R. Vidal: Accurate determination of potential energy curves (preprint) 1985.

(2) C.-L. Chen, B. Maessen, and M. Wolfsberg: Variational calculations of rotational-vibrational energy levels of water (preprint) 1985.

(3) I. P. Hamilton and J. C. Light: On distributed Gaussian bases for multi-dimensional vibrational problems (preprint) 1985.

(4) J. H. Ahlberg, E. N. Nilson, and J. L. Walsh: The Theory of Splines and their applications (Academic: New York 1967).

10. The Proper Choice of the Lagrangian for a Relativistic Particle in External Fields

(C. Leubner)

It is an unsatisfactory feature of the educational literature that renowned authors propose apparently conflicting prescriptions for the construction of an appropriate Lagrangian to describe the interaction of a relativistic point particle with external fields. The point where opinions sharply differ is whether, in the case where the independent parameter is to be the proper time of the particle, the equations of motion should be derived from Hamilton's principle by constrained or unconstrained variation. Therefore, it is shown that there exists a unifying point of view, which allows a consistent derivation of all these seemingly unrelated or even incompatible Lagrangians, which completely clarifies their status and interrelations, and, moreover, provides a sound basis for discussing coherently a multitude of related issues that have emerged in the literature in an often obscure and even misconstrued manner. The results are to appear in the European Journal of Physics.

11. A Note on the Uniform Asymptotic Expansion of Integrals with Coalescing End Point and Saddle points
(C. Leubner)

Together with H. Ritsch of the University of Innsbruck we have introduced a new method for the uniform asymptotic expansion of certain types of contour integrals, one of whose critical points is an end-point of the interval of integration. The method, which is alternative to Bleistein's, has been tested numerically by way of a non-trivial physical example. The results will be published in Journal of Physics A: Mathematical and General.

12. Generalized Stirling Approximations to N!
(C. Leubner)

Generalized asymptotic approximations to $\Gamma(x+1)$, which contain an arbitrary parameter, are derived both from the integral representation of the Gamma function without assuming a knowledge of the Stirling series, and through elementary rearrangements of the Stirling series. By optimizing the arbitrary parameter according to appropriate criteria, several known Stirling-like approximations are recovered in a unifying way. These are as compact as but numerically superior to the standard Stirling approximations, and are meaningful on intervals that even include parts of the negative x-axis. It is pointed out that these results - arrived at by elementary but generally applicable asymptotic techniques - can be exploited in physics teaching to demonstrate the power and utility of asymptotic methods in the analysis of a variety of physics problems. The results are to appear in the European Journal of Physics.

13. Accurate Emission Spectra from Planar Strong Field Wigglers with Arbitrary Field Variation
(C. Leubner)

In collaborative work with H. Ritsch of the University of Innsbruck we showed that the spectral and angular distribution of the single particle wiggler signal can be conveniently evaluated by asymptotic complex contour integration, if the wiggler magnetic field is an arbitrary function of only the coordinate along the wiggler axis. The method is efficient and accurate, especially in the most interesting range of frequencies around the characteristic frequency of the wiggler, where for strong field wigglers the conventional procedure encounters serious computational difficulties. The method exhibits promise for extensions in various directions of experimental interest. The results will appear in Nuclear Instruments and Methods in Physics Research.

14. Dynamical symmetries and equivalent Lagrangians for one-dimensional systems

(C. Leubner)

In collaboration with M. A. M. Marte of the University of Innsbruck we have shown that for one-dimensional Newtonian equations of motion a surjective mapping from the set of dynamical symmetries onto the set of equivalent first-order Lagrangians can be established, where - up to an integration - the Lagrangian associated with a particular dynamical symmetry is explicitly given.

15. On the Relationship of Normal Modes to Local Modes

(I. M. Mills)

A simple model for the effective vibrational Hamiltonian of the XH stretching vibrations in H_2O, NH_3 and CH_4 is considered, based on a Morse potential function for the bond stretches plus potential and kinetic energy coupling between pairs of bond oscillators. It is shown that this model can be set up as a matrix in local mode basis functions, or as a matrix in normal mode basis functions, leading to identical results. The energy levels obtained exhibit normal mode patterns at low vibrational excitation, and local mode patterns at high excitation. When the Hamiltonian is set up in the normal mode basis it is shown that Darling-Dennison resonances must be included, and simple relations are found to exist between the x_{rs}, g_{tt}, and K_{rrss} anharmonic constants (where the Darling-Dennison coefficients are denoted K) due to their contributions from Morse anharmonicity in the bond stretches. The importance of the Darling-Dennison resonances is stressed. The relationship of the two alternative representations of this local mode/normal mode model are investigated, and the potential uses and limitations of the model are discussed.

F. Future Plans

1. Calibration and Data Center Activities

During the coming year we will devote a major effort to the completion of "Microwave Spectral Tables III. Hydrocarbons". In conjunction with this manuscript we will produce a magnetic tape of the combined measured and calculated spectra which is too extensive to publish in printed form. Eventually we will combine this data with the existing files on diatomic and the triatomic species to form the initial spectral line atlas. We will also begin extracting and evaluating data on a new group of organic species. Hydrocarbons containing the heteroatoms, oxygen or nitrogen will be selected for the next review in this series after we examine our files of literature references on these compounds.

In addition to the general search of the microwave literature we will continue searching the astronomy literature for interstellar molecular observations. Due to the rapid increase in new data during the 5 years between revision of the Recommended Rest Frequency publication, we plan to up-date the computer data files on a continuing basis in order to publish subsequent revisions in a shorter time frame. Publication of revisions every two years is the current plan.

Further work is planned in collaboration with NBS/Boulder on developing infrared calibration frequency standards. New heterodyne measurements on hot bands of N_2O will be performed to extend the present calibration tables into the 2800 cm^{-1} region. Preliminary results from this work have already been provided to workers at NBS in support of their work on NO_2. Similar work will also be done on the $\nu_3+2\nu_2$ band of OCS near 1900 cm^{-1} as well as on the fundamental band of NO.

2. Spectroscopy for Environmental Studies

Work on the spectroscopy of molecules of importance in the chemistry of the earth's atmosphere will continue in support of NASA and CMA programs during the coming year. Intensity and frequency measurements will be made on ClO. New infrared diode laser measurements on the spectrum of nitric acid will be made and combined with existing microwave and infrared data to develop an atlas of transition frequencies and intensities for the range 1680-1740 cm^{-1}. Work will also be done on the ν_5 and $2\nu_9$ bands of nitric acid. The analysis of these bands, which span the region from 850 to 930 cm^{-1}, requires the inclusion of a perturbation due to a $\Delta K=\pm 2$ interaction. Similarly, although the ν_3 and ν_4 bands of nitric acid have been assigned, they are found to be perturbed and are still to be satisfactorily analyzed.

The work on the collisional line-shapes of HF and HCl undertaken in support of the NASA project HALOE will be concluded during the coming year. We will examine the effects of collisions on the electronic fine structure of NO as well as for overlapping Q-branch transitions, and make precise frequency measurements on the fundamental band in collaboration with the NBS/Boulder group.

3. Spectroscopy of Hydrogen-Bonded and van der Waals Complexes

As first reported in the report for FY82 the High Resolution Group has embarked on a program of investigating the spectra of weakly bond molecular complexes and the present report indicates the expansion of these efforts. During the coming year we plan to continue to do tunable infrared laser spectroscopy of hydrogen bonded and van der Waals molecules. Using a coolable White cell with the gas under thermal equilibrium conditions investigations of hydrogen-halide complexes will be continued with the difference frequency laser spectrometer while the diode laser spectrometer will be used in the study of heavier complexes (e.g. NO-dimer) as well as for the study of the far-infrared van der Waals modes of HX complexes.

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.

The good performance of the initial version of our pulsed-beam spherical Fabry-Perot cavity microwave spectrometer has prompted us to improve the sensitivity and efficiency of this instrument. Modifications of the hardware in the signal detection and digitization systems coupled with streamlined software will allow more rapid pulsing. Modifications are also planned to improve the search efficiency of the instrument by computer control of a number of current manually performed operations. With these modifications we expect a five-fold improvement in the spectral search over the present value of 100 MHz/day.

Several techniques are under investigation for producing pulsed beams of non-volatile materials e.g. thermo-spray and laser ablation methods, to broaden the range of studies possible with this spectrometer.

In addition to these instrumental improvements planned during the coming year we will engage in spectral studies of hydrogen-bonded species as well as van der Waals complexes. Several of these planned microwave investigations will be carried out in conjunction with the infrared studies done in the group.

The experimental studies planned for next year will be complemented by theoretical investigations. In particular work will continue on the problem of the water dimer.

4. General Spectroscopy

Several projects are planned in the realm of large amplitude motions such as the study of the torsional band of methyl alcohol and the spectrum of methyl amine. These projects will serve to further test the Hamiltonian models for rotation-vibration spectra for the case of large amplitude internal motions.

3. LASER PHOTOCHEMISTRY GROUP

D. F. R. Burgess, Jr., M. P. Casassa, R. R. Cavanagh, L. B. Elwell,
E. J. Heilweil, M. E. Jacox, D. S. King, D. A. Mantell, J. C. Mialocq,
J. Perry, J. C. Stephenson, and A. M. Woodward

A. Introduction

B. Condensed Phase Energy Transfer

1. T_1 (Vibrational Energy Relaxation) times for vibrations on surfaces
2. T_1 times for vibrations in liquids
3. T_1 for vibrations in solids
4. T_2 (Vibrational dephasing) times for vibrations in liquids

C. Desorption of Molecules from Surfaces

D. Dynamics of van der Waals Molecules

E. Matrix Isolation Spectroscopy

1. Fluorine-Atom Reactions
2. Excited Rare-Gas Atom Reaction
3. Vibrational and Electronic Energy Levels of Transient Molecules
4. Reaction Intermediates in the Decomposition of Energetic Materials

F. Future Plans

A. Introduction

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.

The following staff changes have occurred in the year since July 1984. The 1984 annual report mentioned five post doctoral fellows working in this group. One of them (Woodward) remains at NBS as an NRC post-doc. Two (Perry, Mantell) left NBS to take permanent jobs in the private sector. Two (Heilweil and Casassa) agreed to join the Molecular Spectroscopy Division staff. Don Burgess (post-doc, Div. 541) came to NBS in January 1985 to study thermal and laser-induced desorption of molecules from surfaces. A visiting senior scientist, Dr. Jean-Claude Mialocq from CNRS (Saclay, France), spent eleven months on sabbatical at NBS where he did picosecond photochemistry and pulse radiolysis experiments.

B. Condensed Phase Energy Transfer

(M. P. Casassa, R. R. Cavanagh, L. B. Elwell, E. J. Heilweil, J. Perry, J. C. Stephenson, A. M. Woodward)

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.

For simplicity, the experimental results on VET have been organized in four sections: T_1 times for surface vibrations; T_1 for vibrations in liquids; T_1 for vibrations in solids; and T_2 times for vibrations in liquids. This distinction among studies of VET done in various phases of matter is not fundamental. At least for the non-metallic systems we have studied so far, VET is caused by short range forces, and the similarity of results for the same vibration in different phases is striking. This work is supported by AFOSR.

1. T_1 (Vibrational Energy Relaxation) times for vibrations on surfaces

We used an infrared pump/probe method to do 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.

Our initial measurements were on the surface hydroxyls (OH) bound to dispersions of colloidal fumed silica (Degussa Aerosil 200, 120 A diameter particles, 200 m^2/gm surface area). We have since measured T_1 for several different surface vibrations at the solid-vacuum interface and at the solid-liquid interface. We explain the method for the OH-stretch (ν=3750 cm^{-1}) vibration; the same technique was used for all the vibrations we have studied. The surface hydroxyl $v=0\rightarrow1$ transition at the SiO_2-vacuum interface was excited with a strong picosecond IR pulse which transferred up to 10 percent of the hydroxyls from the v=0 to v=1 level. Due to anharmonicity, OH (v=1) does not absorb at the pump frequency, so excitation causes a transient increase in sample transmission, T. As population relaxes, the sample transmission returns to its equilibrium value, T_0; $\ln(T/T_0)$ is proportional to OH (v=1) population. Recovery of sample transmission was monitored by a weak, time-delayed probe pulse derived from the saturating pulse and a variable optical delay. At each time delay (t_D), the probe pulse transmission was measured to 0.3 percent accuracy with pump excitation and with the pump blocked using a dual pyroelectric detector energy ratiometer. A typical data run is shown in Figure 3.1. The population in OH (v=1) decreases exponentially with a characteristic decay time of T_1 = 216 ps.

The picosecond apparatus used in this investigation was based on a modelocked Nd^{+3}:YAG laser. Single 1.06 µm pulses of ~35 mJ and 10 Hz repetition rate pumped a chain of three $LiNbO_3$ crystals (OPA) to parametrically generate tunable infrared picosecond radiation, which had a spectral bandwidth of 15 cm^{-1} FWHM, duration of 20 ps FWHM, and delivered about 400 µJ of pump energy to the sample.

The room temperature results for several surface vibrations, at the solid-vacuum and solid-liquid interface are given in Table 3.1. For all these systems, the bulk substrate SiO_2 was the same (fundamental substrate modes are less than 1200 cm^{-1}). The T_1 lifetime for OH(v=1) on SiO_2 in vacuum corresponds to roughly 2 x 10^4 vibrational periods. In various solvents the OH(v=1) T_1 lifetime decreases as the highest solvent fundamental vibrational mode frequencies approach the 3700 cm^{-1} OH frequency. This is particularly evident for CH-stretch (~3000 cm^{-1}) containing molecules such as CH_2Cl_2 and C_6H_6 where T_1 = 102 ± 20 ps and 87 ± 30 ps, respectively.

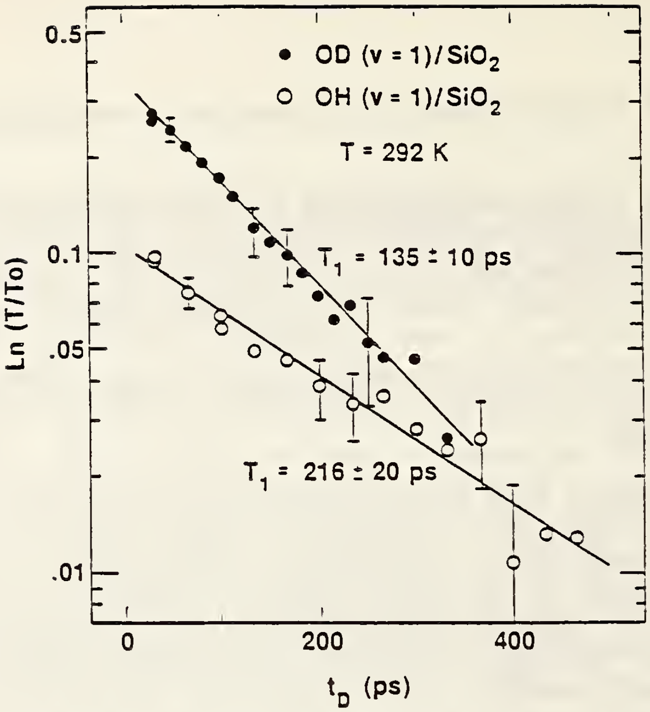


Fig. 3.1. T_1 decay for isolated surface OD(v=1) and OH(v=1) on a dried evacuated SiO_2 disk at T=293K. The exponential recovery of transmission as a function of probe delay (t_D) yields a lifetime of T_1 = 135 ± 10 ps for OD(v=1) and T_1 = 216 ± 20 ps (1σ) for OH(v=1) from a least squares fit.

In the presence of adsorbed H_2O, which possesses a broad, partially overlapping OH absorption with SiOH, T_1 reduces even further to ~56 ps. In this case, direct V-V transfer from the surface OH to adsorbed water may participate in the deactivation process.

Insight into vibrational energy transfer at surfaces may be gained by studying other species bound to the silica substrate. In this way the potential accepting modes of the bulk material remain unchanged while the adsorbate local modes and adsorbate-substrate coupling are modified. The simplest substitution for the OH group is isotopic exchange to OD. In this case T_1 is reduced from 220 ps for SiOH to 150 ps for SiOD (as pressed disks in vacuum). Decay of the lower energy OD quantum into the substrate was expected to require fewer lattice quantum transitions than for OH (i.e., $\Delta v \geq 3$ vs. $\Delta v \geq 4$) and result in faster decay rate. However, the observed isotope effect was smaller than anticipated.

The hydroxyl T_1 lifetime for BOH modified silica (ν_{OH} ~ 3700 cm^{-1}) in vacuum or CCl_4 is found to be ~70 ps. Since the boron mass and coordination to the surface oxygens is different from silicon, changes in the local site bending and stretching frequencies must occur. This surface modification is found to substantially alter the relaxation lifetime of the surface OH species. Both NH-stretching modes of $-NH_2$ were found to saturate to the same extent ($\Delta T/T$ ~ 5%) although time-resolved measurements produced an instrumental pulsewidth-limited response. While precise T_1 values could not be deduced from these results, the two modes apparently exchange population rapidly and have comparable lifetimes ($\leq$20 ps). Attempts to saturate the CH-stretching transitions of -OCH$_3$ were unsuccessful, however. This may imply very fast vibrational relaxation ($T_1 < 5$ ps) for the CH-stretches of chemisorbed methoxy. The above results for adsorbates on SiO$_2$ suggest that increasing the complexity of adsorbate vibrational level structure leads to more rapid vibrational energy relaxation at the silica surface.

We have not yet directly measured where the energy goes when it leaves the initially excited high frequency vibrations. To obtain indirect evidence concerning the effective lattice accepting modes, we studied the isotope and temperature dependence of OH(v=1) relaxation at the SiO$_2$-vacuum interface. The results are shown in Figure 3.2. The solid lines show fits to the data using the theory of multiphonon relaxation in solids. For OH, the observed T dependence is well fit by a n=4 quantum process, i.e. $\nu_{OH}(3750) \rightarrow 4\nu_{lattice}$. For OD the data are best fit by n=3, i.e. ν_{OD} $(2760) \rightarrow 3\nu_{lattice}$.

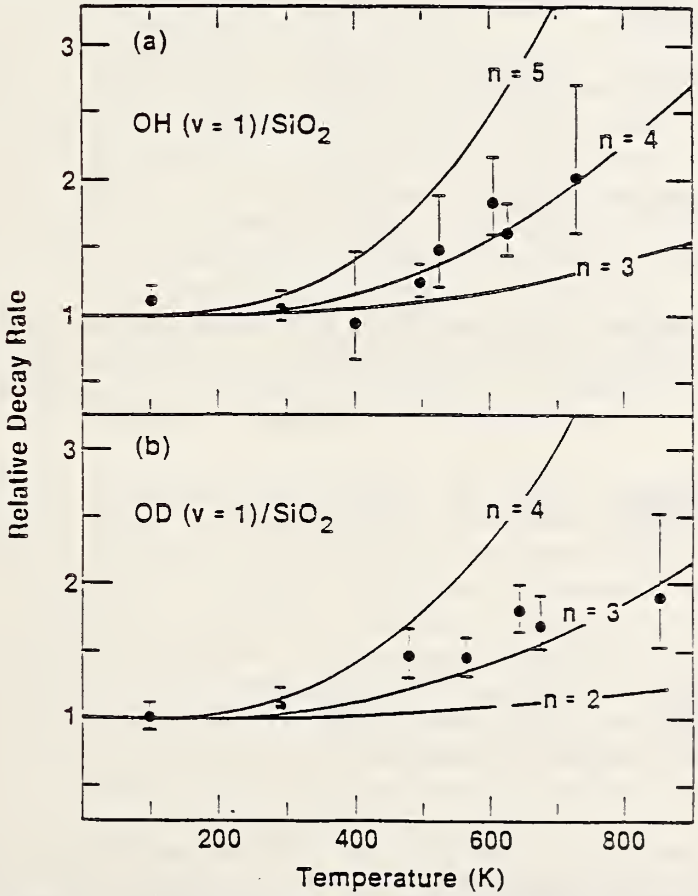


Fig. 3.2 Decay rates, T_1^{-1}, for OH(v=1) and OD(v=1) on a dried evacuated SiO$_2$ disk as a function of temperature T. Rates have been normalized by dividing the OD rates by 1/149 ps = 6.7×10^9 s^{-1}, and the OH rates by 1/220 ps = 4.5×10^9 s^{-1}. Error bars give the 1σ uncertainty in rate. The solid curves give the relative multiphonon relaxation rates vs. T for an n-phonon process (see text).

Table 3.1: T_1 vibrational decay times at room temperature for the various adsorbate/silica systems studied.

System	$\nu(cm^{-1})$	T_1(ps)	$k(10^9\ s^{-1})$	$k'(10^9\ s^{-1})^a$	Notes
SiOH/vacuum	ν_{OH}=3750	220±20	4.9	-	Pressed SiO_2 disk
SiOH/CCl_4	ν_{OH}=3690	159±16	6.3	1.4	Dry SiO_2 dispersion
SiOH/CF_2Br_2	ν_{OH}=3690	140+30	7.1	2.2	"
SiOH/CH_2Cl_2	ν_{OH}=3660	102±20	9.8	4.9	"
SiOH/C_6H_6	ν_{OH}=3625	87±30	11.0	6.1	"
SiOH/C_6D_6	ν_{OH}=3625	80±30	12.0	7.1	"
SiOH/H_2O/CCl_4	ν_{OH}=3690	56±10	18.0	13.0	SiOH T_1, ~5H_2O/100Å^2 physisorbed
SiOD/vacuum	ν_{OD}=2760	155±16	6.5	-	OD T_1 with 67% OH replaced by OD
BOH/vacuum BOH/CCl_4	ν_{OH}=3700	~70	~14.3	-	Early decay time; long time component present
$SiNH_2$/vacuum $SiNH_2$/CCl_4	ν_{NH}=3460 3520	$\lesssim$20	>50	-	Pulsewidth limited signal, ΔT/T ~5% for both stretches
$SiOCH_3$/vacuum	ν=2860 3000	<5(?)	>280(?)	-	No pulse saturation observed for any CH-stretching mode

[a] $k' = k - k_{vacuum}$

Acceptor mode frequencies compatible with this simple theory are also consistent with the known frequencies of modes spatially near and hence likely to be coupled to the surface OH(v=1). For example, the Si-OH stretch occurs at 970 cm^{-1}, the Si-O-H bend at 795 cm^{-1}, and Si-O stretching vibrations produce broad maxima at 800 and 1100 cm^{-1} in the vitreous silica phonon spectrum. The temperature dependence of the multiphonon theory is inconsistent with energy going to the surface Si-OH torsion vibration at 380 cm^{-1} (or to SiOD at ω_i = 270 cm^{-1}). The n=4 process for OH(v=1) and the n=3 process for OD(v=1) are in fact the lowest order processes possible, in keeping with the propensity rule that the most probable relaxation path will require the fewest simultaneous changes of vibrational quantum numbers.

The observation that OD on the surface relaxes faster than OH is qualitatively consistent with the expected increase of T_1 with increasing energy gap between the excited level and the frequency of the accepting modes. Multiphonon theories give the low T rate, $\Upsilon(0)$, as $\Upsilon(0) = a\exp(-b\omega)$ or $\Upsilon(0) = a(\varepsilon)^n$ where ω is the OH or OD frequency, n the order of the process, and the constants a, b, and ε ($\varepsilon < 1$) depend on molecular structure. However, it is surprising that the increase is only a factor of 1.5 (220 ps OH vs. 150 ps OD; ε = .68) when the energy difference is 1000 cm^{-1}. For comparison, measurements of the spin-orbit relaxation of ions in crystals give values of ε in the range 0.037 to 0.2 (i.e., the rate for an n phonon decay is 5 to 27 times faster than an n + 1 phonon decay in the same solid). We used a simple multiphonon relaxation theory to estimate the relative rates for a 3 phonon (OD) and 4 phonon (OH) relaxation of SiO_2. If the accepting modes (ω_i = 930 cm^{-1}) are the same, theory predicts $\Upsilon(0)$ for OD should be 13 times $\Upsilon(0)$ for OH (ε = .077). Although theoretical estimates of the anharmonic coupling strength, and hence of ε, are uncertain, it seems difficult to reconcile the multiphonon theory to both the isotope and temperature dependence.

In addition to the multiphonon theory, we have considered other mechanisms of VET for these surface vibrations. The damping of vibrational energy is <u>not</u> due to coupling to an image dipole formed in the substrate, nor is damping by electron hole pair formation possible for vibrations on a dielectric like SiO_2. Förster energy transfer (site hopping) is not important because of the small transition dipole moments (μ_{OH} = .035 D) and sparse adsorbate density ($\lesssim$ four OH/100Å^2 surface). For molecules like CCl_4 and CF_2Br_2, which have only low frequency vibrations, VET to the solvents is unimportant, although the internal high frequency modes of solvents like C_6H_6 may accept some of the energy.

Any theoretical approach to VET for vibrators on these dielectric surfaces must also take account of the data available for VET in solids and in liquids. Perhaps molecular dynamics simulations and classical trajectory studies will provide a consistent method of understanding the observed T_1 values. Certainly a direct measurement of the pathways (i.e. accepting modes) of VET will be of crucial importance to further the understanding of this subject (c.f. Future Plans).

Spectral linewidths observed in surface vibrational spectroscopy have sometimes been interpreted as T_1 uncertainty broadening. However, the width of the absorption features on silica surfaces must arise from site inhomogeneities or other dephasing processes, since the linewidths corresponding to T_1 are 200 to 2000 smaller than observed. Note that similar remarks pertain to T_1 vs spectral linewidths for the solids and liquids described in the next two sections.

2. T_1 times for vibrations in liquids

Although there have been thousands of measurements of VET rate constants for gas phase molecules where relaxation is caused by bimolecular collisions, there is very little information available ($\lesssim$ 20 measurements) about T_1 times in room temperature liquids.

Over the past nine years, picosecond laser techniques have been used by several research groups (most notably Laubereau, Kaiser, et al., and Chesnoy and Ricard) to measure vibrational energy relaxation times for particular vibrational modes in room temperature liquids. Chesnoy and Ricard measured T_1 for neat liquids of the simple diatomics HCl, DCl, HBr, and DBr. They found that the liquid phase relaxation rate constants were comparable to gas phase rate constants when corrections for dimer formation in the liquids were taken into account.

Kaiser and Laubereau (KL) measured T_1 for the stretching vibrations ($\nu_{CH} \approx 3000\ cm^{-1}$) of eleven different hydrocarbons in solution (mostly dilute in CCl_4). They found T_1 varying from < 2 ps (C_2H_2, CCl_3H) to 100 ps (CH_3CCl_3). The dependence of T_1 on molecular complexity was surprising (i.e. why should a simple molecule with only one high frequency mode like CCl_3H relax rapidly while complicated molecules like acetone or trichloroethane relax 50 times slower?).

We have recently measured T_1 for the OH and OD stretching vibrations of several alcohol and silanol molecules in dilute room temperature CCl_4 solution using the same experimental technique as for the surface studies. In part these experiments were done for comparison to the results of KL. Of particular significance to our program is the comparison between T_1 for vibrations such as OH, OD, and NH_2 bound to the surface of a dielectric such as SiO_2, and T_1 for these same functional groups attached to a small molecule (dissolved in a liquid like CCl_4 which has vibrational frequencies comparable to those of SiO_2). If coupling to nearest neighbor vibrational motions determines the VET rates, then those small molecules may exhibit similar lifetimes to the surface systems.

The results we have obtained to date are shown in Table 3.2. T_1 times for the OH (~3690 cm^{-1}) and OD (~2720 cm^{-1}) stretching vibrations bound to the Si atoms of silanols (in CCl_4) are long. The T_1 values are similar to those for OH and OD bound to the Si atoms on a silica surface either at

Table 3.2 Vibrational relaxation times for OH(v=1) and OD(v=1) bonds of alcohols and silanols dilute in CCl_4 at T = 295K.

Alcohols	T_1(ps)		Silanols	T_1(ps)
Me_3COH	<15	$\longleftrightarrow$	Me_3SiOH	205
Me_3COD	<15	$\longleftrightarrow$	Me_3SiOD	245
Et_3COH	<15	$\longleftrightarrow$	Et_3SiOH	185
Et_3COD	<20	$\longleftrightarrow$	Et_3SiOD	224
ϕOD	<15		ϕ_3SiOH	206
C_6F_5OD	<15		ϕ_3SiOD	292
CH_3OH	<30		$\phi_2Si(OH)_2$	85
CD_3OH	73			
CH_3OD	52		$\phi_2Si(OD)_2$	134
CD_3OD	79			
C_2H_5OH	70			

Accuracy ±20%

the vacuum interface or interacting with liquid CCl_4. For the surface species in vacuum, OD relaxes 50% faster than OH; for the liquid silanols the OH relaxation rate is systematically slightly faster than the OD rate.

The relaxation rates for OH (~3620 cm^{-1}) and OD (~2680 cm^{-1}) stretches in alcohols are much faster than for the corresponding silanols. For most alcohols T_1 was too fast for us to measure accurately ($T_1 \leq 15$ ps); only for deuterated methanols and ethanol (OH) was T_1 long enough to be determined. For the four instances where we studied both silanols and the corresponding carbinols (i.e. Si substituted for central C), T_1 is at least twelve times shorter for the OH or OD groups when bound to C than when bound to Si. We are presently trying to interpret these results in terms of coupling to specific adjacent vibrational modes and determine if these rates relate to the chemical properties of these molecules.

All the T_1 results to date have been obtained with the one color IR pump/probe method. With the aid of a new low f-number Raman spectrometer (acquired in August, 1985), we hope to do further experiments on VET in liquids, using the technique of IR vibrational excitation followed by spontaneous anti-Stokes Raman scattering (SPARS) probing (with harmonics of the Nd-YAG) of population in particular vibrational levels of these and other systems. For example, if we probe the OH, NH, or OD vibrations initially populated by the IR pulse, then we should obtain the same T_1 values deduced from the IR probe experiments. This will be an independent verification of these results. Of more importance, the SPARS experiments should permit us to identify the pathways of energy transfer (i.e., what are the lower frequency accepting modes) during the relaxation. For instance, using the IR pump/SPARS probe method, KL found that T_1 for the CH-stretch in ethanol is 40 ps, and we found T_1 for the OH stretch is 70 ps. If the CH stretching modes are transiently populated following excitation and relaxation of the higher frequency OH-stretch, we should be able to identify the rise and fall times of population in those modes. Of course, by tuning our OPA to pump CH stretches, we could also independently do the KL experiments.

3. T_1 for vibrations in solids

The IR pump/probe technique described above was also used to determine T_1 times for hydroxyl stretching vibrations in both amorphous and crystalline solids. T_1 times for hydroxyl groups coordinated to atoms (ions) in a variety of crystals have been studied in order to assess the importance of different local environments, including the mass of the metal atoms (heavy atom effect) on VET. It may be easier to model, e.g. via molecular dynamics simulations, the relaxation of bonds in these crystalline materials than for liquids or amorphous solids like fused silica.

The temperature dependence ($T \leq 1450K$) of the relaxation rate (T_1^{-1}) of OH (v=1) impurity oscillators inside fused silica is given in Figure 3.3. Note that the intrinsic vibrational relaxation rate for the bulk OH at room temperature is twice as fast as that for the surface OH on SiO_2. The T-dependence is perfectly fit by the multiphonon relaxation theory for an $n = 4$ process, i.e. ν_{OH} (3690) $\longrightarrow 4\nu_{lattice}$. The OH impurity concentration in fused silica is so small ($\leq$ 460 ppm) that no dependence of T_1 on OH concentration was observed.

The room temperature relaxation times for OH(v=1) ions inside samples of crystalline mica have very recently been measured. In these crystals, OH is part of the unit cell, and the interatomic distances, the vibrational frequencies and the orientation of the OH bonds with respect to the crystallographic axes are known. In the mineral muscovite, formula $[O_{10}\ Al_3\ Si_3\ (OH)_2\ K]_2$, the OH groups have a frequency of 3630 cm^{-1}. There are four equivalent hydroxyls per unit cell, located in a plane such that each is hexagonally surrounded by O atoms, and each OH is coordinated to two Al ions. For these OH groups, T_1 = 100 ±20ps. In the mineral biotite, Mg ions are substituted for some of the Al ions in muscovite, and two

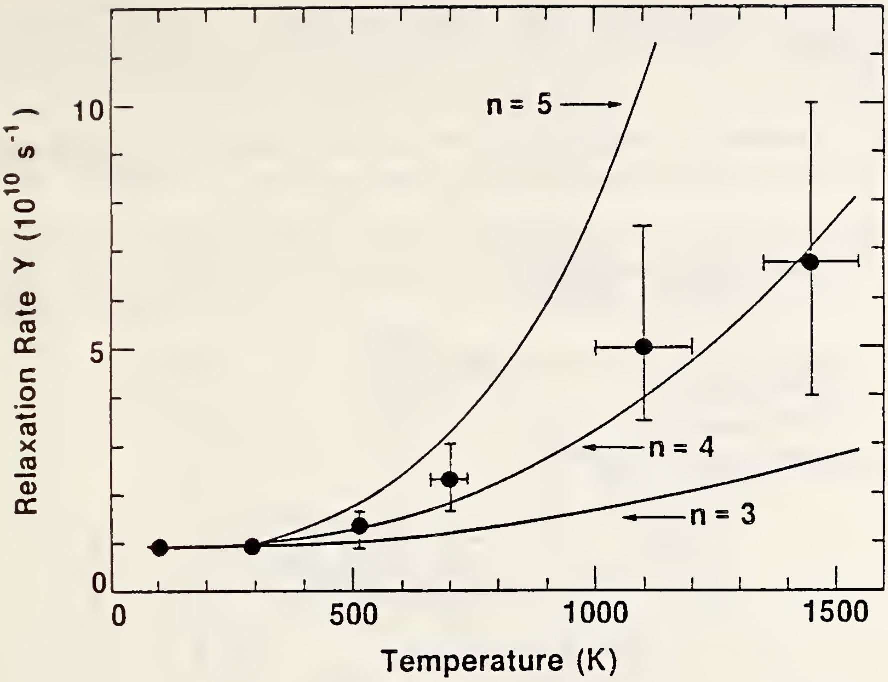


Fig. 3.3. Temperature dependence of the vibrational relaxation rate, $1/T_1$, of OH (v=1) impurity oscillators in bulk fused silica. The solid curves give the relative multiphonon relaxation rates vs. T for an n-phonon process (see text).

different OH species (ν=3660, 3590 cm^{-1}) occur. For the 3660 cm^{-1} vibration, T_1 = 210 ± 20 ps. These results are too recent to permit a detailed interpretation at this time. It should be emphasized that the high frequency lattice vibrations in these crystals are similar to those of fused SiO_2, and the measured T_1 values are similar to the values found for the surface OH on SiO_2, for the bulk OH in SiO_2, and for OH bound to Si atoms of silanol molecules in liquid CCl_4.

4. T_2 (Vibrational dephasing) times for vibrations in liquids

Picosecond coherent anti-Stokes Raman scattering (CARS) determined the dephasing times (T_2) for vibrations in simple liquids. Dephasing rates ($2/T_2$) were determined at T=295K for the symmetric stretch of CS_2 (ν_1=656 cm^{-1}) as a function of mole fraction in several solvents, and as a function of temperature in neat CS_2. Also, the dephasing rate of the ring breathing mode of benzene (ν = 991 cm^{-1}) was studied as a function of its dilution in CS_2.

Since neither the apparatus nor the results have previously been described in an Annual Report, details of both will be given below. We do not anticipate any further studies of dephasing rates. However, the apparatus used for the T_2 measurements, with some modification, will be used in several future experiments, e.g. measurements of T_1 for CO(v=1) on Pt(111) and measurements of vibrational predissociation times for van der Waals molecules.

The apparatus is shown in Figure 3.4. Two dye lasers of independently tunable wavelength (via 3 plate intracavity birefringent filters)

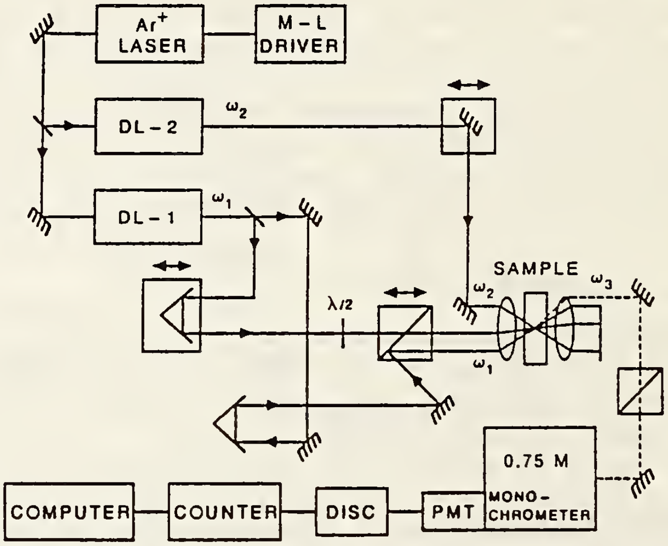


Fig. 3.4. Schematic diagram of apparatus used to measure T_2 for vibrations in simple liquids by picosecond CARS.

are synchronously pumped by a modelocked Ar^+ laser operating at 82 MHz. Tunable dye laser pulses at that repetition rate had about 0.6 nJ energy, an autocorrelation width (FWHM) of 8 ps, and a spectral bandwidth (FWHM) of 2.5 cm^{-1}. If the pulses were Gaussian, this would correspond to a $\Delta\nu\Delta t$ product of 0.42, very close to the transform limit. The width of the cross correlation was about the same as the autocorrelation. A cw modelocked Nd-Yag laser (scheduled for delivery in November 1985) will replace the Ar^+ laser in future experiments. Uncompressed dye laser pulses of 0.5 ps duration have been reported with (doubled) Nd-Yag pumping.

In our CARS experiment, the frequency difference between the dye lasers ($\omega=\omega_1-\omega_2$) was chosen to be resonant with the vibrational mode to be studied. Pulses at ω_1 and ω_2, vertically polarized and overlapped in time were incident on the sample at the phase-matching angle. The pair of pump pulses creates a coherent vibrational excitation in the liquid at frequency $\omega_1-\omega_2$. At a delayed time t_D a probe pulse at frequency ω_1, horizontally polarized, is sent through the sample in the correct propagation direction for phase matching the anti-Stokes frequency $\omega_3=2\omega_1-\omega_2$. A CARS signal (different in both frequency and propagation direction from the other beams) is generated by this pump pulse. The intensity (i.e. pulse energy) of the CARS signal decays in time after the pump pulses as $S(t_D) = \exp(-2t_D/T_2)$. The CARS signal, spatially and spectrally filtered to eliminate scattered dye laser light, is detected by a cooled photomultiplier operated in the pulse counting mode, and the count rate is constantly stored in a computer. When necessary, neutral density filters are inserted in the CARS beam to keep the count rate much less than 82 mHz.

A typical experimental run to determine T_2 for the symmetric stretch of liquid CS_2 is shown in Figure 3.5. Counts were summed for 10 sec at each delay stage position t_D.

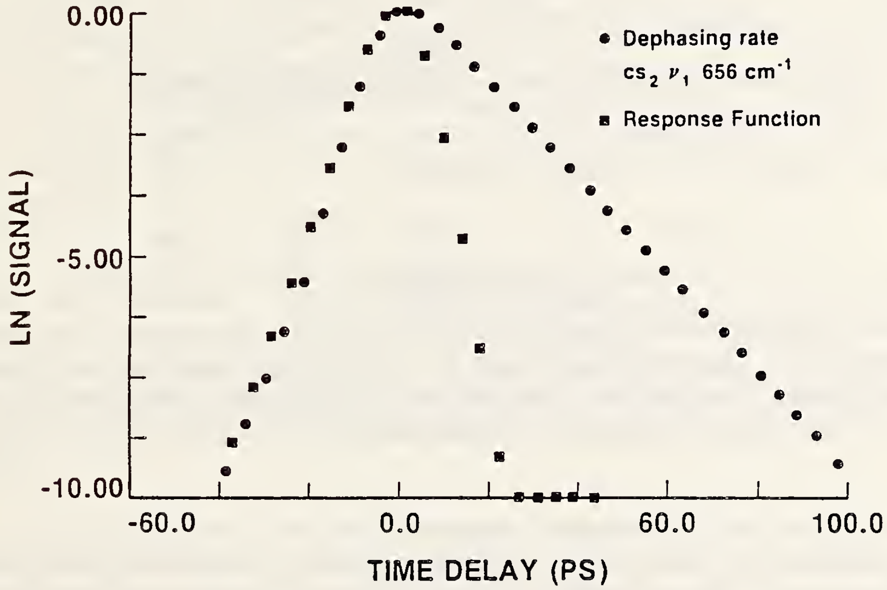


Fig. 3.5. Typical experimental run for the determination of the vibrational dephasing time T_2 for the totally symmetric stretching vibration ν_1=656 cm^{-1} of CS_2 in the liquid state.

The CARS signal decays exponentially over at least 10 e-folding times, with a characteristic decay time $T_2/2 = 10.2 \pm 0.2$ ps. This result for neat CS_2 agrees with previous work. Also shown in Figure 3.5 is the measured apparatus response function for this experiment. For $t_D > 10$ ps, the third order response function has a characteristic exponential decay time (1/e point) of 1.8 ps. Therefore, if the CARS signal is sufficiently strong, one may determine values of $T_2/2$ almost as short as this response time, despite the fact that the cross correlation FWHM is 8-9 ps. The shortest T_2 we report below is 5.2 ps.

A summary of the room temperature dephasing rates of $CS_2(100)$ in various liquid mixtures is shown in Figure 3.6. When CS_2 is diluted in CCl_4, the dephasing rate decreases compared to the pure CS_2 rate. On dilution in benzene, T_2 for CS_2 (100) is constant. Nitrobenzene, which has a large permanent dipole moment, and ethanol, which can form hydrogen bonds to other liquids, significantly decrease the dephasing rate of CS_2 (100). This is probably due to the stronger long range forces that these molecules can exert on CS_2.

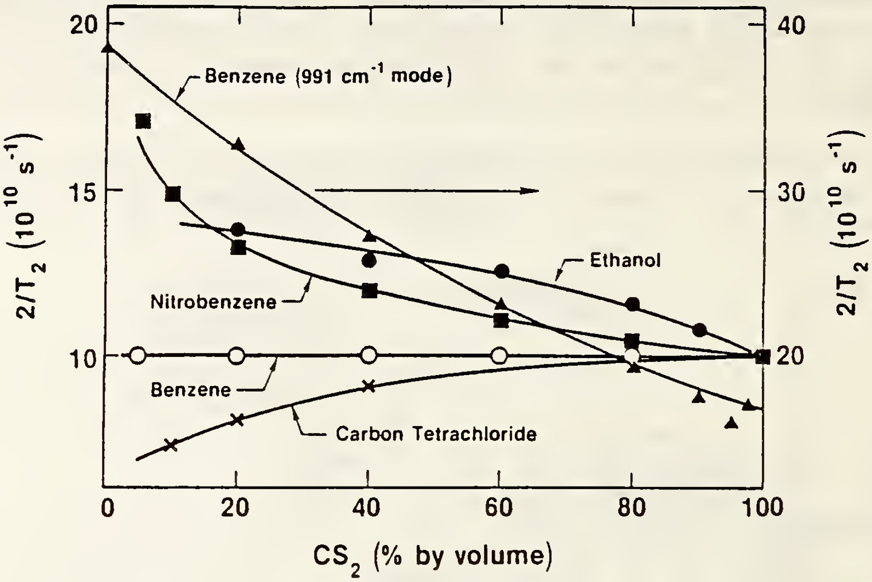


Fig. 3.6. Room temperature dephasing rates ($2/T_2$) of CS_2 in the totally symmetric vibrational state ν_1 = 656 cm^{-1} in various liquid mixtures. The points designated by filled triangles (Δ) are for the ring breathing mode of benzene (ν = 991 cm^{-1}) in CS_2.

Also shown in Figure 3.6 is the dephasing rate of the ring breathing mode of benzene (ν=991 cm^{-1}) in CS_2. Our result for pure benzene (T_2 = 5.2 ps) agrees with previous measurements. As benzene becomes more dilute in CS_2, $2/T_2$ decreases. At low concentrations, so that each benzene molecule is surrounded by CS_2, T_2 increases by a factor of 2.5 (T_2 = 12 ps). This is completely different behavior from the relaxation of $CS_2(100)$ for which T_2 was independent of CS_2/benzene ratio.

We are presently working on the interpretation of these data. Although the data in Figure 3.6 do not give straight lines, it nevertheless appears that all the rates are consistent with an isolated binary collision (IBC) expression of the form

$$2/T_2 = \rho\ x\ k_{ii}\ g_{ii}(o) + \rho\ (1-x)\ k_{ij}\ g_{ij}(o)$$

where x is the mole fraction of the molecule for which T_2 was determined, ρ the liquid density, $g_{ij}(\sigma)$ the radial distribution function at separation σ, and k the bimolecular dephasing rate constants (cm^3/molecules/sec).

We have also measured the dephasing rate of neat CS_2 as a function of temperature from its freezing point at T=165K to T=298K. Over the range 210K < T < 300K the rate decreases; then as T decreases further, $2/T_2$ increases from $8.2 \times 10^{10} s^{-1}$ at 210K to $11.2 \times 10^{10} s^{-1}$ at T = 170K. These time-domain data may be compared to earlier frequency domain results for the isotropic Raman linewidth $\Delta\nu$ of CS_2(100). In principle, $2/T_2 = \Delta\nu$ (FWHM). The agreement is only fair. In this case the picosecond measurements are probably more accurate, since the linewidths are narrow (hence difficult to resolve), and since the slope of the line in Figure 3.5 can probably be determined with more accuracy than a Lorentzian can be fit to the Raman spectral line. We are presently interpreting these temperature-dependent results.

These T_2 experiments have supported the T_1 measurements which have been done or are planned. Both T_1 and T_2 experiments in liquids (or at the solid/liquid interface) can make use of similar theoretical treatments (which we are now attempting). The T_2 experiments have played a crucial role in developing and testing our ability to use the synch-pumped lasers which (when amplified) will form the basis for many future T_1 measurements.

C. Desorption of Molecules from Surfaces

(D. F. R. Burgess, Jr., R. R. Cavanagh, L. B. Elwell, D. S. King and D. A. Mantell)

A dedicated experimental facility including surface sensitive analysis (e.g., mass spectrometer, argon ion sputtering, LEED and Auger electron spectrometer), computer controlled data acquisition and sub-Doppler (250 MHz) laser resolution is being applied to the study of the thermal desorption of molecules chemisorbed on well characterized surfaces. Results in past years have emphasized the NO/Ru(001) system.

In FY'85 measurements of the internal state distributions for NO desorbing from a saturation coverage of NO on Pt(111) were published as a communication in J. Chem. Phys. Results for an extensive study of the NO coverage dependence, over a ten-fold range in coverage, and the influence of co-adsorbates has been submitted to J. Chem. Phys. 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.

The results of a series of thermal desorption experiments following saturation coverage of NO on Pt(111) are shown in Figure 3.7. The solid curve is a thermal desorption spectrum obtained using a mass spectrometer to measure the total NO desorption as a function of increasing surface temperature. The data points (with 2 sigma error limits) give the measured rotational temperatures describing the NO species desorbed during intervals of 20 K (during a period of 2 sec) during the desorption heating ramp. There are two distinct desorption features for the NO/Pt(111) system and from this figure it becomes obvious that the rotational temperature of the desorbing species follows the instantaneous surface temperature for both features. All this data fits in the narrow range of having the rotational temperature being equal to 95±5% of the surface temperature.

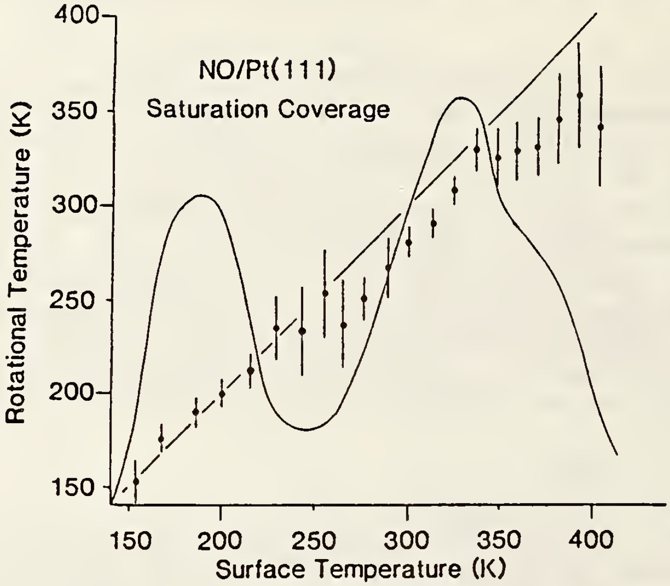


Fig. 3.7. Dependence of rotational temperature of NO desorbed from a saturation covered Pt(111) surface at various substrate temperatures.

Despite the fact that these results are consistent with the expectations from transition state theory, such a theory would lead to the additional expectation of a desorbing angular flux described by the cosine law and a Maxwellian kinetic energy distribution at the surface temperature. Preliminary results on Doppler profile measurements for NO desorbing from saturation coverages from Pt(111) indicate that these expectations are not upheld. These measurements show equivalent Doppler profiles for NO species desorbing in all final rotational states in the range of $2.5<J<15.5$, with energies from $13<E_r<426$ cm^{-1}, indicating no dependence of final kinetic energy on rotational state. Both the rotational state distributions and the dependence of kinetic energy on final rotational state are markedly different for the reactive NO/Ru(001) versus the non-reactive NO/Pt(111) systems.

Thermal desorption samples processes occurring under "equilibrium" conditions; this is to say that a heating rate of 10K/sec is much slower than molecular energy transfer processes in condensed phases. We have initiated a study of direct desorption processes following rapid heating of the surface using non-resonant laser irradiation. Here it is hoped that the short time scales for heating, i.e., 1-10 nsec. might allow desorption to compete favorably with other energy exchange or relaxation processes. Progress to date includes the assembly of an ultra-high vacuum chamber designed for laser-heating/final-state resolved measurements. Initial measurements have focussed on obtaining reproducible laser desorption signals and achieving an understanding of the dependence of desorption probability versus laser pulse energy. This work is supported by DOE.

D. Dynamics of van der Waals Molecules
(M. P. Casassa, L. B. Elwell, D. S. King, J. C. Stephenson and A. M. Woodward)

These experiments represent a new direction of research, in part an outgrowth of infrared multiphoton photodissociation experiments. The experiments consist of the characterization of the time scales and final state distributions in the dissociation of van der Waals complexes excited to well-defined vibrational or electronic states. The systems studied during FY '85 included the electronic predissociation of NO-Ar, and the vibrational predissociation of both NO-ethylene and NO-NO. The van der Waals species were formed in a pulsed free jet expansion. Mass spectrometric techniques have been used to characterize the cluster distributions formed in our beam as a function of backing gas composition and pressure. The dynamics studies consisted of a one-photon laser excitation to a predissociating state, followed by measurements of the rotational (J), spin-orbit (Ω), and lambda doublet (Λ^+/Λ^-) distributions of the NO photoproducts via laser excited fluorescence of the A--X transition at 226 nm. The spatial distribution of J-vectors (alignment) and the velocity distribution (both speed and angular flux) were determined by polarization and Doppler techniques.

NO-Ar undergoes an electronic excitation to the NO-like 3sσ A state at excitation frequencies near 44,200 cm^{-1}. Although excited Π states of the NO-Ar species are stable and exhibit discrete electronic absorption spectra, the $A^2\Sigma$ state is distinctly different. This is a Rydberg state, with an electronic orbital radius that extends well beyond the NO-Ar separation in the electronic ground state. Thus, in the Franck-Condon excitation process, the excited state created through the absorption process is more analogous to NO$^+$-Ar, which should be more tightly bound and have a shorter van der Waals radius. The result of this is that there is a predissociative curve crossing involving the ground state potential energy surface. The NO fragments formed in this predissociation are predominantly in the electronic ground state (>99%) and exhibit Doppler profiles that indicate that the lifetime of the electronically excited parent is substantially less than a rotational period -- i.e., on the order of or less than a few periods of the van der Waals vibration. Very little of the total available energy appears as rotational excitation of the fragments -- only about 0.5%. Presumably this reflects a constraint imposed in the conservation of angular momentum.

There has been substantial recent theoretical interest in the vibrational predissociation of van der Waals molecules, but very few experiments that have looked at either the final state distributions or obtained real time measurement of the dissociation lifetimes. Earlier measurements (by Hoffbauer, Liu, Giese and Gentry and by Bomse, Cross and Valentini) of the kinetic energy released in the dissociation of the ethylene dimer excited at 950 cm^{-1} to the ethylene ν_7 mode indicated, in consonance with theoretical expectations, that most of the available excess energy went into rotational excitation of the two ethylene fragments. In our experiments on NO-ethylene excited to the same ethylene-like ν_7 mode by our short pulse CO_2 laser we found very little rotational excitation in the NO fragment and very little kinetic energy released. Equal populations were found in the two NO lambda doublets. This contrasts with the disequilibrium of lambda states found in the products of the prompt electronic photodissociations of HOH and HONO and in many direct collisional H-atom abstraction reactions. Presumably, most of the available excess energy (i.e., roughly 50%) went into excitation of a-axis rotation in the ethylene fragment. Doppler profiles were measured for various orientations of the electric vector of the pump laser and the directions of propagation of both the pump and probe lasers. Equivalent Doppler profiles, of 0.060cm^{-1}FWHM, were obtained for NO products under all conditions. This observation requires the distribution of NO velocities to be spatially isotropic, i.e, not aligned with respect to the pump laser electric vector. Similar spatial flux isotropy was reported for the ν_7 predissociation of the ethylene dimer; spatially anisotropic flux distributions have however been reported for prompt photodissociation processes. Real time measurements of the appearance of the NO fragment, in a dual laser pump/delayed laser probe experiment, proved that the lifetime of the vibrationally excited van der Waals complex was less than 10 ns. The isotropic flux suggests that the vibrationally excited complexes survive more than one rotational period. At the temperature of our beam, the average rotational period is ~35 psec., implying a lower limit of ≈ 50 psec on the predissociation lifetime of the excited complexes.

In the vibrational predissociation of the nitric oxide dimer, following excitation by a frequency doubled short pulse CO_2 laser at 1870 cm^{-1}, the total distribution of available energy was determined. The rotational and spin-orbit states of both NO photofragments (for values of internal energy <426 cm^{-1}), are described by a rotational temperature of 110 K. This corresponds to only 20% of the available excess energy going into rotational excitation of the two fragments in dramatic contrast to the results obtained on the ethylene dimer. The two lambda doublet states were observed to be statistically populated and the relative populations of the two spin-orbit states were consistent with a spin-orbit temperature equal to the rotational temperature, indicating equilibration of the electronic spin- and nuclear rotation angular momenta in this reaction. This is an unusual instance, where a singlet parent dissociates to form two doublet state fragments since in previous examples (e.g., including CH_3ONO, HONO, and dimethyl methoxy phosphate) apparent selection rules favored one spin-orbit component. Real time measurements of the fragment appearance times indicated that the vibrationally excited complexes dissociate within 10 nsec. We determined the NO fragment flux to be spatially isotropic by measuring Doppler profiles at various experimental configurations. This is similar to our results on ethylene-NO and previous results on ethylene dimer and implies a lower limit on the predissociation lifetime of ~ 50 psec.

It is possible for us to probe the photodissociation dynamics of the NO-ethylene van der Waals complex following excitation to several different vibrational states. Of particular interest are the results following excitations at 1870 and 1900 cm^{-1} to either the NO stretch or the ethylene ($\nu_7+\nu_8$) combination band, respectively. Here there are several lower frequency vibrational modes that might act as receptors for the available excess energy -- on the order of 1500 cm^{-1}. These mode specific experiments are in progress. In addition, experiments are in the planning stages (see section F) to determine the lifetimes of these vibrationally excited species using psec lasers for excitation and probing.

E. Matrix Isolation Spectroscopy
(M. E. Jacox)

The assembly and testing of the vacuum systems and the cryogenic cell for use with the high resolution Bomem interferometer have been completed. Experimental studies using this apparatus are scheduled to begin in September.

With the help of Dr. Thomas Buckley, Chemical Thermodynamics Division, and Mr. Ricardo Metz, a summer worker in the Chemical Kinetics Division, substantial progress has been made in the software development for use with the Ebert visible-ultraviolet scanning monochromator. As this is written, it is planned to resume the long-suspended studies of the ultraviolet absorption spectra of transient molecules in the near future. The work is supported by ARO.

1. Fluorine-Atom Rections

A major effort was the preparation of a review paper, entitled "Spectroscopy and Photochemistry of Free Radicals Formed by the Reaction of F Atoms with Small Molecules," which has recently been published in Reviews of Chemical Intermediates. This paper provides a comprehensive review of both gas-phase and matrix isolation studies of the various types of F-atom reactions (e.g., addition, H-atom abstraction) which have yielded spectroscopic or photochemical data for the primary free radical products.

Because hydrogen-atom abstraction from a generalized molecule, RH, in an argon matrix leads to the formation of hydrogen-bonded R•••HF, this review has included an assessment of the extent of perturbation of the HF-stretching vibration of R•••HF species which results from trapping of the complex in an argon matrix. Also included is a summary of shifts in the molecular vibrations, observed in solid argon, upon hydrogen-bonding of various types of molecules with HF.

Studies of the reaction of F atoms with methyl chloride, bromide, and iodide were completed. Evidence was obtained for a steric effect on the mechanism of F-atom reaction with these molecules, with two major reaction channels for each system. Attack of the F atom at the halogen position results in the formation of the CH_3XF addition product, which has a moderately strong X-F bond and is photochemically stable at wavelengths as short as 250 nm. F-atom reaction with a hydrogen atom of the methyl halide results in the stabilization of a weakly bound $F\cdots HCH_2X$ complex, intermediate to the formation of $H_2CX\cdots HF$ in the solid. For all of the species studied except CH_3Cl, the barrier to the decomposition of this complex is sufficiently great to require exposure of the solid deposit to visible light for the production of $H_2CX\cdots HF$. A paper presenting these results in detail is scheduled to appear in an October issue of Journal of Chemical Physics.

Studies of the reaction of F atoms with formic acid were initiated, with the objectives of determining whether the $H-CO_2$ structure has a ground-state potential minimum and of obtaining the spectra of the important combustion intermediates cis- and trans-HOCO in solid argon. (Previous studies in this laboratory had yielded the infrared spectra of these two species in solid CO, with which HOCO would be expected to hydrogen-bond.) Although some of the isotopic substitution studies, useful for a final normal coordinate analysis, remain to be completed, the following conclusions are evident:

(1) If the $H-CO_2$ structure has a ground-state potential minimum, it is formed with too much energy for stabilization in this system.

(2) Evidence for the formation of an $HCOOH\cdots F$ intermediate when the F atom attacks the OH bond of HCOOH is provided by the appearance of a high yield of $CO_2\cdots HF$, with little evidence for isolated CO_2, in the initial deposit.

(3) F atoms abstract H directly from the C-H bond of HCOOH, leading to the stabilization of isolated HOCO, as well as of $HOCO\cdots HF$.

(4) Trans-HOCO is more stable than the cis-rotamer.

Preliminary studies of the important F + SiH_4 reaction system indicated that extensive reaction occurs.

2. Excited Rare-Gas Atom Reaction

The interaction of excited argon atoms with formic acid was found to lead to the stabilization of trans-HOCO in solid argon. Studies of this reaction system were extremely valuable in the detailed assignment of absorptions in the corresponding F-atom reaction study to isolated HOCO and to HOCO···HF.

The interaction of excited argon atoms with silane was found to provide a relatively "clean" yield of SiH_2, with only weak contributions of other products to the observed infrared spectrum.

3. Vibrational and Electronic Energy Levels of Transient Molecules

A paper entitled "Ground-State Vibrational Energy Levels of Polyatomic Transient Molecules," summarizing both gas-phase and inert matrix data for almost 500 species containing from 3 to 16 atoms, was published in the October 1984 issue of the Journal of Physical and Chemical Reference Data. In keeping with the rapid pace of new developments in this field, on May 1 a supplement containing data for 76 molecules which had appeared in the literature since August 15, 1984, was prepared for distribution with the reprints. An up-to-date digital record of developments in this fast-moving field is being maintained, and in one or two years it is planned to publish a supplement.

A proposal entitled "Spectroscopic Properties of Excited Electronic States of Small Polyatomic Transient Molecules" was submitted to the Office of Standard Reference Data, and beginning on September 1 will be supported for a period of two years. The output of this project will be a critically evaluated compilation of the experimentally determined spectroscopic properties of the bound and dissociative excited electronic states of covalently bonded transient molecules containing from three to six atoms. Spectroscopic data observed for transient molecules in the gas phase and in dilute solid solution in the rare gases or in non-polar small-molecule solvents will be included. The extent of deviation of the transition origins, vibrational fundamental frequencies, and radiative lifetimes of transient molecules observed in these media from the values reported for the gas-phase species will be assessed, in order to provide an estimate of the expected deviations for molecules for which gas-phase data are not available.

4. Reaction Intermediates in the Decomposition of Energetic Materials

With support from the Army Research Office, studies of the infrared and ultraviolet spectra of reaction intermediates derived from the decomposition of benzene and nitrobenzene are being pursued. Spectroscopic identifications are also being sought for a number of other small free radicals which play important roles in the decomposition of explosive or propellant molecules.

Preliminary infrared studies have been made of the photodecomposition of benzene isolated in solid argon by 254-, 122-, and 105-107-nm radiation. There is evidence for the stabilization of at least four products: phenyl radical, benzyne (C_6H_4), and two or more other species, one of which photodecomposes when the sample is exposed to the full light of the medium-pressure mercury arc.

Preliminary studies were also conducted of the photodecomposition of nitrobenzene isolated in solid argon, using the highly dilute Ar:nitrobenzene = 2000 samples which could be prepared in a conventional sampling system. Photolysis sources were 254-nm mercury-arc radiation and a beam of excited argon atoms, which provides a source of energy in the 11.5-11.8 eV range. Infrared absorptions of new products did not appear in either system. Previous studies had indicated that in the 254-nm spectral region the most important photodecomposition process is O-atom detachment, but that some NO_2 is also produced. No photodecomposition products were detected in the preliminary experiments. Since O atoms can diffuse from the site of their photoproduction in solid argon, failure to detect nitrosobenzene or O-atom reaction products suggests that previous studies may have overestimated the extent of O-atom photodetachment in the primary decomposition of nitrobenzene. Phenyl radical and NO_2, products of the other primary photodecomposition process, would be expected to undergo cage recombination to re-form nitrobenzene or, possibly, to form the previously unobserved species phenyl nitrite. The negative results obtained in these preliminary studies are most consistent with the formation and recombination of phenyl radical and NO_2. Experiments with more concentrated nitrobenzene samples will be necessary in order definitively to exclude the formation of nitrosobenzene and/or phenyl nitrite under these conditions. Construction of an auxiliary vacuum manifold to permit higher concentration studies of low vapor pressure materials is in progress.

In a search for infrared absorptions of the H_2CN free radical, which may play an important role in the decomposition of RDX and HMX, studies of the infrared spectra of the products of the H + HCN reaction were initiated, using a microwave discharge through an Ar:H_2 mixture as the H-atom source. Rather weak infrared absorptions of CN and of three other products were detected. Positive identification of these three products, which differ in their photodecomposition thresholds on exposure of the sample to filtered mercury-arc radiation, must await the completion of planned isotopic substitution studies.

F. Future Plans

1. 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? Experiments are planned to answer these questions.

We have measured vibrational relaxation rates for high frequency vibrations on dielectric surfaces at the solid/vacuum and solid/liquid interface, in liquids, in amorphous and crystalline dielectric solids. We do not have one simple theory to interpret all the results in a consistent fashion. It appears qualitatively that one may interpret all the results in simple terms of masses connected by springs. However 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 linewidths observed for high frequency vibrations on metals really are 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.

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 is to use the same technique for ordered monolayers on large metal single crystals under UHV conditions. A third approach involves IR excitation of a molecule 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 laser pulses of suitable energy, bandwidth, frequency, and duration. The present Nd-Yag pumped OPA setup has several important limitations. Only frequencies $\nu_{IR} > 2600$ cm^{-1} can be generated, which restricts us to high frequency vibrations. However, because of its large transition dipole moment, and because of the wealth of surface information available, we want to study CO on metals. This requires $\nu_{IR} \approx 2000$ cm^{-1}, not possible with the present setup. Also, the pulse duration of 15-20 ps with the present system is too long for many experiments (e.g. NH_2 on SiO_2, and probably CO on metals). The broad spectral bandwidth from the OPA is also undesirable for many reasons (e.g., for the experiment to work an extremely large anharmonicity is required).

Therefore, in future T_1 experiments we will produce tunable IR radiation by generating the difference frequency , $\omega_{IR} = \omega_1 - \omega_2$, between two visible laser pulses in non-linear crystals. For frequencies $\omega_{IR} \geq 1800$ cm^{-1} we will use $LiIO_3$ and for lower frequencies $900 < \omega_{IR} < 1800$ we have tried $AgGaS_2$. We are trying two approaches to generate the necessary visible pulses to be used for mixing. At a 20 Hz repetition rate we will amplify the outputs of both synch-pumped tunable dye lasers so that each has an energy of 0.5 mJ/pulse (as of 7/85 one of the two necessary amplifiers was operational). An alternative is to double the Nd^{+3}:YAG light to synchronously pump a dye laser cavity. The dye laser output should be of significantly shorter duration than the 532 nm pumping pulses. The tunable IR, generated by difference frequency mixing ($\omega_{IR} = \omega_{532} - \omega_{dye}$) should have the duration of the input dye pulse. Both difference frequency schemes should be capable of generating 1-10 μJ pulses in the 5 μm region. This should be sufficient to perform experiments described below.

It is conceptually straightforward to do the one color IR pump/probe transmission IR experiment to measure T_1 for CO (v=1, ω= 2000 cm^{-1}) on dispersed Pt particles supported on a SiO_2 disk. The transmission IR spectra of such samples have been extensively studied over the last 30 years. During the past year we have attempted this type of experiment for higher frequency vibrations (3000-4000 cm^{-1}) of molecules chemisorbed on dispersed metals (M-OH, M-NH, M-C_2H_2) without success. Two major problems - sample damage by the pump pulse and excessive scattering of pump light into the probe detector - have been solved by improved sample preparation. However, it is difficult to chemisorb these species in sufficient concentrations for study. Previous work shows that this should not be a problem for CO on metal surfaces. Also, molecules which absorb in the high frequency range tend to have relatively low vibrational transition dipole moments compared to CO chemisorbed on metals. Thus CO/metal systems offer important advantages. We expect in 1986 to perform the simple pump/probe experiments to measure T_1 for CO(v=1) bound to a variety of dispersed supported metals.

In principle the IR transient saturation experiment is applicable to any sample for which ordinary IR absorption spectroscopy is possible, including monolayers on metal single crystals. For most vibrations on single crystals, infrared reflection-absorption spectroscopy (IRAS) requires the detection of very small absorptions, typically 2×10^{-4}. With our present detectors and poorly behaved OPA pulses, we can only detect transmission changes greater than 0.3%; to determine the slope of the ln (T/T_0) plot (i.e. T_1) presently requires a change in T (caused by the pump) of at least 1.5%. The present apparatus thus has two orders of magnitudes less sensitivity than that necessary to measure T_1 for typical surface vibrations. We expect that our sensitivity can be significantly improved since other laboratories have claimed 1 part in 10^5 using pulsed lasers. In fact, for CO on metals, sensitivity limitations are not as severe since absorptions of 1-2% are usually reported in IRAS experiments. We are working toward attempting to measure T_1 for CO on Pt(111) or related metal single crystal surfaces using the IR pump/probe method. Better laser pulses, better pulsed IR detection and signal averaging, and significant additional surface preparation and characterization (e.g. high resolution IRAS capability) equipment will be needed.

A direct measurement of the pathways (accepting modes) involved in the VET experiments requires a determination of population in different sample vibrational modes. Time-dependent Raman or IR spectroscopy may be used. For samples of good optical quality, such as colloidal silica particles suspended in CCl_4, or for the liquid samples of R_3Si-OH molecules (which may be models for the surface vibrations), we will perform IR pump/SPARS probe experiments (using either OPA/532 nm or IR difference frequency systems) in 1986. To decrease background signals from the thermal population in very low energy modes the samples may be cooled (as done for the CS_2 T_2 experiments). It is likely that other samples (pressed disks, dispersed supported metals) will scatter too much visible light to permit detection of the expected weak SPARS signals. For these samples 2 color IR transmission spectrosocpy (pump one mode, probe another) may be used. This approach is likely to be successful only for a few surface species where energy flows from one high frequency vibration to a neighboring high frequency mode before dissipating to the low frequency ($\nu < 1200\ cm^{-1}$) lattice modes. As an alternative to SPARS probing of vibrational population (e.g. OH v=1), we may try CARS probing. The CARS method has the advantage of generating more detected signal photons per pulse, but the disadvantage of requiring large excited state densities and three coincident laser pulses.

To date our surface T_1 measurements have been for molecules on collidal SiO_2, a surface which has little catalytic activity. One way we hope to explore the relation between VET and surface chemistry is to study T_1 for systems with important catalytic activity. For instance, the hydroxyl groups inside zeolite catalysts are associated with active Brönsted acid sites, and there have been many transmission IR studies of these OH sites in the 3700 cm^{-1} region. In collaboration with Dr. R. Wormsbecher at W. R. Grace (Columbia, MD) we hope to measure T_1 times for OH stretching vibrations in a number of zeolites of different catalytic activity.

2. Dynamics of van der Waals Molecules

The same synch-pumped picosecond laser apparatus which will generate IR pulses suitable for studying VET rates for bonds on metal surfaces, will also generate pulses suitable for doing VET studies involving the photodissociation of van der Waals molecules. An example of a van der Waals experiment which we should do in 1986 is the photodissociation of $NO{\cdot}C_2H_4$ by $\nu_{IR} = 1900\ cm^{-1}$

$$\begin{array}{llll}
C_2H_4{\cdot}NO & \xrightarrow{1900cm^{-1}} C_2H_4(\nu_7+\nu_8){\cdot}NO & \xrightarrow{\tau} & C_2H_4 + NO\ (J,\Omega,\Lambda) \\
 & \xrightarrow{1870cm^{-1}} \quad C_2H_4{\cdot}NO(v=1) & \xrightarrow{\tau} & C_2H_4 + NO\ (J,\Omega,\Lambda)
\end{array}$$

There is a significant controversy about the value of τ, the predissociation lifetime. The photodissociation spectrum in the C_2H_4 ν_7 region is a Lorentzian (FWHM = $6cm^{-1}$), which has been interpreted as implying τ = 0.9 ps. Our time-resolved measurements of product appearance using nanosecond lasers proved that $\tau < 10$ ns. However our measurement of isotropic flux distribution suggested that $\tau \geq \tau_r$, where the rotational time of $NO{\cdot}C_2H_4$ in our beam is $\tau_r = 35$ ps.

We will generate tunable IR at 1900 or 1870 cm^{-1} by generating the difference frequency in $LiIO_3$ of the two amplified synch-pumped lasers. One of them (at λ = 575 nm) is frequency doubled; the λ = 288 nm is summed with Nd-Yag (1.06 μm) in a KD*P crystal to generate light at 226 nm (P_1 head = 44176 cm^{-1}) suitable for LEF detection of the NO photoproduct on the $\tilde{A}\leftarrow\tilde{X}$ transition. Measurement of the NO LEF signal vs. pump/probe delay time (t_D), will determine τ for excitation of C_2H_4 $(\nu_7+\nu_8)\cdot NO$ at 1900 cm^{-1} compared to $C_2H_4\cdot NO(v=1)$ at 1870 cm^{-1}. It will be interesting to see if the product yield has an exponential build-up as $NO(t) \propto [1-\exp(-t/\tau)]$, as predicted by statistical theories, and to see if there is any relationship between τ and photodissociation line widths. Excitation of the out-of-plane ν_7 motion which corresponds to the reaction coordinate, may give a short τ, while there may be a significantly longer time for NO stretching energy to flow into the van der Waals bond leading to dissociation. Similar experiments are planned in which C-H stretching modes of van der Waals clusters will be excited with picosecond IR pulses. The necessary 3 µm light will be produced by the same dye lasers by difference frequency generation.

3. Desorption of Molecules from Surfaces

Several years ago we undertook a joint research project involving staff and expertise of the Molecular Spectroscopy and Surface Science Divisions of the Center for Chemical Physics to examine in greater detail molecular dynamics at the gas-surface interface. The thrust of this program was to use laser based, state and velocity selective diagnostics to study molecules being thermally desorbed from well-characterized single crystal metal surfaces in an ultra high vacuum environemnt. The results of our work on NO/Ru(001) and NO/Pt(111) have been published and are reviewed herein. What is important about these experiments is that they are extremely, perhaps uniquely, sensitive to the interactions between gas molecules and different metallic surfaces.

The future directions of this research effort can be broken up into two branches. First, in view of the marked differences for NO/Pt, where there is only simple molecular desorption, versus Ru, where decomposition competes with desorption, during FY'86 we plan to explore the desorption of NO from 1) co-adsorbed layers of NO and ammonia on Pt(111) where there appears to be a co-operative interaction during the desorption process; and 2) Ir(111) where a major source of the desorbing NO is from atom-atom recombination. Although all our present work has emphasized interactions with the NO adsorbate, we hope to acquire a second dye laser to enable us to extend our laser probe capabilities into the vacuum ultra-violet and study the molecule-surface dynamics of other, chemically interesting species such as hydrogen and CO.

Thermal desorption studies are sensitive to the molecular dynamics and energy flow in the region of the top of the chemisorption potential energy well - a region important in the making and breaking of chemical bonds. In the thermal desorption experiment the heating rates traditionally used are much slower (e.g. ~10 K/sec.) than other molecular relaxation processes, which is good if one's goal is to study the dynamics of a highly energetic system under "equilibrium" conditions. A deeper level of understanding can be obtained regarding molecule-surface energy transfer by attempting to study non-equiblibrium conditions, such as might be achieved following laser irradiation of the adsorbate covered surface.

We hope during FY'86 to successfully characterize the internal state distributions, kinetic energy and angular flux distributions of the NO driven off a Pt(111) surface by non-resonant laser excitation at 532 nm. Estimates of the anticipated signal levels for desorption of 10^{-4} of a monolayer per laser shot indicate that we should be able to determine the vibrational as well as rotational partition functions. These experimental results will provide a stringent test of the theoretical treatments currently being applied to model laser-surface heating and energy transfer processes.

4. Matrix Isolation Studies

The high sensitivity and extended spectral range afforded by the Bomem interferometer will be crucial to the study of a number of important systems during the coming year. Among the first systems to be studied will be the photodecomposition of acetylene to produce HC_2 and C_2^-. Electronic transitions for both have recently been reported near 4000 cm^{-1}. Observation of the absorptions resulting from these electronic transitions in a rare-gas matrix will aid in the definitive identification of the C_2^- transition and in the assignment of the bands arising from vibrationally unexcited HC_2, which has an unusually low ground-state bending vibrational frequency.

Priority will also be given to the studies of the H + HCN reaction, in which the greater sensitivity of the Bomem interferometer will be valuable for the definitive assignment of the infrared spectra of H_2CN and of cis- and trans-HCNH. A search will also be made for near infrared transitions of these species, each of which, like the isoelectronic species HCO, may have a low-lying electronic transition.

As reported one year ago, the feasibility of detecting the infrared and electronic spectra of molcular ions produced by codepositing a beam of excited neon atoms with a suitable precursor molecule isolated in solid neon has been demonstrated. The energy range accessible using excited neon atoms (16.6-16.8 eV) will substantially broaden the range of molecules whose ions are accessible over that covered in earlier experiments in this laboratory using excited argon atoms, permitting a search for such important ions as HCO^+, H_2O^+, NH_3^+, and CH_4^+. These long-planned studies have been deferred until they could be conducted on the Bomem interferometer, since the enhanced sensitivity of this instrument is especially important when liquid helium must be used as the coolant. It is hoped that studies of these experiental systems can proceed during FY'86. Such studies may provide much previously inaccessible information on the vibrational and electronic spectra of molecular ions, important in a variety of high energy systems ranging from combustion to high-speed flight.

The higher sensitivity of the Bomem interferometer will permit studies of such other important classes of molecule as carbon-13 substituted species present in natural abundance and products of O-atom reactions in discharge sampling experiments. Observations of the carbon-13 species will aid in product identification and will provide valuable data for infrared spectral analysis. Since water and oxygen impurities generally lead to the formation of O atoms in discharge sampling experiments, the greater sensitivity of the Bomen inteferometer will both facilitate and mandate a series of studies of the reactions of O atoms with small molecules. Such studies of the reactions of O atoms with benzene and with nitrobenzene form an important part of the current program of research being supported by the Army Research Office.

Preliminary studies have indicated that species of formula HCN_2 are stabilized by the reaction of photochemically generted CH with a nitrogen matrix. Further studies will be conducted in order to obtain a definitive identification of this product, which may play important roles in processes as diverse as the decomposition of explosive or propellant molecules and the generation of "prompt" NO on atmospheric combustion of hydrocarbons.

In order to obtain as complete as possible a characterization of the spectra of the products of elementary reactions of silane, studies will be continued not only on the reaction of excited argon atoms and of F atoms with silane, but also on the corresponding H-, Cl- and O-atom reactions.

Because F-atom reaction studies have provided an extremely valuable tool for obtaining free radical spectra, they will continue. Emphasis will be placed on studies of the ultraviolet absorption spectra of the products of F-atom reaction with such species as CH_3NO_2, CH_3CHO, CH_3CN, and HCOOH, for which infrared studies have provided definitive identifications of free radicals.

As it becomes possible to stabilize a wide variety of molecular ions and O-atom reaction products in rare-gas matrices, it will be increasingly important to determine their laser-excited fluorescence spectra, in order to provide a more complete characterization of their energy levels and to establish a basis for their detection in atmospheric and combustion systems. This need will mandate construction of a laser-excited fluorescence system dedicated to matrix isolation studies. This system will also permit unique experiments to determine previously inaccessible low-lying molecular electronic states; cage recombination of molecular fragments formed on laser photodissociation of the matrix-isolated molecule may populate such low-lying states, which may then be deactivated by fluorescence or phosphorescence.

4. QUANTUM CHEMISTRY GROUP

H. Basch, P. Jasien, P. S. Julienne, M. Krauss,
F. H. Mies and W. J. Stevens

A. Introduction

B. Electronic Structure

1. Theoretical Proton Affinities
2. Hydrogen Bonding of Water and Methanol with Formamide
3. Localized Electron Pair Polarizabilities
4. Binding of Pt Complexes to DNA
5. Reaction Field Methods
6. Relative Energetics of Dipeptide Conformers

C. Scattering in the Presence of Radiation

1. Radiative Redistribution
2. Application of Generalized Multichannel Quantum Defect Theory (MCQDT)
3. Product Distributions in Molecular Photodissociation
4. Atomic Lineshapes and Resonance Fluorescence Spectra
    a. Continuum-continuum Matrix Elements in Atomic Lineshape Theory
    b. Impact Limit in Weak Laser Fields
    c. Impact Limit and Pressure Broadening of Mollow Sidebands in Intense Fields

D. Multiphoton Effects in Resonance Fluorescence Spectra

E. Future Plans

A. Introduction

Atomic and molecular electronic structure and scattering methods are developed and applied to chemical and spectroscopic problems where experiments are difficult to perform or so complicated that the theory is needed to model the results.

The electronic structure method and code development and applications now include chemical problems with large molecular systems including models of biomolecules. The applications to the biotechnology area utilize the recently acquired IBM-4381 in the Molecular Structure and Modeling Facility (MSMF) and are described in part in the competence summary.

B. Electronic Structure

1. Theoretical Proton Affinities

(W. J. Stevens, P. Jasien)

A combination of several state-of-the-art ab initio quantum chemistry methods has been applied to the quantitative determination of the proton affinities of small molecules containing the Group VI elements, O, S, Se, and Te. Several series of molecules have been studied including CX, CX_2, OCX, and H_2CX (where X is the Group VI atom). Comparisons with available experimental data are very good, and the estimated accuracy of the theoretical results is ± 2.5 kcal/mole. These are the first such accurate calculations ever carried out for compounds containing selenium and tellurium. In addition to the proton affinities, trends down the Periodic Table are now available for favored protonation sites, vibrational frequency shifts upon protonation, and structural distortions due to protonation.

Compact effective potentials (CEP), which were developed at NBS, allow the chemically unimportant core electrons to be eliminated from the molecular wavefunctions with little loss of accuracy. Thus, all of the Group VI elements were treated as six electron atoms. Relativistic effects are incorporatd through the use of Dirac-Fock atomic wavefunctions in the determination of the core potentials.

Full analytic energy gradient geometry optimizations of all neutral and protonated species were carried out at the single configuration self-consistent-field (SCF) level using accurate "double-zeta plus polarization" basis sets. At the optimized geometries, harmonic force constants were determined from numerical first derivatives of the analytic energy gradients, and zero-point vibrational energy contributions to the proton affinities were calculated. Electron correlation energy contributions were evaluated by configuration interaction calculations including all single and double excitations from the single configuration SCF wavefunctions.

This work is described in: P. G. Jasien and W. J. Stevens, J. Chem. Phys. 83, 2984 (1985).

2. Hydrogen Bonding of Water and Methanol with Formamide

(W. J. Stevens and P. Jasien)

The characterization of the hydrogen bonding between water and formamide has been of considerable interest to experimentalists and theoreticians alike. This interest stems from the fact that formamide may be viewed as the simplest molecule containing a peptide linkage. As such, the formamide-water complex provides the simplest model for the hydration of proteins.

We have carried out detailed calculations on several conformers of the formamide-water complex at a level of accuracy significantly beyond all previous theoretical studies. Full gradient energy optimizations using double-zeta plus polarization basis sets were carried out for each conformer. The effects of electron correlation were determined by configuration interaction including all single and double excitations from the SCF configuration.

These accurate calculations show hydrogen bonding of water to the carbonyl group to be favored by about 0.5 kcal/mol over bonding to the amide group. However, a cyclic structure in which the water is hydrogen bonded to the carbonyl and amide groups simultaneously is found to be most stable (9.5 kcal/mol) and is a likely candidate for molecular beam microwave spectrocopic studies.

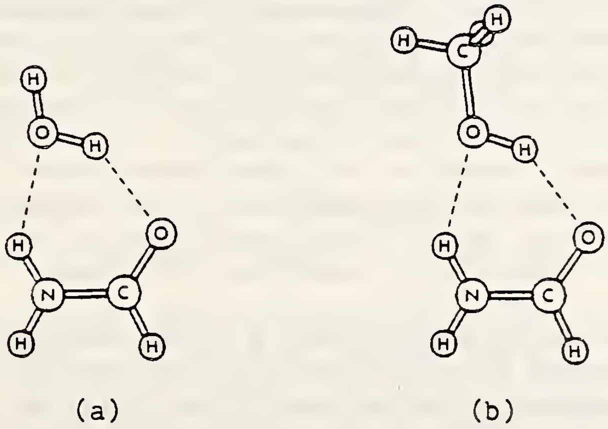


Fig. 4.1. Most stable hydrogen-bonded complexes of (a) water-formamide and (b) methanol-formamide illustrating near coincidence of the two structures.

Calculations were also carried out on methanol-formamide complexes to determine if any fundamental differences exist in the hydrogen bonding of the alcohol versus the water. The results show virtually identical structural and energetic behavior of the methanol-formamide complexes when compared to the water-formamide complexes. Again, the cyclic, doubly hydrogen-bonded conformer is the most stable. Figure 4.1 shows the striking similarity of the two cyclic structures.

The systematic study of basis sets, geometry optimizations, and correlation energy for these hydrogen bonded complexes have allowed us to set up general guidelines for future calculations of this type.

3. Localized Electron Pair Polarizabilities

(W. J. Stevens, P. Jasien)

The coupled, perturbed Hartree-Fock method (CPHF) has been used to calculate the dipole polarizabilities of several prototypical non-aromatic molecules containing H, C, O, and N. The list of molecules studied and the principal components of their calculated polarizability tensors are shown in Table 4.1. All calculations were carried out with triple-zeta basis sets augmented by two polarization functions on each atomic center. The resulting polarizabilities are very close to the Hartree-Fock limit of accuracy, which is generally within 15% of experimental values for the isotropic part.

It is possible to transform the Hartree-Fock molecular orbitals, via a unitary transformation, into localized orbitals that can be identified as bonds and lone pairs. The same unitary transformation may be applied to the orbital components of the CPHF molecular polarizability. In this way, electron-pair polarizability tensors may be derived that are transferable from molecule to molecule. Preliminary transferability studies have been made using average bond and lone pair polarizabilities extracted from the saturated molecules listed in Table 4.1. Table 4.2 compares spherically averaged CPHF polarizabilities to polarizabilities obtained as a sum of transferable bond and lone pair components. The agreement is within a few percent. Anisotropic behavior and unsaturated bonds are still under investigation but show similar promise. A functional group analysis (e.g. methyl group, hydroxyl group, amide group) may be required in order to take full advantage of anisotropic tensor contributions.

Transferable polarizabilities are a key ingredient in the ab initio reaction field method being developed by the Quantum Chemistry Group. A reaction field computer code will allow the study of very large molecular systems by treating a small portion fully quantum mechanically while representing the surrounding environment by a distribution of polarizable point multipoles. The distribution of the point multipoles and their polarizabilities will be determined from ab initio calculations on prototypical molecules and fragments whose properties are assumed to be transferable.

Table 4.2. A comparison of CPHF molecular polarizabilities and polarizabilities constructed from transferrable average bond and lone-pair contributions.

Molecule	$\bar{\alpha}_{CPHF}(Å^3)$	$\bar{\alpha}_{TRANS}(Å^3)$
CH_4	2.28	2.27
CH_3OH	2.87	2.98
C_2H_5OH	4.58	4.63
C_2H_6	3.99	3.95
C_3H_8	5.68	5.62
C_2H_6O	4.58	4.73

4. Binding of Pt Complexes to DNA
(H. Basch, M. Krauss, W. J. Stevens)

The binding of the Pt diamine moiety to DNA was found to occur predominantly in a cis intrastrand chelate between neighboring guanine bases. The stereospecificity of the binding was recently called into question by the observation of anti-tumor properties for both cis and trans Pt diammine ascorbate molecules. Calculations of the relative trans effects and binding energies for the carbon and oxygen ligand binding sites have shown that the carbon site is less labile than the ammonia ligand. As a result cis chelates can be formed with the DNA in reaction with either the cis or trans Pt ascorbate molecules.

Substituted amines have also been considered in the binding of $Pt(R\text{-}NH_2)_2^{2+}$ to one or two imidazole ligands. The imidazole is used to model the N7 binding site in guanine. The binding energies for $R=CH_3$ or cyclopropyl are found to each reduce in turn by 6% from the unsubstituted values for R=H. These relatively slight variations in binding energy are not expected to play a role in the binding behavior of the substituted Pt amines to DNA. Steric effects are now being modeled to analyze the effect of the aliphatic substitution. Preliminary results indicate that steric effects are not significant for $R = CH_3$ or cyclopropyl. This work is supported by the National Foundation for Cancer Research.

5. Reaction Field Methods

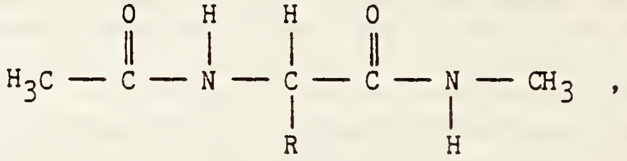
(W. J. Stevens, H. Basch, M. Krauss)

All-valence-electron quantum mechanical self-consistent-field (SCF) calculations are limited to relatively small prototypes of biomolecular systems. Using the compact effective potentials (CEP), calculations are possible at the double zeta level of basis set for molecules with 30 to 40 atoms. Systematic generation of the CEP for the elements between Na and Rn has been continued so that calculations including metal atoms can now be done with a consistent, accurate set of CEP. Nontheless, calculations on systems of the order of 1000 atoms are desirable and the reaction field method will approximate the SCF for such a system. The system is divided into two regions. In the quantum mechanical (QM) region all valence electrons are treated explicitly, while in the classical (CM) region, the charge distribution contributes to the SCF hamiltonian through the interaction of localized molecular orbital charges, moments, and polarizabilities centered at the orbital centroids of the QM charge distribution. At the boundary between the QM and CM regions, effective fragment potentials (EFP) emulate the exchange and orbital exclusion of the orbital paris that are treated classically. Approximate EFP have been generated for the interaction of non-bonded systems and are now being tested for multimers of formamide and imidazole.

6. Relative Energetics of Dipeptide Conformers

(M. Krauss, W. J. Stevens)

Double zeta level SCF calculations have been completed for a number of conformers of the dipeptides,



$$H_3C - \overset{\overset{O}{\|}}{C} - \overset{\overset{H}{|}}{N} - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - \overset{\overset{O}{\|}}{C} - \underset{\underset{H}{|}}{N} - CH_3 \ ,$$

with R = H (glycine-GLY), CH_3 (alanine-ALA), CH_2OH (serine-SER), CH_2SH (cysteine-CYS), $CH_2CO{\cdot}OH$ (aspartic acid-ASP). The conformer geometries are at equilibrium positions obtained with the molecular mechanics ECEPP code (ECEPP data supplied by Dr. S. Chin, IBM Kingston) or at published quantum optimized structures. In addition to providing data for the reaction field code development, these calculations offer a comparison of energetics with the available quantum and the classical mechanics values as seen in Table 4.3.

The agreement with the quantum results of Schäfer et. al. is reasonably good. Since the presently used basis is more flexible, this implies that the larger molecules allow for considerable basis superposition and improved conformational energetics. For GLY 3d polarization functions were added to all heavy atoms except the two methyl carbons. The second GLY conformer was then found to be lowest in energy. This result can be rationalized in terms of the importance of H-bonding in the conformers. The GLY-1 conformer contains a seven member ring with the amide hydrogen of one amide group bonded to the carbonyl oxygen in the other amide group. Double zeta calculations have been found to overestimate H-binding, and adding polarization functions provides lower and more accurate SCF values.

The comparison with the ECEPP energy orderings is not as good. However, comparison with an empirical method requires the evaluation of the dispersion interaction. Simple London type dispersion calculations for all non-bonded interactions shows very little variation with conformation. For example, the dispersion energy difference between the C1, C2, and C6 conformers of GLY is less than 0.2 kcal/mole. More accurate analyses of the correlation energy are sufficiently difficult that this estimate suggests much effort would not be rewarded. The discrepancy with classical energetics at specific conformers is likely to remain. Whether the topography of a ψ, φ map will be qualitatively different, needs to be explored for specific dipeptides.

Table 4.3. Comparison of Dipeptide Conformer Energetics Energy (kcal/mole)

Peptide	Conformer	DZ	DZP	Ref. 1	Ref. 2	Ref. 3
GLY	QM1	0.0	0.5		0.0	0.0
	QM2	0.02	0.0		0.8	0.8
	QM3	4.5	3.8		4.7	1.0
	QM4	4.0	3.2		4.3	1.2
	C1	0.3		0.0		
	C2	0.0		0.7		
	C6	8.7		1.7		
	C8	7.7		5.1		
ALA	QM1	0.0			0.0	0.0
	QM2	0.5			1.4	0.4
	QM3	2.6			2.6	8.8
SER	C1	0.0		0.0		
	C2	3.8		1.2		
CYS	C1	0.0		0.0		
	C3	4.2		0.2		
ASP	C1	2.8		0.0		
	C3	0.0		0.3		

1. Calculations with ECEPP; communicated by S. Chin, Kingston, IBM.
2. J. N. Scarsdale, C. V. Alsenoy, V. J. Klimkowski, L. Schäfer, and F. A. Momany, J. Chem. Phys. 105, 3438 (1983).
3. S. S. Zimmerman, M. S. Pottle, G. Nemethy, and H. A. Scheraga, Macromolecules 10, 1 (1977).

C. Scattering in the Presence of Radiation

1. Radiative Redistribution

(P. Julienne)

We have continued close coupled scattering calculations to calculate the fine structure branching ratios to ^2P j=1/2 and j=3/2 when a Na atom is excited to a dissociative $^2\Sigma$ or $^2\Pi$ state during a collision with a rare gas perturber atom, He, Ne, or Ar. We have also predicted the alignment (orientation) of the ^2P j=3/2 atom if a linearly (circularly) polarized photon is absorbed. These calculations have been carried out in conjunction with Drs. Linda Vahala and Mark Havey of Old Dominion University, Norfolk, Va., and have successfully explained Dr. Havey's radiative redistribution experiments. These calculations and experiments study the molecular dynamics which occur between the time a photon is absorbed into a particular molecular state and the time it is re-emitted later as fluorescence. The nonadiabatic dynamics describe the way in which the coupling of orbital, spin , and nuclear rotation angular momenta changes as the excited atoms separate. This work is supported by AFOSR.

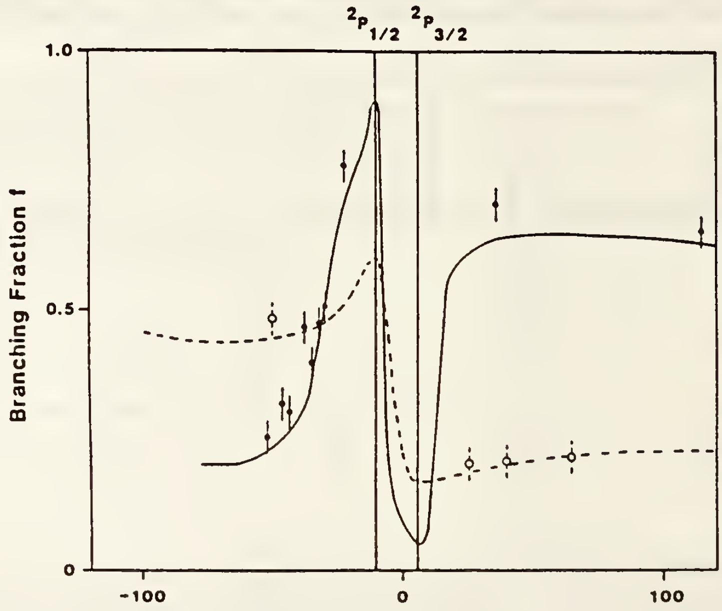


Fig. 4.2. Branching fraction f into Na $^2P(j=1/2)$ when Na ^2P j=3/2 or 1/2 is produced following excitation of Na(^2P) by photon absorption in the wings of the Na $^2P \leftarrow {}^2S$ transition broadened by collisions with Ar (solid line and filled circles) or He (dashed line and open circles). The detuning Δ is measured relative to the mean energy of the fine structure doublet. The lines give the results of close coupled scattering calculations using ab initio potentials. The points represent the measured values.

2. Application of Generalized Multichannel Quantum Defect Theory (MCQDT)

(P. S. Julienne, F. H. Mies)

The generalized MCQDT applied to molecular potentials gives a way of relating the transition amplitudes for the closely related processes of photodissociation and radiative redistribution. The theory also permits, for suitable systems, the factorization of the transition amplitude matrix for both phenomena into separate factors representing short range Franck-Condon excitation and nonadiabatic final state interactions which occur at longer range and control the distribution of product states. We have tested this factorization for the Na(^{2}P) + rare gas system studied above by applying the recoil limit for fine structure branching and polarization. The recoil limit for fine structure branching applies at sufficiently high fragment relative separation velocity, and was found to apply at much lower relative fragment kinetic energies for the light collision partner He than for Ar. Significant departures from the recoil limit apply at thermal energies, reflecting the influence of the molecular potentials on the nonadiabatic dynamics. An invited paper on the MCQDT analysis of molecular dissociation was presented at the International Conference on the Physics of Electronic and Atomic Collisions.

3. Product Distributions in Molecular Photodissociation

(P. S. Julienne and F. H. Mies)

For some time we have been using close coupled scattering calculations to calculate the nonadiabatic free-free redistribution phenomena. We are now generalizing our close coupling scattering codes to incorporate weak coupling to a bound state so we can calculate bound-free matrix elements for a final close coupled scattering state. This will enable us to calculate product distributions in molecular photodissociation. We have obtained the photodissociation code of Singer, Freed, and Band, and it is running on the University of Maryland VAX + FPS array processor computer system. We are currently implementing the renormalized Numerov algorithm of this code in our close coupling scattering code on the NBS CYBER 205 supercomputer. This work is supported by AFOSR.

4. Atomic Lineshapes and Resonance Fluorescence Spectra

(F. H. Mies and P. S. Julienne)

We are progressively expanding the capabilities of our close-coupled scattering codes to include many aspects of radiative coupling and laser-induced phenomena in molecular continuum spectroscopy. The programs incorporate the effects of non-adiabatic couplings and the resultant breakdown of the Born-Oppenheimer approximation. We directly extract the photon scattering cross-sections and redistribution spectra from the close-coupling codes, without any commitment to perturbation theory. Also we can systematically increase the intensity of the pumping laser field and achieve saturation. Our calculations yield the resultant non-linear response of the absorption cross-sections in the presence of inelastic collisions. Further we have begun to incorporate two separate laser fields into our calculations. At present the second field is treated as weak and allows us to extract the resonance fluorscence spectrum in the presence of saturation by the pumping laser field. We are now calculating the pressure-broadened half-widths of the three peaked Mollow lineshape for the resonant transition in Sr. The following are four separate accomplishments associated with this program for FY85. This work is supported by AFOSR.

a. Continuum-continuum Matrix Elements in Atomic Lineshape Theory (F. H. Mies and P. S. Julienne)

The calculation of the pressure-broadened lineshape for the atomic transition $A_i + \hbar\omega_L \rightarrow A_f^*$ requires the evaluation of the following continuum-continuum matrix element

$$S_{fi}^{rad} = -i\pi\hbar \, \langle \psi_f^-(E^-) | \Omega_L | \psi_i^+(E^+) \rangle. \tag{1}$$

where the field-free multichannel wavefunctions $\psi^\pm$ incorporate non-adiabatic effects and the breakdown of the usual Born-Oppenheimer Approximation. This expression applies in the weak-field limit, when the Rabi frequency Ω_L associated with the photon $\hbar\omega_L$ is very small and when the radiative scattering matrix element S_{fi}^{rad} can be evaluated in perturbation theory. The precise details of the lineshape analysis depends on the extent to which the incident photon is detuned from the exact atomic resonance energy $\hbar\omega_{fi}^o = (E_f^* - E_i)$,

$$\Delta_{fi} = \omega_L - \omega_{fi}^o \tag{2}$$

In the wings of the line, where Δ_{fi} is very large compared to the homogeneous width of the atomic transition, the absorption coefficient is directly proportional to the radiative scattering cross section determined by the transition matrix elements in Eq. (1). The impact approximation to the pressure-broadened half-width in the vicinity of the line center can can also be expressed in terms of S_{fi}^{rad}.

For dipole allowed atomic transitions the radiative matrix element which defines the pressure-broadened atomic lineshape is only conditionally convergent. Using a commutator technique to redefine the integral we can isolate, and ultimately reject, the contribution of an indeterminant asymptotic surfce integral which is associated with the energy normalization of the continuum wavefunctions which describe the binary collision of the atom and its perturber. The remaining contributions to the atomic lineshape are absolutely convergent. Since the transformed integrals apply as well to the multichannel wavefunction they encompass the effects of non-adiabatic and inelastic scattering. Further we show the relationship of the commutator integral to the exact requirements of close-coupled scattering theory for radiatively-induced collisions. This scattering analysis suggests that we should interpret the convergent lineshape as an expression of multichannel inelastic collisions between field-dressed atomic states. The same interpretation applies both in the impact and the static limit. We would advocate that, since stable close-coupling codes are required to generate the multichannel wavefunctions in Eq. (1), it is a simple matter to merely expand the set of coupled equations to directly include the radiative coupling between channel states as required by the dressed atom boundary conditions and completely avoid explicit numerical quadrature of the multichannel matrix elements in Eq. (1).

b. Impact Limit in Weak Laser Fields
(F. H. Mies and P. S. Julienne)

Care must be taken when one attempts to apply the perturbation expression near the impact limit for allowed transitions. As the detunings $\Delta_{f'i'}$ approach zero, the major contributions to the matrix element (1) occur in the asymptotic regions R=∞ and S_{fi}^{rad} becomes proportional to $1/\Delta_{f'i'}$,

$$S_{fi}^{rad}\ (\Delta_{f'i'}\rightarrow 0) \sim \sum_{f'} \sum_{i'} \frac{\langle \psi_{f'} | \Omega_r | \psi_{i'} \rangle}{2\Delta_{f'i'}}\ [S_{f,f'}\delta_{f,f'}S_{i'i}] \quad . \qquad (3)$$

This divergent limiting form is predicted by the impact theories of Shafer and Gordon and Ben-Reuven. In fact we can numerically extract this matrix element from the full close-coupling codes for small $\Delta_{f'i'}$ and then employ these same impact theories to obtain accurate estimates of the collisional half-widths of pressure broadened lines. Note that the near resonance photon simultaneously causes a collective coupling among <u>all</u> the asymptotic channel states $\psi_{fi'}$ and $\psi_{i'}$ and we can never factor Eq. (3) into distinct products of initial and final state terms.

We have performed multichannel close-coupled calculations of the $Sr(^1S) \rightarrow Sr(^1P)$ transition broadened by Ar. A comparison of the exact close-coupled raditive scattering matrix elements to eq. (3) confirms the validity and utility of our numerical procedures for obtaining pressure broadened half-widths in the weak field limit. This procedure should enjoy substantial application throughout lineshape theory.

c. Impact Limit and Pressure Broadening of Mollow Sidebands in Intense Fields

(F. H. Mies)

Our close-coupled procedures for evaluating S_{fi}^{rad} avoid any commitment to weak fields or perturbative estimates of S_{fi}^{rad}. Of course, in the weak field limit, we should choose a representative Rabi frequency sufficiently small to insure that Eq. (1) remains linearly proportional to Ω_L and yet sufficiently large to insure numerical accuracy of the close-coupled radiative scattering matrix elements. As long as the magnitude of S_{fi}^{rad} remains below about 10^{-3} there seems to be a one-to-one correspondence to Eqs. (1) and (3).

Of course true deviations from linearity must ultimately prevail as the actual field strength increases. Such effects become particularly important in the impact limit, and ultimately become manifest as pronounced sidebands in the fluorescence spectrum of the pressure-broadened atomic lineshape symmetrically located at frequencies $\pm\Omega_L$ from the scattered Raleigh line.

Experimental observations of the three-peaked Mollow lineshape have been made for Sr+Ar. We have made some preliminary calculations for Sr+Ar in the strong-field limit and confirm that our close-coupling procedures reproduce the dressing of the asymptotic Sr states and yields a three-level version of Eq. (3). We are now in the process of calculating the complete impact limit half-width for each of the separated peaks as well as the expected polarization properties of the intense field fluorescence.

In addition to the spectrum there have been experimental estimates (and semiclassical calculations) of the inelastic collisional energy transfer between the dressed Sr atomic states which causes collisional redistribution of the resonance fluorescence. These cross-sections are also being extracted from our calculations.

D. Multiphoton Effects in Resonance Fluorescence Spectra

(F. H. Mies)

Until now we have only allowed for a single photon transition in our close-coupled equations. In order to calculate the redistribution spectrum in intense fields we have introduced a second laser field with Rabi frequency Ω_P and frequency ω_P. So far we have only permitted a weak probe intensity Ω_P and have obtained a beautiful mapping of the Mollow lineshape for Sr+ Ar as a function of the probe detuning.

In view of our encouraging results with a weak probe field our ultimate goal is to also saturate this field and examine the close-coupled calculations for effects associated with four wave mixing. Again, such effects have been observed in Sr + Ar and we are confident that our techniques can derive reliable estimates of the appropriate cross-sections.

E. Future Plans

In the area of electronic structure calculations the Quantum Chemistry Group intends to move ahead in 1) the development of the reaction field methods and code, 2) the calculation of accurate prototype energy and properties for amides and nucleic acid components, and 3) model problems on H-bonding in enzymes, metal binding to both proteins and nucleic acids, and the analog behavior of phosphates and vandates in nucleus-substrate binding.

The reaction field development is the major thrust. As we improve the methods and the code we intend to apply the model calculations in category three to enzyme binding and spectroscopy problems. In the interim calculations in category two will provide insight into polarizabilities and dispersion interactions in large aromatic systems, the electronic structure of phosphorus and vanadium five-coordinate molecules, accurate hydrogen-bonding energies comparing H, O, and S sites, and metal binding to small amides and isolated nucleic acid bases.

Future plans in the scattering analysis call for further development and implementation on the CYBER 205 of efficient numerical algorithms for calculating accurate photodissociation transition amplitudes to a manifold of strongly coupled final states. Such codes enable us to calculate product state distributions following photodissociation. Initial calculations will be on diatomic systems with later generalization to small polyatomic systems. Specific calculations are planned for the NaK molecule in conjunction with experimental studies to be done at the University of Maryland. In addition to our numerical studies, we also will continue to develop an analytic half-collision theory of photodissociation and photo-assisted collisions based on generalized multichannel quantum defect theory. This approach leads to much insight into photodissociation dynamics and suggest various limiting approximations which need further testing, such as recoil or frame transformation approximations for product alignment or fine structure branching. We will also continue to develop the nonadiabatic theory of atomic line broadening in two areas. First, we will study the Lorentzian asymmetry of the core profile. Second, we will incorporate the effect of strong laser fields, including the effect of collisions in broadening the Mollow line shapes and the effect of AC Stark shifts in modifying inelastic collision cross sections.

5. PUBLICATIONS

(a) Publications of Past Year

Casassa, M. P., Heilweil, E. J., Stephenson, J. C., and Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation of Molecules on Surfaces: Hydroxyl Groups on Silica Surfaces," J. Vac. Soc. Tech. A3, 1655 (1985).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Temperature Dependence of the Vibrational Population Lifetime of OH(v=1) in Fused Silica," Chem. Phys. Letters, 117, 185 (1985).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Vibrational Deactivation of Surface OH Chemisorbed on SiO_2: Solvent Effects," J. Chem. Phys. 82, 5216 (1985).

Heilweil, E. J., Casassa, M. P., Cavanagh, R. R., and Stephenson, J. C., "Vibrational Energy Relaxation of Adsorbates on Surfaces," SPIE Proceedings 533, 15 (1985).

Heilweil, E. J., Casassa, M. P. , Cavanagh, R. R., and Stephenson, J. C., "Picosecond Vibrational Energy Relaxation of Surface Hydroxyl Groups on Colloidal Silica," J. Chem. Phys. 81, 2856 (1984).

Hougen, J. T. and Ohashi, N., "Group Theoretical Treatment of the Planar Internal Rotation Problem in $(HF)_2$," J. Mol. Spectrosc. 109, 134-165 (1985).

Hougen, J. T., "Summary of Group Theoretical Results for Microwave and Infrared Studies of H_2O_2," Can. J. Phys. 62, 1392-1402 (1984).

Jacox, M. E., "Ground-State Vibrational Energy Levels of Polyatomic Transient Molecules," J. Phys. Chem. Ref. Data 13, 945-1068 (1984).

Jacox, M. E., "Spectroscopy and Photochemistry of Free Radicals Formed by the Reaction of F Atoms with Small Molecules," Rev. Chem. Intermed. 6, 77-120 (1985).

Julienne, P. S., "Collision Induced Radiative Transitions at Optical Frequencies," in Phenomena Induced by Intermolecular Interactions, ed., by G. Birnbaum (Plenum Press, 1985).

King, D. S. and Stephenson, J. C., "Kinetic Energy Disposal in the Unimolecular IRMPD of Methyl Nitrite," Chem. Phys. Letts. 114, 461 (1985).

King, D. S. and Stephenson, J. C., "Infrared Multiphoton Dissociation of Methyl Nitrite in a Molecular Beam; Internal States of the Nitric Oxide Fragment," J. Chem. Phys. 82, 2236 (1985).

King, D. S., Mantell, D. A., and Cavanagh, R. R., "NO Thermally Desorbed from a Saturation Coverage on Pt(111): Internal State Distributions," J. Chem. Phys. 82, 1046 (1985).

King, D. S., "Product State and Kinetic Energy Distributions in the Ultraviolet Photodissociation of the NO-Ar van der Waals Molecule," J. Chem. Phys. 82, 3629 (1985).

King, D. S. and Stephenson, J. C., "Energy Distribution in the Nitric Oxide Fragments from the ν_7 Vibrational Predissociation of NO-C_2H_4," J. Chem. Phys. 82, 5286 (1985).

Krauss, M. and Stevens, W. J., "Electronic Structure of FeO and RuO," J. Chem. Phys. 82, 5584 (1985).

Lovas, F. J., "Microwave Spectra of Molecules of Astrophysical Interest XXII. Sulfur Dioxide (SO_2)," J. Phys. Chem. Ref. Data 14, 395-488 (1985).

Lovas, F. J., "Microwave Spectra of Atmospheric Species," Proc. of CMA/NBS Workshop on Atmospheric Spectra, (ed., by A. Weber, June 1985) p. IIIA14.

Lovas, F. J., "Critically Evaluated Microwave Spectral Data," Proc. of CMA/NBS Workshop on Atmospheric Spectra, (ed., by A. Weber, June 1985) p. IV21.

Maki, A. G., "Infrared Spectra and Atmospheric Chemistry," Proc. of CMA/NBS Workshop on Atmospheric Spectra, (ed., by A. Weber, June 1985) p. IIIB1.

Maki, A. G., Pine, A. S., and Dang-Nhu, M., "A Doppler-Limited Study of the Infrared Spectrum of Allene from 2965 to 3114 cm^{-1}," J. Mol. Spectrosc. 112, 459-481 (1985).

Maki, A. G. and Wells, J. S., "High Resolution Spectrum of the ν_5 Band of Nitric Acid (HNO_3) Near 880 cm^{-1}," J. Mol. Spectrosc. 108, 17-30 (1984).

Mies, F. H., "Adiabatic Analysis of Distant Perturbations: Application to Herzberg-Teller Vibronic Coupling Theory," Molec. Phys. 54, 1423-1436 (1985).

Mies, F. H. and Julienne, P. S., "A Molecular Half Collision Analysis of Atomic Lineshapes in Spectral Lineshapes," Vol. 3, (ed., F. Rostas) W. de Gruyter and Co., Berlin, pp. 393-420 (1985).

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. Biomol. Struct. Dynam. 2, 1157 (1985).

Ohashi, N. and Hougen, J. T., "The Torsional-Wagging Tunneling Problem and the Torsional-Wagging-Rotational Problem in Hydrazine," J. Mol. Spectrosc. 112, 384-400 (1985).

Petersen, F. R., Wells, J. S., Jennings, D. A., and Maki, A. G., "Improved Deuterium Bromide 1-0 Band Molecular Constants from Heterodyne Frequency Measurements," J. Mol. Spectrosc. 107, 48-61 (1984).

Pine, A. S., Fried, A., and Elkins, J. W., "Spectral Intensities in the Fundamental Bands of HF and HCl," J. Mol. Spectrosc. 109, 30-45 (1985).

Pine, A. S., Lafferty, W. J., and Howard, B. J., "Vibrational Predissociation, Tunneling and Rotational Saturation in the HF and DF Dimers," J. Chem. Phys. 81, 2939-2950 (1984).

Pine, A. S., "Tunable Laser Spectroscopy of Upper Atmospheric Molecules," Proc. of CMA/NBS Workshop on Atmospheric Spectra, (ed., by A. Weber, June 1985) p. III B8.

Pollock, C. P., Petersen, F. R., Jennings, D. E., Wells, J. S., and Maki, A. G., "Absolute Frequency Measurements of the 00°2-00°0, 20°1-00°0 Bands of N_2O by Heterodyne Spectroscopy," J. Mol. Spectrosc. 107, 62-71 (1984).

Raab, M. and Weber, A., "Amplitude Modulated Heterodyne Polarization Spectroscopy," J. Opt. Soc. Am. B2, 1476 (1985).

Ratcliff, L., Konowalow, D. D., and Stevens, W. J., "Transition Moments for Low-Lying Excited States in NaK," J. Mol. Spectrosc. 110, 242 (1985).

Rumble, J. R., Jr., Stevens, W. J., and Truhlar, D. G., "Effective Electron Correlation in the Target Wavefunction on Electron-Molecule Scattering," J. Phys. B17, 315 (1984).

Snyder, L. E., Henkel, C., Hollis, J. M., and Lovas, F. J., "Observations of the SiO_2 Radical Toward IRC + 10216 at 1.27 Centimeters," Astrophys. J. (Letters) 290, L29-L33 (1985).

Stevens, W. J., Basch, H., and Krauss, M., "Compact Effective Core Potentials and Efficient Shared-Exponent Basis Sets for the First- and Second-Row Atoms, Li-Ar," J. Chem. Phys. 81, 6026 (1984).

Suenram, R. D., Lovas, F. J., and Stevens, W. J., "Reaction Products from a Microwave Discharge of N_2 and H_2S, The Microwave Spectrum Two Conformers of Sulfur Diimide (H-N=S=N-H)," J. Mol. Spectrosc. (1985).

Weber, A., "Proceedings of the CMA/NBS Workshop on Atmospheric Spectra," November 3-4, 1983, (June 1985).

Wells, J. S., Jennings, D. A., Hinz, A., Murray, J. S., and Maki, A. G., "Heterodyne Frequency Measurements on N_2O at 5.3 and 9.0μm," J. Opt. Soc. Am. B2, 857-861 (1985).

(b) Publications in Progress

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. (in press).

Basch, H., Krauss, M., and Stevens, W. J., "Cation Binding Effect on H-Bonding," J. Am. Chem. Soc. (submitted).

Basch, H., Krauss, M., Stevens, W. J., and Cohen, D., "Binding of $Pt(NH_3)_3^{2+}$ to Nucleic Acid Bases," J. Inorg. Chem. (submitted).

Basch, H., Krauss, M., Stevens, W. J., and Cohen, D., "Electronic and Eleometric Structures of $Pt(NH_3)_2^{2+}$, $Pt(NH_3)_2Cl_2$, $Pt(NH_3)_3X$, $Pt(NH_3)_2XY$ (X,Y = OH^-, H_2O)," Inorg. Chem. (submitted).

Basch, H. Krauss, M., and Stevens, W. J., "Cation Binding Effect on H-Bonding," J. Am. Soc. (submitted).

Bodaness, R. S., Heller, D. F., Krasinski, J., and King, D. S., "Direct Two-Photon Excitation of the Tumor Localizing Photo-Sensitizer Hematoporphyrin Derivative at 750 nm via the Soret Band System," J. Biological and Biochemical Sciences (WERB review).

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 Surfaces: Isotope and Temperature Dependence," Phys. Rev. Lett. (submitted).

Casassa, M. P., Heilweil, E. J., Stephenson, J. C., and Cavanagh, R. R., "Time-Resolved Measurements of Vibrational Relaxation at Surfaces," J. Electronic Spectry. (accepted).

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. (in press).

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

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. <u>B</u>, (in press).

Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer," J. Mol. Spectrosc. (accepted).

Howard, B. J. and Pine, A. S, "Rotational Predissociation and Libration in the Infrared Spectrum of Ar-HCl," Chem. Phys. Letters (submitted).

Jacox, M. E., "Comparison of the Ground-State Vibrational Fundamentals of Diatomic Molecules in the Gas Phase and in Inert Solid Matrices," J. Mol. Spectrosc. 113, (in press).

Jacox, M. E., "Reaction of F Atoms with Methyl Halides. Vibrational Spectra of CH_3XF and of $H_2CX\cdots HF$ Trapped in Solid Argon," J. Chem. Phys. 83, (in press).

Jasien, P. G. and Stevens, W. J., "Calculated Proton Affinities for Some Molecules Containing Group VI Atoms," J. Chem. Phys. (in press).

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. (in press).

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. (in press).

King, D. S. and Cavanagh, R. R., "Laser Studies of Molecule-Surface Interactions," Review prepared for Springer Series in Chemical Physics (submitted).

Krauss, M., Stevens, W. J., and Basch, H., "Relativistic Effective Potential SCF Calculations of AgH and AuH," J. Comp. Chem. (in press).

Lovas, F. J., "Recommended Rest Frequencies for Observed Interstellar Molecular Microwave Transitions," J. Phys. Chem. Ref. Data (submitted).

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

Mialocq, J.-C. and Stephenson, J. C., "Picosecond Laser Study of the Collisionless Photodissociation of Dimethylnitramine at 266 nm," Chem. Phys. Lett. (submitted).

Mialocq, J.-C. and Stephenson, J. C., "Picosecond Laser Induced Fluorescence Study of the Collisionless Photodissociation of Nitrocompounds at 266 nm" Chem. Phys. (in WERB review).

Mies, F. H., Julienne, P. S., Band, Y. B., and Singer, S., "A Convergent Analysis of Radiative Matrix Elements in Atomic Lineshape Theory," J. Phys. B (submitted).

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. Biomol. Str. Dyns. (in press).

Ohashi, N., Lafferty, W. J., and Olson, W. B., "Fourier Transform Far Infrared Spectrum of Hydrazine," J. Mol. Spectrosc. (submitted).

Pine, A. S., Maki, A. G., and Chou, N.-Y., "Pressure Broadening, Lineshapes, and Intensity Measurements in the 2←0 Band of NO," J. Mol. Spectrosc. (in press).

Pine, A. S. and Fried, A., "Self Broadening in the Fundamental Bands of HF and HCl," J. Mol. Spectrosc. (in press).

Pine, A. S. and Howard, B. J., "Hydrogen-Bond Energies of the HF and HCl Dimers from Absolute Infrared Intensities," J. Chem. Phys. (submitted).

Rosenkrantz, M. E. and Krauss, M., "Damped Dispersion Interaction Energies for He-H_2, Ne-H_2, and Ar-H_2," Phys. Rev. (submitted).

Suenram, R. D., Lovas, F. J., and Pickett, H. M., "Millimeter Wave Spectrum of Peroxynitric Acid," J. Mol. Spectrosc. (submitted).

Thompson, G. A., Maki, A. G., and Weber, A., "The Infrared Spectrum of GeO," J. Mol. Spectrosc. (submitted).

Vahala, L., Julienne, P. S., and Havey, M. D., "Nonadiabatic Theory of Fine-Structure Branching Cross Sections for NaHe, NaNe, and NaAr," Phys. Rev. A (submitted).

Wells, J., Hinz, A., and Maki, A. G., "Heterodyne Frequency Measurements on N_2O Between 1257 cm^{-1} and 1340 cm^{-1}," J. Mol. Spectrosc. (in press).

6. TALKS

Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Molecules on Surfaces," 31st National Meeting of the American Vacuum Society, Reno, NV, December 1984.

Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," Gordon Conference on Dynamics of Gas-Surface Interactions, New London, NH, July 1985.

Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," Exxon Research and Engineering Co., Annandale, NJ, May 1985.

Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," IBM Watson Research Center, Yorktown Heights, NY, June 1985.

Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," General Motors Research Labs, Warren, MI, May 1985.

Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," Sandia National Laboratory, Livermore, CA, May 1985.

Casassa, M. P., "Time-Resolved Measurements of Vibrational Relaxation on Surfaces," Aerospace Corporation, Los Angeles, CA, May 1985.

Casassa, M. P., "Dynamics of Vibrational Energy in Molecules: Vibrational Relaxation of Molecules Chemisorbed on Surfaces," Sandia National Laboratory, Albuquerque, NM, March 1985.

Casassa, M. P., "Picosecond Measurements of Vibrational Relaxation on Surfaces," Surface Science Division, National Bureau of Standards, Gaithersburg, MD, February 1985.

Casassa, M. P., Heilweil, E. J., Cavanagh, R. R., and Stephenson, J. C., "Vibrational Energy Relaxation of Adsorbates on Surfaces," Symposium on Surface Bonds, ACS National Meeting, Chicago, IL, September 1985.

Heilweil, E. J., "Time-Resolved Vibrational Energy Decay of Surface Adsorbates," Microphysics of Adsorbates Conference, Santa Fe, NM, February 1985.

Heilweil, E. J., "Time-Resolved Vibrational Energy Decay of Surface Adsorbates," Sandia National Labs, February 1985.

Heilweil, E. J., "Time-Resolved Vibrational Energy Decay of Surface Adsorbates," Howard University, April 1985.

Heilweil, E. J., "Vibrational Energy Decay of Surface Adsorbates," Virginia Commonwealth University, April 1985.

Heilweil, E. J., "Vibrational Energy Decay of Surface Adsorbates," Time-Resolved Vibrational Spectroscopy Conference, Bayreuth, West Germany, June 1985.

Heilweil, E. J., "Picosecond Vibrational Relaxation of Adsorbates at Colloidal Interfaces," Gordon Research Conference, Chemistry at Interfaces, July 1985.

Hougen, J. T., "Point-Groups, Permutation-Inversion Groups and Extended Groups," IMS Colloquium, Okazaki, Japan, November 1984.

Hougen, J. T., "The Philosophy and Mathematics of Constructing Effective Hamiltonians for Molecules with Large Amplitude Vibrational Motions," Seminar for the Theoretical Group at IMS, Okazaki, Japan, November 1984.

Hougen, J. T., "Selected Topics from Atomic and Molecular Spectroscopy," IMS, Okazaki, Japan, November 1984.

Hougen, J. T., "The Avoided Crossing Technique of Meerts and Ozier: Its Application to A values and Barrier Heights, and One Selection Rule Puzzle," Seminar for the High Resolution Group at IMS, Okazaki, Japan, December 1984.

Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems," Seminar for High Resolution Group at IMS, Okazaki, Japan, December 1984.

Hougen, J. T., "Application of Vibration-Rotation Tunneling Theory to the Gas Phase Water Dimer Spectrum," Molecular Spectroscopy Division Seminar, NBS, January 1985.

Hougen, J. T., "Tunneling Motion in the Water Dimer," Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, CA, April 1985.

Hougen, J. T., Four lectures on "Group Theory in Molecular Spectroscopy," at the Chemistry Department, University of California, Berkeley, CA, April 1985.

Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer," Washington Meeting of the American Physical Society, Washington, D.C., April 1985.

Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems, as Applied to the Water Dimer," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Hougen, J. T. and Ohashi, N., "The Torsional-Wagging Tunneling Problem and Torsional-Wagging-Rotatinal Problem in Hydrazine," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Hougen, J. T., "The Use of Extended Permutation-Inversion Groups for Constructing Hyperfine Hamiltonians for Symmetric Top Internal Rotor Molecules Like H_3C-SiH_3," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Hougen, J. T., "Symmetry Beyond Point Groups in Molecular Spectroscopy," Department of Chemistry, University of Chicago, Chicago, IL, July 1985.

Hougen, J. T., "Symmetry Beyond Point Groups in Molecular Spectroscopy," Seventeenth International Symposium on Free Radicals, Granby, CO, August 1985.

Hougen, J. T., "A Generalized Internal Axis Method for High Barrier Tunneling Problems, As Applied to the Water Dimer," American Chemical Society, Chicago, IL, September 1985.

Hougen, J. T., "The Use of Extended Permutation-Inversion Groups for Constructing Hyperfine Hamiltonians for Symmetric-Top High-Barrier Internal Rotor Molecules," Ninth Colloquium on High Resolution Molecular Spectroscopy, Riccione, Italy, September 1985.

Howard, B. J. and Pine, A. S., "Near-Infrared Spectra of Rare-Gas-HCl Complexes," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Jacox, M. E., "Spectroscopic Studies of the Early Stages in the Decomposition of Energetic Materials," Workshop on the Initiation of the Chemical Decomposition of Energetic Materials, Office of Naval Research, Annapolis, MD, October 1984.

Jacox, M. E., "Spectroscopy of Intermediates in the Decomposition of Energetic Materials. Experimental Studies at the National Bureau of Standards," Workshop on Diagnositics for Ignition Mechanisms, Army Research Office, Aberdeen, MD, November 1984.

Jacox, M. E., "Spectra of Free Radicals Formed in the Primary Reaction of F Atoms with the Substituted Methanes," 7th Winter Fluorine Conference, Division of Fluorine Chemistry, American Chemical Society, Orlando, FL, February 1985.

Jacox, M. E., "Dolphus E. Milligan - A Scientific Retrospective," Dedication Symposium, Dolphus E. Milligan Science Research Institute, Atlanta University Center, Atlanta, GA, March 1985.

Jacox, M. E., "Matrix Isolation Studies of the Decomposition and Ionization of Small Molecules at Energies Between 11.5 and 16.8 eV," Symposium on Ultraviolet Photochemistry, 68th Canadian Chemical Conference, Kingston, Ontario, Canada, June 1985.

Jacox, M. E., "Spectra of Free Radicals Formed in the Primary Reaction of F Atoms with the Methyl Halides," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Jacox, M. E., "Spectra of Free Radicals Formed in the Primary Reaction of F Atoms with the Substituted Methanes," 5th International Colloquium on the Spectroscopy of Matrix Isolated Species, Fontevraud, France, July 1985.

Jacox, M. E., "The Vibrational Spectrum of the COOH Free Radical Trapped in Solid Argon," 17th International Symposium on Free Radicals, Granby, CO, August 1985.

Jacox, M. E., "Vibrational and Electronic Spectra of Transient Species Trapped in Solid Argon and Neon," Symposium on Theoretical and Experimental Studies of Transient Species, 190th National Meeting of the American Chemical Society, Chicago, IL, September 1985.

Jasien, P. G. and Stevens, W. J., "Proton Affinities of Some Molecules Containing Group VI Atoms," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Jennings, D. E., Weber, A., and Brault, J. W., "Fourier Transform Raman Spectroscopy of H_2 and D_2 in Flames," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Julienne, P. S., "Theory of Atomic Collisions in Laser Fields," Physics Department Seminar, University of Missouri, Rolla, MO, October 1984.

Julienne, P. S., "Nonadiabatic Half-Collision Theory of Line Broadening, Laser-induced Collisions, and Photodissociation," Atomic and Molecular Theory Group Seminar, Lawrence Livermore Laboratory, Livermore, CA, December 1984.

Julienne, P. S., "Analytic Multichannel Theory of Molecular Dissociation," International Conference on the Physics of Electronic and Atomic Collisions," Stanford University, Palo Alto, CA, August 1985.

King, D. S., "State Selective Studies of Molecular-Surface Dynamics," Optical Society of America National Meeting, San Diego, CA, October 1984.

King, D. S., "State Selective Studies of Molecule-Surface Interactions," University of California, Irvine, CA, November 1984.

King, D. S., "Dynamics in Chemical Bond Breaking Processes," Molecular Spectroscopy Division Seminar, NBS, February 1985.

King, D. S., "Energy Distributions in Thermally Desorbed Molecules," Conference on the Dynamics of Molecular Collisions, Utah, July 1985.

Krauss, M., "Electronic Structure of Metal Oxides," IBM, Kingston, NY, February 1985.

Krauss, M., "Effective Potentials in Quantum Chemistry," Rensselaer Polytechnical Institute, NY, April 1985.

Lafferty, W. J. and Olson, W. B., "High Resolution Spectrum of the ν_2 and ν_3 Bands of HOCl," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Lovas, F. J. and Suenram, R. D., "Pulsed Beam Microwave Study of the van der Waals Complex $Ar \cdots CH_2CHCN$," Spring Meeting of the American Physical Society, Crystal City, MD, April 1985.

Lovas, F. J., "Rotational Studies of Weakly-Bound Molecules by Conventional and Fourier Transform Microwave Spectroscopy," Institut für Physikalische Chemie der Universität Kiel, Kiel, Germany, September 1985.

Lovas, F. J. and Suenram, R. D., "Pulsed Beam Microwave Study of the van der Waals Complexes Ar···CH_2CHCN and Kr···OCS," Ninth Colloquium on High Resolution Molecular Spectroscopy, Riccione, Italy, September 1985.

Lovejoy, R. W., Schaeffer, R. D., and Olson, W. B., "High Resolution Infrared Spectrum on SiH_3D," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Maki, A. G., "Laboratory Studies of Atmospheric Molecules at NBS," Workshop on the Spectroscopic Studies of Atmospheric Species, NASA-Langley Research Center, Hampton, VA, October 1984.

Maki, A. G., Pine, A. S., Wells, J. S., Jennings, D. A., Fayt, A., and Goldman, A., "Laboratory Studies of the Infrared Spectra of Atmospheric Species," Topical Meeting on Optical Remote Sensing of the Atmospheric, Incline Village, Nevada, January 1985.

Maki, A. G. and Pine, A. S., "Pressure Broadening and Intensity Measurements lor the 2-0 Band of NO," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Mies, F. H., "Collisional Redistribution of Resonant Radiation in Intense Laser Fields," Conference on Dynamics of Molecular Collisions, Snowbird, Utah, July 1985.

Ohashi, N., Lafferty, W. J., and Olson, W. B., "Far-Infrared Spectrum of the Torsional Band of Hydrazine," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Pine, A. S., "Difference-Frequency Laser Spectroscopy of Hydrogen-Bonded and van der Waals Complexes," Joint MIT-Harvard Physical Chemistry Colloquium, Harvard University, Cambridge, MA, December 1984.

Pine, A. S., "High-Resolution Studies of Predissociation in Hydrogen-Bonded and van der Waals Complexes," Chemistry Department, University of California, Berkeley, CA, January 1985.

Pine, A. S., "Infrared Spectroscopy of Hydrogen-Bonded and van der Waals Complexes Using a Difference-Frequency Laser," Western Spectroscopy Association Meeting, Asilomar, CA, February 1985.

Pine, A. S., "Difference-Frequency Laser Spectroscopy of Hydrogen-Bonded and van der Waals Complexes," American Physical Society Spring Meeting, Washington, D.C., April 1985.

Pine, A. S. and Fried, A., "Intensities and Self-Broadenings in HF and HCl," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Stevens, W. J., "Compact Effective Potentials and Basis Sets," IBM Laboratories, Kingston, NY, October 1984.

Stevens, W. J., "Cation Binding Effect on Inidizole Tautomerism," 5th International Congress on Quantum Chemistry, Montreal, Canada, August 1985.

Suenram, R. D. and Lovas, F. J., "Microwave Spectrum of the Ar•••Acrylonitrile van der Waals Complex" 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Stephenson, J. C., "Vibrational Energy Transfer," Chemistry Department, Howard University, April 1985.

Stephenson, J. C., "Vibrational Energy Transfer in Adsorbates on Surfaces," Chemistry Department, MIT, May 1985.

Stephenson, J. C., "Vibrational Energy Transfer in Adsorbates on Surfaces," Gordon Conference on Molecular Energy Transfer, July 1985.

Stephenson, J. C., "Vibrational Relaxation of Chemical Bonds in Liquids and on Surfaces," International Conference on Photochemistry, June 1985.

Thompson, G. A., Maki, A. G., and Weber, A., "More Diode Laser Spectra of Diatomic Molecules," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Thompson, G. A., Maki, A. G., and Weber, A., "Infrared Measurements of High Temperature Diatomic Species," XVII European Congress on Molecular Spectroscopy, Madrid, Spain, September 1985.

Weber, A., Lafferty, W. J., and Olson, W. B., "High Resolution Infrared Spectrum of Cyanogen," 40th Symposium on Molecular Spectroscopy, Columbus, OH, June 1985.

Weber, A., Jennings, D. E., and Brault, J. W., "Fourier Transform Raman Spectroscopy of Gases," XVII European Congress on Molecular Spectroscopy, Madrid, Spain, September 1985.

Weber, A., Jennings, D. E., and Brault, J. W., "Fourier Transform Raman Spectroscopy of Gases," Ninth Colloquium on High Resolution Molecular Spectroscopy, Riccione, Italy, September 1985.

Weber, A., "Recent Work in High Resolution Molecular Spectroscopy at NBS," Physics Department, University of Bayreuth, Bayreuth, Germany, September 1985.

7. MOLECULAR SPECTROSCOPY DIVISION SEMINARS

Allen, L. C., Department of Chemistry, Princenton University, Princenton, NJ, "Electronic Mechanism of Carbonic Anhydrase," March 1985.

Andrews, L., Department of Chemistry, University of Virginia, Charlottesville, VA, "High and Low Energy Species: Spectroscopy of Molecular Ions and HF Complexes in Solid Argon," November 1984.

Band, Y. B., Ben-Gurion University, Israel, "Optical Properties of Molecules with Large Excited State Absorption," July 1985.

Band, Y. B., Ben-Gurion University, Israel, "Photodissociation of Diatomic Molecules to Atoms with Non-vanishing Angular Momentum," July 1985.

Bowen, K. H., Department of Chemistry, Johns Hopkins University, Baltimore, MD, "Negative Ion Photoelectron Spectroscopy of Negative Cluster Ions," May 1985.

Evenson, K., Time and Frequency Division, NBS, Boulder, CO, "Tunable Far Infrared Spectroscopy," November 1984.

Fraser, G. T., Chemistry Department, Harvard University, MA, "Nonrigidity and Vibrational Predissociation in Ammonia van der Waals Complexes," March 1985.

Herman, R., Physics Department, Penn State University, "Collisional Interference in the Vibration-Rotation Spectra of H_2 and HD," October 1984.

Hirota, E., Institute for Molecular Science, Myodaiji, Okazaki, Japan, "Infrared Laser Kinetic Spectroscopy," April 1985.

Hochstrasser, R. M., Department of Chemistry, University of Pennsylvania, PA, "Ultrafast Relaxation Processes in Condensed-Phase Molecular Systems," May 1985.

Howard, B. J., Physical Chemistry Laboratory, Oxford University, England, "IR Studies on Intermolecular Interactions in Weakly Bound Species," April 1985.

Jackson, W. M., Chemistry Department, Howard University, "Laser Studies of Reaction Dynamics in Gases and on Surfaces," September 1985.

Kunz, T., Department of Chemistry, Rice University, Houston, TX, "Photochemistry of Formyl Fluoride," February 1985.

Ladik, J., University Erlangen-Nürnberg, Germany, "Quantum Theory of Polymers: Solid State Aspects," September 1985.

Mills, I. M., University of Reading, England, "Molecular Vibrations Seen as Local Modes," April 1985.

Moore, R., Department of Chemistry Virginia Commonwealth University, VA, "Picosecond Intermolecular Vibrational Relaxation in the Gas Phase," January 1985.

Pickett, H. M., Jet Propulsion Laboratory, Pasadena, CA, "Spectroscopy in the World Above One Terahertz," March 1985.

Schweitzer, E., Chemistry Department, MIT, Cambridge, MA, "Spectroscopic Probes of Infrared Multiphoton Dissociation," February 1985.

Shostak, S., University of Rochester, Rochester, NY, "Studies of Infrared Laser Excited Molecules by MBER and Maser Spectroscopy," February 1985.

van Duijnen, P., Theoretical Chemistry Group, Laboratory of Chemical Physics, Cromingen, The Netherlands, "Reaction Field Hamiltonians and Applications to Biomolecules," June 1985.

8. 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.

Bevan, John W., Chemistry Department, Texas A & M University, worked with W. J. Lafferty and W. B. Olson on the Fourier transform infrared spectra of hydrogen bonded molecules.

Bodaness, Robert S., National Institutes of Health, worked with D. S. King on laser photosensitization processes in biological samples.

Chou, N.-Y., Chemistry Department, Howard University, worked with A. S. Pine on collisional line broadening problems.

Ho, P.-T., Electrical Engineering Department, University of Maryland, worked with J. C. Stephenson on research with picosecond lasers.

Hollis, Jan Michael, NASA/Goddard Space Flight Center, works with F. Lovas and R. Suenram on software development for automated microwave spectrometer and collaborates on astronomical studies.

Howard, Brian, Oxford University, Oxford, England, worked with A. S. Pine on high resolution infrared spectroscopy of the rare gas-HCl van der Waals molecules.

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.

Leubner, Christoph, J., Institut für Theoretische Physik, Universität Innsbruck, Austria, worked with J. T. Hougen on improved least squares determination of potential energy surfaces from spectroscopic data.

Lovejoy, Roland W., Chemistry Department, Lehigh University, works with B. Olson on the infrared spectrum of deuterated silanes.

Mialocq, John-Claude, Department de Physico-Chemie, Centre d'Etudes Nucleaires de Saclay, France, worked with J. C. Stephenson on problems of vibrational relaxation, photo-dissociation, and fluorescence and absorption spectroscopy on a picosecond time scale.

Mills, Ian M., Department of Chemistry, Reading University, Reading, England, worked with W. J. Lafferty on the spectroscopy of hydrogen bonded molecules and the theoretical relationships between normal and local mode models of molecular vibrations.

Ohashi, Nobukimi, Kanazawa University, Physics Department, Japan, works with A. S. Pine, J. T. Hougen, W. J. Lafferty and B. Olson on high resolution infrared spectroscopy of hydrazine and of hydrogen bonded molecules.

Sattler, Joseph P., Harry Diamond Laboratories, U. S. Army, collaborates with W. Lafferty and A. Maki on precise line frequency measurements in the infrared.

Vahala, Linda L., Physics Department, Old Dominion University, Norfolk, VA, worked 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.

Wofford, Billy A., Chemistry Department, Texas A & M University, worked with W. J. Lafferty and W. B. Olson on the Fourier transform infrared spectra of hydrogen bonded molecules.

S-114A (REV. 2-80)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR-86/3313	2. Performing Organ. Report No.	3. Publication Date JANUARY 1986

TITLE AND SUBTITLE

Technical Activities 1985 - Molecular Spectroscopy Division

. AUTHOR(S)

A. Weber

. 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

. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

. 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 technical activities of the NBS Molecular Spectroscopy Division during Fiscal Year 1985. These activities span experimental and theoretical research in high resolution molecular spectroscopy, quantum chemistry, and laser photochemistry, 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.

2. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

Environmental spectroscopy; hydrogen-bonded molecules; energy transfer; surface desorption studies; picosecond spectroscopy; quantum chemistry; multiphoton effects; and scattering theory.

3. 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

110

15. Price