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COLUMBUS OHIO ON 17-21 JUNE 1985(U) OHIO STATE UNIV
COLUMBUS DEPT OF CHEMISTRY I N RAO 21 JUN 85
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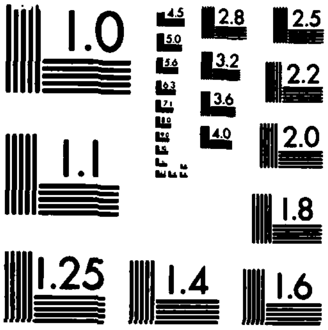

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AD-A160 415

Fortieth

symposium on

MOLECULAR SPECTROSCOPY

THE OHIO STATE UNIVERSITY

June 17-21, 1985

Under the Sponsorship of
the Department of Physics
the Department of Chemistry
the Graduate School
the Office of Academic Affairs
of the University
and
the U.S. Army Research Office
the U.S. Air Force Office of Scientific Research

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INFORMATION

ACCOMMODATIONS: The check-in for dormitory accommodations is located in Drackett Tower (6) on Curl Drive. Curl Drive is a one-way street going north from West Woodruff Avenue.

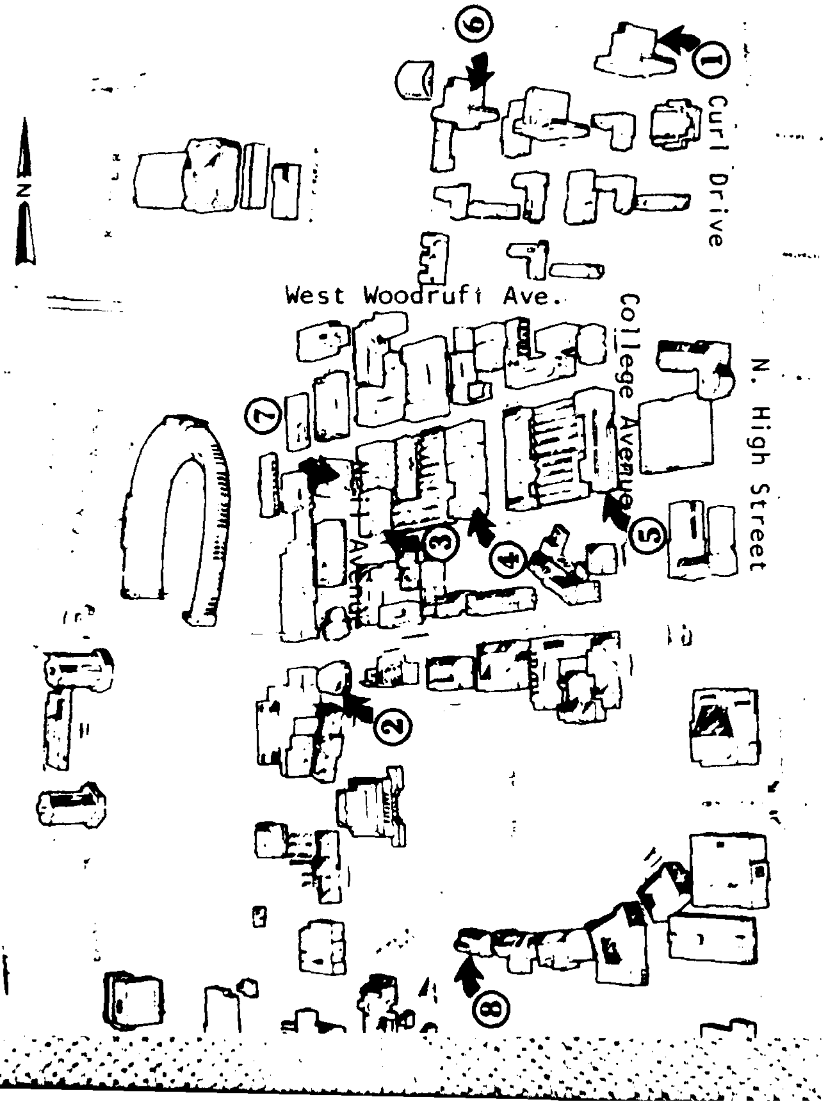
BANQUET: This will take place at the Faculty Club (8) on Wednesday, June 19, 1985. RECEPTION: 6:00-7:00 p.m. BANQUET: 7:00 p.m. Dr. N. Bloembergen, Gerhard Gade University Professor, Harvard University, Cambridge, Massachusetts, will be the speaker.

MAIL: Address your mail for delivery during the Symposium to: c/o MOLECULAR SPECTROSCOPY SYMPOSIUM, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210, U.S.A.

PARKING: Please purchase your parking permits when you check into the dorms or at the Registration Desk. These permits allow you to park in the Tuttle-Woodruff parking lot only. The permits must be displayed on the front windshield of your car. Please follow all traffic rules to avoid the issuance of tickets.

REGISTRATION: The Registration Desk will be located in Room 1036, Physics Laboratory. It will be kept open between 8:30 a.m.--noon and 1:00--4:30 p.m., Monday through Friday. The registration fee is $60.00 per participant and $50.00 if paid by June 1. The special rate of $20.00 per Graduate Student will be reduced to $18.00 if paid by June 1. Please send the completed registration form along with your check by June 1. This is a new procedure.

SESSIONS: They will be held in: Independence Hall (2), Physics Lab (4), and Evans Lab (5). Digits in parentheses correspond to the campus map below:



THE OHIO STATE UNIVERSITY

1	Taylor Tower
2	Independence Hall
3	Post Office
4	Physics Laboratory (Smith Lab.)
5	Evans Laboratory
6	Drackett Tower (Check-In)
7	Electronics Laboratory
8	Faculty Club

SECURITY CLASSIFICATION OF THIS PAGE

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Recent years have witnessed the devlopment of powerful experimental techniques that have allowed the observation of finer details of molecular spectra with a resolution not conceived as possible even in the recent past. Therefore, in interpreting the laboratory data it has become necessary to re-examine the theory.

275

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PLANS FOR THE 1986 SYMPOSIUM (JUNE 16-20, 1986)

Alan Carrington from Oxford, G. Herzberg from Ottawa, E. W. Schlag from München, and Richard N. Zare from Stanford have already accepted to be Invited Speakers. Abstracts of Contributed Papers in the proper format (see on the back of this page) are due at The Ohio State University on March 1, 1986.

Professors Russell Pitzer, Terry Miller, and Weldon Mathews of the Chemistry Department at The Ohio State University write: "The 1986 Molecular Spectroscopy Symposium will celebrate an important event, the dedication of the new OSU Laser Spectroscopy Facility housed in the new Chemistry building. We believe that this facility will do much to enhance the long tradition of spectroscopy at OSU, as symbolized by the annual Molecular Spectroscopy Symposium."

PROFESSORS HARALD H. NIELSEN AND DAVID M. DENNISON REMEMBERED.

Harald H. Nielsen
(1903-1973)

Department of Physics
The Ohio State University

David M. Dennison
(1900-1976)

Department of Physics
The University of Mich

START HERE

THIS DIMENSION MUST BE PRESERVED FOR EVERY ABSTRACT

8 in. (=20 cm)

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HIGH RESOLUTION FOURIER SPECTROSCOPY OF THE Ar^+ LASER 5145 Å EXCITED I_2 FLUORESCENCE SPECTRUM

R. BACIS, S. CHURASSY, R. W. FIELD, J. B. KOFFEND, AND J. VERGES

This preliminary work demonstrates the feasibility of obtaining a high resolution spectrum of cw laser excited fluorescence using a Fourier spectrometer.

Using 1.3W of 5145 Å multimode power from an Ar^+ laser, fluorescence is excited mainly via the P(13) and R(15) (43,0) lines. Nearly all of the [illegible] fluorescence lines [P(13), P(17), R(11), R(15)] originating from v' = 43 are observe[illegible] 85. Their recorded full width at half maximum in the 7000-8000 cm^{-1} regi[illegible]

Rotational relaxation (ΔJ' - [illegible] rous odd-J" satellite lines. The usual parameters are obtain[illegible] rotation-vibration levels of I_2 $X^1\Sigma^+$ through v" = 85.

The vibrational line intens[illegible] the alternation pattern predicted by the Franck-Condon factors of Tellingh[illegible] [illegible]ne agreement between measured and calculated intensities is only qualitative for [illegible]gh v" values. This has important implications with respect to the I_2 laser gain measurements discussed in the following talk.

This sample abstract gives the required format

---

[1] J. Tellinghuisen, J. Quant. Spect. Rad. Transf. 19, 149 (1978).

Will be copied photographically

Address of Bacis and Churassy: Laboratoire de Spectrométrie Ionique et Moléculaire 43, bd du 11 Novembre 1918, 69621 - Villeurbanne, France.
Address of Field and Koffend: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
Address of Verges: Laboratoire Aimé Cotton - C.N.R.S. II, Bâtiment 505, 91405 - Orsay, France.

Time required: 15, 10 or 5 min.

* Session in which paper is recommended for presentation:_____

Chemical formulas & sketches of molecular structures for larger molecules:

PLEASE NOTE:

1. Use good quality bond paper and an electric typewriter when preparing your Abstract. In the space for title and abstract you may include tables, equations and line drawings.
2. Send an original and one copy.
3. Please use a larger envelope for mailing. Do not fold.
4. Underline the name of the person who will be presenting the paper.
5. Include only the TITLE, AUTHORS' NAMES, and TEXT in the abstract. The author's affiliation should be given separately, as shown in the example.
6. Supply chemical formulas and rough sketches of structures of the larger molecules. This information is useful in arranging sessions.

General categories of sessions:

(1) Electronic (large molecules)
(2) Electronic (small molecules)
(3) Electronic (theory)
(4) Energy transfer
(5) High resolution IR & THEORY
(6) Laser spectra
(7) Liquid state
(8) Matrix spectra
(9) Microwave
(10) Molecular beam
(11) Raman spectra
(12) Solid state (electronic)
(13) Solid state (infrared)
(14) Techniques
(15) Vibrational analysis

PLEASE CHOOSE ONE OF THESE FIFTEEN CATEGORIES FOR YOUR PAPER AND GIVE THAT INFORMATION IN THE PLACE WHERE THE * APPEARS ABOVE. THANK YOU.

MONDAY, JUNE 17, 1985 -- 9:15 A.M.

Auditorium, Independence Hall

Chairman: S. LESLIE BLATT, Department of Physics, The Ohio State University, Columbus, Ohio.

Plenary Session

MA1. INFRARED SPECTROSCOPY FOR UPPER ATMOSPHERIC MEASUREMENTS........................40 min.

MARY ANN H. SMITH, Chemistry and Dynamics Branch, Atmospheric Sciences Division, NASA, Langley Research Center, Hampton, Virginia, 23665.

MA2. LATEST DEVELOPMENTS IN THE TECHNIQUES OF FOURIER TRANSFORM SPECTROSCOPY................40 min.

JYRKI KAUPPINEN, Department of Physics, University of Oulu, Linnanmaa, SF-90570, Oulu 57, Finland.

MA3. WORKING AT THE PHOTON LIMIT WITH A HIGH RESOLUTION FOURIER TRANSFORM SPECTROMETER......40 min.

JAMES W. BRAULT, Kitt Peak National Observatory, 950 North Cherry Avenue, Tucson, Arizona 85726.

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MONDAY, JUNE 17, 1985 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman: KOICHI M.T. YAMADA, Erstes Physikalisches Institut, Universität zu Köln, West Germany.

ME1. HIGH RESOLUTION SPECTRUM OF THE C-O STRETCHING BAND OF C-13 METHANOL........15 min.(1:30)

I. MUKHOPADHYAY, R. M. LEES, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada, E3B 5A3; and W. LEWIS-BEVAN, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6.

ME2. INFRARED AND MILLIMETER SPECTRA OF METHYLAMINE..............................15 min.(1:47)

R. M. LEES, K.V.L.N. SASTRY, J. S. PITRE, T. J. NOBLE, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada, E3B 5A3; and W. LEWIS-BEVAN, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6.

ME3. ANALYSIS OF THE STIMULATED RAMAN SPECTRUM OF THE $\nu_{16}/\nu_2+\nu_{18}$ FERMI DIAD OF BENZENE...15 min.(2:04)

P. ESHERICK, A. OWYOUNG, Sandia National Laboratories, Albuquerque, New Mexico, 87185; and J. PLÍVA, Department of Physics, Pennsylvania State University, University Park, Pennsylvania, 16802.

ME4. THE ROTATION-VIBRATION SPECTRUM OF CYANAMIDE AND CARBODIIMIDE..............15 min.(2:21)

M. BIRK and M. WINNEWISSER, Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, Federal Republic of Germany. Paper presented by K. BLOM.

ME5. HIGH RESOLUTION INFRARED SPECTRUM OF CH_2NH...................................15 min.(2:38)

L. HALONEN, Department of Physical Chemistry, University of Helsinki, SF-00170 Helsinki, Finland; and G. DUXBURY, Department of Physics, University of Strathclyde, Glasgow G4 ONG, Scotland.

Intermission

ME6. A GENERALIZED INTERNAL AXIS METHOD FOR HIGH BARRIER TUNNELING PROBLEMS AS APPLIED TO THE WATER DIMER..15 min.(3:15)

JON T. HOUGEN, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

ME7. THE TORSIONAL-WAGGING TUNNELING PROBLEM AND TORSIONAL-WAGGING-ROTATIONAL PROBLEM IN HYDRAZINE...15 min.(3:32)

NOBUKIMI OHASHI, Department of Physics, Faculty of Science, Kanazawa University, Kanazawa, Ishikawa, 920, Japan; and JON T. HOUGEN, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

ME8. FAR-INFRARED SPECTRUM OF THE TORSIONAL BAND OF HYDRAZINE...................15 min.(3:49)

N. OHASHI, Department of Physics, Faculty of Science, Kanazawa University, Kanazawa, 920, Japan; W. J. LAFFERTY, and W. B. OLSON, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

ME9. HIGH RESOLUTION SPECTRUM OF THE ν_2 AND ν_3 BANDS OF HOCl....................15 min.(4:06)

W. J. LAFFERTY and W. B. OLSON, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

ME10. VIBRATION ROTATION SPECTRA AND THE HARMONIC FORCE FIELD OF HOCl............15 min.(4:23)

CATHERINE M. DEELEY, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6; and IAN M. MILLS, Department of Chemistry, The University of Reading, Whiteknights, Reading, Berkshire, England, RG6 2AD.

ME11. COLLISION INDUCED ROTATIONAL SPECTRUM OF NONPOLAR HYDROCARBONS AND THEIR MIXTURES WITH ARGON...10 min.(4:40)

R. COHEN and W. PRINGLE, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457.

ME12. OBSERVATION OF COLLISIONAL LINE MIXING IN A CO_2 Q-BRANCH USING A DIODE LASER...Arrived Late..15 min.(4:49)

L. STROW, Department of Physics, University of Maryland Baltimore County, Catonsville, Maryland, 21228; and B. GENTRY, NASA/Goddard Space Flight Center, Code 615.2, Greenbelt, Maryland, 20771.

MONDAY, JUNE 17, 1985 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman: JOHN PARSON, Department of Chemistry, Ohio State University, Columbus, Ohio.

MF1. MEASUREMENT OF THE ν_2 PERPENDICULAR BENDING MODE OF Ar-HCl BY INTRACAVITY FAR INFRARED LASER STARK SPECTROSCOPY..........15 min.(1:30)

D. RAY, R. L. ROBINSON, D. H. GWO, and R. J. SAYKALLY, Department of Chemistry, University of California-Berkeley, Berkeley, California, 94720.

MF2. INTRACAVITY FAR INFRARED LASER STARK SPECTROSCOPY OF SUPERSONIC MOLECULAR BEAMS..........15 min.(1:47)

D. RAY, R. L. ROBINSON, D. H. GWO, and R. J. SAYKALLY, Department of Chemistry, University of California-Berkeley, Berkeley, California, 94720.

MF3. LASER SPECTROSCOPY OF PHOTOLYTICALLY PRODUCED FREE RADICALS..........15 min.(2:09)

YEN-CHU HSU, RICHARD A. KENNEDY, and TERRY A. MILLER, Department of Chemistry, Ohio State University, Columbus, Ohio, 43210.

MF4. NEAR-INFRARED SPECTRA OF RARE GAS-HCl COMPLEXES..........15 min.(2:21)

B. J. HOWARD, Physical Chemistry Laboratory, Oxford University, Oxford, OX1 3QZ, England; and A. S. PINE, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

MF5. ARGON ISOTOPE EFFECT IN THE MICROWAVE SPECTRA OF ArDF..........15 min.(2:38)

BRIAN L. COUSINS and JAMES M. LISY, Department of Chemistry, University of Illinois, Urbana, Illinois, 61801.

MF6. EVIDENCE FOR A MAGNETIC OCTUPOLE INTERACTION IN THE HYPERFINE SPECTRUM OF NaBr..........15 min.(2:55)

J. CEDERBERG, D. NITZ, A. KOLAN, T. RASMUSSON, K. HOFFMAN, and S. TUFTE, Department of Physics, St. Olaf College, Northfield, Minnesota, 55057.

Intermission

MF7. MICROWAVE SPECTRUM AND STRUCTURE OF THE Ar•••ACRYLONITRILE VAN DER WAALS COMPLEX..........15 min.(3:30)

R. D. SUENRAM and F. J. LOVAS, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

MF8. DIODE LASER SPECTROSCOPY OF VAN DER WAALS COMPLEXES..........15 min.(3:47)

G. HAYMAN, J. HODGE, B. HOWARD, Physical Chemistry Laboratory, Oxford University, Oxford, OX1 3QZ, England; T. DYKE, Department of Chemistry, University of Oregon, Eugene, Oregon, 97403; and J. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

MF9. CONFORMATIONAL ANALYSIS OF GUAIAZULENE IN ITS GROUND AND SECOND EXCITED SINGLET STATE..........15 min.(4:04)

M. M. CARRABBA, T. M. WOUDENBERG, and J. E. KENNY, Department of Chemistry, Tufts University, Medford, Massachusetts, 02155.

MF10. SATURATION STUDIES OF EXCITED-STATE DYNAMICS OF GUAIAZULENE..........15 min.(4:21)

M. M. CARRABBA, T. M. WOUDENBERG, and J. E. KENNY, Department of Chemistry, Tufts University, Medford, Massachusetts, 02155.

MF11. FLUORESCENCE QUANTUM YIELDS OF SINGLE VIBRONIC LEVELS OF GUAIAZULENE..........15 min.(4:38)

T. M. WOUDENBERG and J. E. KENNY, Department of Chemistry, Tufts University, Medford, Massachusetts, 02155.

MF12. FAR-INFRARED SPECTROSCOPY OF Ar-HCl..........(Paper Arrived Late)..........20 min.(4:55)
(Formerly RE6)

M. D. MARSHALL, A. CHARO, H. O. LEUNG, and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

MONDAY, JUNE 17, 1985 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chairman Before Intermission: M. C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois.

Chairman After Intermission: RAMACHANDRA R. DASARI, Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

MG1. DISCRETE TRANSFORM OF MOLECULAR M CHANGING KERNELS BY STARK SUBLEVEL ECHOES........15 min.(1:30)

J. M. LIANG, L. A. SPINELLI, J. E. THOMAS, R. R. DASARI, and M. S. FELD, Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

MG2. ABSORPTION ATTENUATION MEASUREMENT OF ATMOSPHERE FOR 4416A OF He-Cd LASER IN SHANGHAI REGION........10 min.(1:47)

CAI PEIPEI, SHANXIONG SHEN, ZHANG HANSHENG, and I-SHAN CHENG, Department of Physics, East-China Normal University, Shanghai, 200062, People's Republic of China.

MG3. PROPAGATION OF INFRARED RADIATION IN SHANGHAI REGION........10 min.(1:59)

SHANXIONG SHEN, YU HAI-PING, I-SHAN CHENG, Department of Physics, East-China Normal University, Shanghai, 200062, People's Republic of China.

MG4. THE INTERPRETATION OF OVERTONE SPECTRA: MODE-MODE COUPLINGS IN THE TRIHALOMETHANES........15 min.(2:11)

W. H. GREEN, W. D. LAWRANCE, C. B. MOORE, Department of Chemistry, University of California-Berkeley, Berkeley, California, 94720; and J. S. WONG, IBM Instruments, Orchard Park, P.O. Box 332, Danbury, Connecticut, 06810.

MG5. INTERACTIONS OF PO RADICALS WITH ATMOSPHERIC GASES........15 min.(2:28)

K. N. WONG, W. R. ANDERSON, A. J. KOTLAR, M. A. DEWILDE, and L. J. DECKER, U. S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, 21005.

MG6. THE COLLISIONAL QUENCHING OF ELECTRONICALLY EXCITED NITROGEN........15 min.(2:45)

D. H. KATAYAMA, Ionospheric Physics Division, Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731.

Intermission

MG7. TRANSLATIONAL ENERGY DEPENDENCE OF THE ELECTRONIC QUENCHING OF I_2(B) AND Br_2(B) BY He........15 min.(3:15)

J. P. NICOLAI and M. C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616.

MG8. ROTATIONAL ENERGY TRANSFER AND ELECTRONIC SELF QUENCHING RATES FOR Br_2(B)...15 min.(3:32)

L. J. VAN DE BURGT and M. C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616.

MG9. LASER EXCITATION AND EMISSION SPECTRA FOR Br_2 IN AN ARGON MATRIX........15 min.(3:49)

L. J. VAN DE BURGT, J. P. NICOLAI, and M. C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616.

MG10. VIBRATIONAL LEVEL STRUCTURE AND IVR IN S_1 p-DIFLUOROBENZENE........15 min.(4:06)

R. A. COVELESKIE, D. A. DOLSON, K. W. HOLTZCLAW, D. B. MOSS, and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47401.

MG11. VIBRATIONAL PREDISSOCIATION AND IVR FROM THE VAN DER WAALS COMPLEX OF PARA-DIFLUOROBENZENE AND Ar........15 min.(4:23)

D. L. CATLETT, JR., D. KRAJNOVICH, and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

MG12. VIBRATIONAL ENERGY TRANSFER IN S_1 PARA-DIFLUOROBENZENE BY COLLISIONS WITH Ar........15 min.(4:40)

D. L. CATLETT, JR. and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

MG13. CIS-TRANS ISOMERIZATION OF GLYOXAL IN A SUPERSONIC EXPANSION........15 min.(4:57)

J. R. JOHNSON, D. KRAJNOVICH, K. W. BUTZ, and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

TUESDAY, JUNE 18, 1985 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairman Before Intermission: M. J. CLOUTER, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada.

Chairman After Intermission: L. STROW, Department of Physics, University of Maryland Baltimore County, Catonsville, Maryland.

TA1. THE ν_3 AND ν_1 BANDS OF THE $^{16}O^{16}O^{18}O$ AND $^{16}O^{18}O^{16}O$ ISOTOPIC SPECIES OF OZONE .... 15 min.(8:30)

J.-M. FLAUD, C. CAMY-PEYRET, A. PERRIN, Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, Campus d'Orsay, 91405 Orsay, France; V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; C. P. RINSLAND, and M.A.H. SMITH, NASA/Langley Research Center, Atmospheric Sciences Division, Mail Stop 401 A, Hampton, Virginia, 23665.

TA2. IDENTIFICATION OF ^{18}O-ISOTOPIC LINES OF OZONE IN INFRARED GROUND-BASED SOLAR ABSORPTION SPECTRA .... 10 min.(8:47)

C. P. RINSLAND, M.A.H. SMITH, NASA/Langley Research Center, Atmospheric Sciences Division, Mail Stop 401 A, Hampton, Virginia, 23665; V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; J.-M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, Campus d'Orsay, 91405 Orsay, France; and G. M. STOKES, Battelle Observatory, Battelle Pacific Northwest Laboratories, P.O. Box 999, Richland, Washington, 99352.

TA3. TEMPERATURE DEPENDENCE OF N_2-BROADENED HALFWIDTHS OF OZONE .... 10 min.(8:59)

R. R. GAMACHE, Center for Atmospheric Research, University of Lowell, Lowell, Massachusetts, 01854; and L. S. ROTHMAN, Optical Physics Division, Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731.

TA4. BALLOON-BORNE ATMOSPHERIC INFRARED EMISSION SPECTRA OBTAINED WITH THE SCRIBE INTERFEROMETER .... 15 min.(9:11)

L. S. ROTHMAN, G. A. VANASSE, Optics Division, Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731; F. H. MURCRAY, F. J. MURCRAY, and D. G. MURCRAY, Department of Physics, University of Denver, Denver, Colorado, 80208.

TA5. CALCULATED ENERGY LEVELS AND INTENSITIES FOR THE ν_1 AND $2\nu_2$ BANDS OF HDO .... 10 min.(9:28)

A. PERRIN, J.-M. FLAUD, and C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, Campus d'Orsay, 91405 Orsay, France.

TA6. THE SECOND TRIAD OF INTERACTING STATES OF $H_2{}^{18}O$. LINE POSITIONS AND INTENSITIES FOR THE $3\nu_2$, $\nu_1 + \nu_2$ AND $\nu_2 + \nu_3$ .... 10 min.(9:40)

J.-P. CHEVILLARD, J.-Y. MANDIN, J.-M. FLAUD, and C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, Campus d'Orsay, 91405 Orsay, France.

Intermission

TA7. ATMOSPHERIC WATER VAPOR ABSORPTION AT 1.3 μm .... 15 min.(10:10)

S. L. BRAGG and J. D. KELLEY, McDonnell Douglas Research Laboratories, P.O. Box 516, St. Louis, Missouri, 63166.

TA8. ANALYSIS OF ν_2 OF D_2S .... 15 min.(10:27)

JAMES R. GILLIS, RONALD D. BLATHERWICK, and FRANCIS S. BONOMO, Department of Physics, University of Denver, Denver, Colorado, 80208.

TA9. ENERGY LEVELS AND BAND STRENGTHS OF CARBON DIOXIDE CALCULATED BY DIRECT NUMERICAL DIAGONALIZATION .... 10 min.(10:44)

RICHARD B. WATTSON, Visidyne, Inc., 5 Corporate Place, S. Bedford St., Burlington, Massachusetts, 01803; and LAURENCE S. ROTHMAN, Optics Division, Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731.

TA10. INTENSITY AND PRESSURE BROADENING MEASUREMENTS IN THE ν_3 FUNDAMENTAL OF CO_2 .... 10 min.(10:56)

J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

TA11. MOLECULAR PARAMETERS FOR CARBON DIOXIDE BANDS IN THE 2.86-3.18 μm SPECTRAL REGION....................10 min.(11:08)

D. CHRIS BENNER, V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; and C. P. RINSLAND, NASA/Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665.

TA12. LINE POSITION MEASUREMENTS OF $^{13}C^{16}O_2$ AND $^{13}C^{16}O^{18}O$ AT ELEVATED TEMPERATURES IN THE 2.8 μm REGION....................10 min.(11:20)

MARK P. ESPLIN, Stewart Radiance Laboratory, Utah State University, Bedford, Massachusetts, 01730; and JOHN P. MYCROFT, Optical Physics Division, U. S. Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01731.

TA13. CO_2 BAND INTENSITIES IN THE 9.4 AND 10.4 μm REGIONS....................10 min.(11:32)

M. S. ABUBAKAR and J. H. SHAW, Department of Physics, Ohio State University, Columbus, Ohio, 43210.

TA14. A CHARGE FLOW MODEL FOR THE HIGHER DERIVATIVES OF THE MOLECULAR DIPOLE MOMENT....................15 min.(11:44)

JEFFREY L. HYLDEN, Naval Research Laboratory, Code 6833, Washington, D.C., 20375; and JOHN OVEREND, deceased November 28, 1984.

TA15. OXYGEN-BROADENED LINEWIDTHS OF CARBON DIOXIDE....................10 min.(12:01)
(Last Minute Addition)

E. ARIE, N. LACOME, P. ARCAS, and A. LEVY,
Laboratoire d'Infrarouge, associe au C.N.R.S.,
Universite de Paris XI, Batiment 350, 91405 Orsay,
Cedex, France

TUESDAY, JUNE 18, 1985 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chairman Before Intermission:	LOUIS BRUS, AT&T Laboratories, Murray Hill, New Jersey.
Chairman After Intermission:	MARILYN E. JACOX, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland.

TB1. INFRARED MATRIX ISOLATION INVESTIGATION OF THE MOLECULAR COMPLEXES OF SILICON AND GERMANIUM TETRAFLUORIDES WITH WEAK LEWIS BASES .... 15 min. (8:30)

BRUCE S. AULT, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

TB2. INFRARED MATRIX ISOLATION STUDIES OF THE COMPLEXES OF THE HYDROGEN HALIDES WITH SUBSTITUTED CYCLOPROPANES .... 15 min. (8:47)

CANDACE E. TRUSCOTT and BRUCE S. AULT, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

TB3. INFRARED SPECTROSCOPIC STUDIES OF MATRIX ISOLATED COMPLEXES OF ClF WITH SELECTED LEWIS BASES .... 15 min. (9:04)

NICHOLAS P. MACHARA and BRUCE S. AULT, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

TB4. VIBRATIONAL SPECTRA OF FREE RADICALS FORMED IN THE PRIMARY REACTION OF F ATOMS WITH THE METHYL HALIDES .... 15 min. (9:21)

MARILYN E. JACOX, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

TB5. FTIR SPECTRUM OF CARBON-13 SUBSTITUTED SiC_2 TRAPPED IN ARGON AT 8 K .... 15 min. (9:38)

RICHARD A. SHEPHERD and W.R.M. GRAHAM, Department of Physics, Texas Christian University, Fort Worth, Texas, 76129.

Intermission

TB6. ESR SPECTRA OF $Ag_3(^2A_1)$ IN AN N_2 MATRIX .... 15 min. (10:10)

K. KERNISANT, G. A. THOMPSON, and D. M. LINDSAY, Department of Chemistry, City University of New York, City College, New York, New York, 10031.

TB7. ESR OF HSiO AND Si_2 MOLECULES AT 4°K .... 10 min. (10:27)

R. J. VAN ZEE and W. WELTNER, JR., Chemical Physics Center and Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

TB8. ESR OF $V(CO)_n$ (n=1 to 3) MOLECULES AT 4°K .... 15 min. (10:39)

R. J. VAN ZEE, S.B.H. BACH, and W. WELTNER, JR., Chemical Physics Center and Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

TB9. ELECTRONIC STATES OF MATRIX-ISOLATED NI ATOMS: A MAGNETIC CIRCULAR AND LINEAR DICHROISM STUDY .... 15 min. (10:56)

JAN PYKA, MARTIN VALA, MARC EYRING, Department of Chemistry, University of Florida, Gainesville, Florida, 32611; JEAN-CLAUDE RIVOAL, and CHRISTIAN GRISOLIA, Laboratoire d'Optique Physique, ESPCI, Paris, 75231, France.

TB10. HYBRID EXCITED ELECTRONIC STATES IN SEMICONDUCTOR CRYSTALLITES OF DIAMETER ~ 15-50Å .... 15 min. (11:13)

LOUIS BRUS, AT&T Bell Laboratories, Murray Hill, New Jersey, 07974.

TB11. A SPECTROSCOPIC STUDY OF THE SPIN DIPOLAR INTERACTIONS OF THE EXCITED TRIPLET STATE OF DIPHENYLMETHYLENE .... 15 min. (11:30)

DANIEL J. GRAHAM, Department of Chemistry, West Virginia University, Morgantown, West Virginia, 26506.

TB12. ELECTRONIC SPECTRA OF Re^{4+} AND Ir^{4+} DOPED IN THE DISTORTED OCTAHEDRAL HOSTS .... 15 min. (11:47)

R. K. YOO, B. A. KOZIKOWSKI, and T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

TUESDAY, JUNE 18, 1985 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chairman Before Intermission:	W. E. ERNST, Institut für Molekülphysik, Freie Universität Berlin, D-1000 Berlin 33, Germany.
Chairman After Intermission:	J. A. COXON, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada.

TC1. PHOTOIONIZATION SPECTRUM OF TRIPLET RYDBERG STATES OF H_2....................10 min.(8:30)

R. D. KNIGHT and LIANG-GUO WANG, Department of Physics, Ohio State University, Columbus, Ohio, 43210.

TC2. OBSERVATION OF THE AUTOIONIZING GERADE TRIPLET RYDBERG SERIES IN H_2.........15 min.(8:42)

R. KACHRU and H. HELM, Molecular Physics Department, Chemical Physics Laboratory, SRI International, Menlo Park, California, 94025.
Presented by D. L. HUESTIS.

TC3. PROBING EXCITED STATES OF NO INVOLVED IN MULTISTATE INTERACTIONS USING THE OODR-MPI TECHNIQUE..15 min.(8:59)

W. Y. CHEUNG, W. A. CHUPKA, S. D. COLSON, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut; D. GAUYACQ, Laboratoire de Photophysique moleculaire, CNRS, Orsay, France; PH. AVOURIS, and J. J. WYNNE, IBM T.J. Watson Research Center, Yorktown Heights, New York.

TC4. DETECTION OF THE $L'^{2}\Phi$ STATE OF NO...15 min.(9:16)

M. R. TAHERIAN and T. G. SLANGER, Chemical Physics Laboratory, SRI International, Menlo Park, California, 94025.
Presented by D. L. HUESTIS.

TC5. ABSORPTION CROSS SECTION MEASUREMENTS OF OXYGEN IN THE WAVELENGTH REGION 195-241 nm OF THE HERZBERG CONTINUUM...15 min.(9:33)

A.S.C. CHEUNG, K. YOSHINO, W. H. PARKINSON, and D. E. FREEMAN, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts, 02138.

Intermission

TC6. SCHUMANN-RANGE ABSORPTION BANDS OF $^{18}O_2$..................................15 min.(10:05)

K. YOSHINO, D. E. FREEMAN, A.S.C. CHEUNG, and W. H. PARKINSON, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts, 02138.

TC7. PERTURBATIONS IN THE B STATE OF S_2..15 min.(10:22)

K. RAGHUVEER and A. SMITH, Department of Chemistry, Drexel University, Philadelphia, Pennsylvania, 19104.

TC8. AN EXTENSION OF THE ROTATIONAL ANALYSIS OF THE B $^3\Pi$ - X $^1\Sigma^+$ TRANSITION OF BCl ....10 min.(10:39)

LISA HAMILTON and C. WELDON MATHEWS, Department of Chemistry, Ohio State University, Columbus, Ohio, 43210.

TC9. LASER SPECTROSCOPY OF RARE EARTH OXIDES: RECENT RESULTS...................15 min.(10:51)

C. LINTON, D. M. GAUDET, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada, E3B 5A3; A. HOCQUET, P. CARETTE, Laboratoire de Spectroscopie des Molécules Diatomiques, Université de Lille I, 59655 Villeneuve d'Ascq, France; H. SCHALL, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; and M. DULICK, Ionospheric Physics Division, Air Force Geophysics Laboratory/LID, Hanscom Air Force Base, Bedford, Massachusetts, 01731.

TC10. DIPOLE MOMENTS OF THE GROUND AND FIRST EXCITED VIBRATIONAL STATES OF ^{35}ClO...10 min.(11:08)

D. J. YARON, K. I. PETERSON, and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

TC11. LINE STRENGTH OF THE ATOMIC CHLORINE $^2P_{1/2} \leftarrow {}^2P_{3/2}$ SPIN ORBIT TRANSITION.... 5 min.(11:25)

A. C. STANTON and J. WORMHOUDT, Aerodyne Research, Inc., 45 Manning Road, Billerica, Massachusetts, 01821.

TC12. HYPERFINE STRUCTURE OF BaI $X^2\Sigma^+$...15 min.(11:32)
(Formerly FC6)

W. E. ERNST, J. KÄNDLER, and J. LÜDTKE, Institut für
Molekülphysi', Freie Universität Berlin Arnimallee 14,
D-1000 Berlin 33, Germany.

TC13. HIGH RESOLUTION SPECTROSCOPY OF $Sr^{79}Br$ AND $Sr^{81}Br$: $B^2\Sigma^+ - X^2\Sigma^+$
ROTATIONAL ANALYSIS AND HYPERFINE STRUCTURE...............................15 min.(11:49)
(Formerly FC7)

W. E. ERNST and J. O. SCHRÖDER, Institut für Molekülphysik,
Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33,
Germany.

TUESDAY, JUNE 18, 1985 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman: RANDALL D. KNIGHT, Department of Physics, Ohio State University, Columbus, Ohio.

TE1. THE EQUILIBRIUM STRUCTURE OF PROTONATED NITROGEN DETERMINED FROM HIGH RESOLUTION INFRARED SPECTROSCOPY..15 min.(1:30)

J. C. OWRUTSKY, C. C. MARTNER, N. H. ROSENBAUM, L. M. TACK, R. J. SAYKALLY, Department of Chemistry, University of California-Berkeley, Berkeley, California, 94720; and C. S. GUDEMAN, IBM-Thomas J. Watson Research Center, Yorktown Heights, New York, 10598.

TE2. MEASUREMENT OF THE ROTATIONAL SPECTRUM OF H_2O^+ BY LASER MAGNETIC RESONANCE..15 min.(1:47)

S. E. STRAHAN, R. P. MÜLLER, and R. J. SAYKALLY, Department of Chemistry, University of California-Berkeley, Berkeley, California, 94720.

TE3. MEASUREMENT OF THE ROTATIONAL SPECTRUM OF OH^+ AND OD^+ BY LASER MAGNETIC RESONANCE..15 min.(2:04)

M. GRUEBELE, R. P. MÜLLER, and R. J. SAYKALLY, Department of Chemistry, University of California-Berkeley, Berkeley, California, 94720.

TE4. OBSERVATION OF OH^+ AND H_2O^+ INFRARED FUNDAMENTAL BANDS......................15 min.(2:21)

M. W. CROFTON, R. S. ALTMAN, M.-F. JAGOD, B. D. REHFUSS, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TE5. EXPERIMENTAL DETERMINATION OF THE H_3O^+ GROUND STATE INVERSION SPLITTING......15 min.(2:38)

DI-JIA LIU and TAKESHI OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

Intermission

TE6. SPECTACULARLY INTENSE INFRARED VIBRATIONAL TRANSITIONS IN SPATIALLY DEGENERATE ELECTRONIC STATES..15 min.(3:10)

B. SCHARF, Department of Chemistry, Ohio State University, Columbus, Ohio, 43210 and Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel; and TERRY A. MILLER, Department of Chemistry, Ohio State University, Columbus,Ohio, 43210.

TE7. IMPROVEMENTS IN THE VIBRATION INTERVAL PREDICTIONS FOR H_3^+..................15 min.(3:27)

G. D. CARNEY, Department of Chemistry, Allegheny College, Meadville, Pennsylvania, 16335; and S. ADLER-GOLDEN, Spectral Science Inc., 111 South Bedford Street, Burlington, Massachusetts, 01803.

TE8. INFRARED EMISSION SPECTRA OF H_2, H_3 AND H_3^+ FROM A HYDROGEN DISCHARGE AT VARIOUS PRESSURES..15 min.(3:44)

W. A. MAJEWSKI, J.K.G. WATSON, and J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

TE9. THE $_2$ AND $_3$ BANDS OF H_2D^+ AND D_2H^+.................................15 min.(4:01)

S. C. FOSTER, A.R.W. MCKELLAR, and J.K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

TE10. ASTRONOMICAL DETECTION OF THE $1_{10} \rightarrow 1_{11}$ TRANSITION OF H_2D^+..................15 min.(4:18)

T. G. PHILLIPS, D. A. BLAKE, J. KEENE, G. W. Downs Laboratory of Physics, California Institute of Technology, Pasadena, California, 91125; R. C. WOODS, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, 53706; and E. CHURCHWELL, Department of Astronomy, University of Wisconsin, Madison, Wisconsin, 53706.

TE11. THE MICROWAVE SPECTRUM OF SO^+..15 min.(4:35)

H. E. WARNER, N. CARBALLO, and R. C. WOODS, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, 53706.

TE12. A STUDY OF MOLECULAR ION DISTRIBUTION IN THE POSITIVE COLUMN OF D.C. GLOW DISCHARGES BY DIODE LASER SPECTROSCOPY...........................15 min.(4:52)

FU-SHIH PAN and TAKESHI OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TE13. MARK W. CROFTON and TAKESHI OKA (See page 159 for title and abstract) (5:09)

TUESDAY, JUNE 18, 1985 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman: R. H. SCHULER, Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana.

SEMINAR OF INVITED PAPERS ON TIME RESOLVED RAMAN SPECTROSCOPY

TF1. TIME-RESOLVED RESONANCE RAMAN OF PHOTOTRANSIENTS..................30 min.(1:30)

M. A. EL-SAYED, Department of Chemistry and Biochemistry, University of California, Los Angeles, California, 90024.

TF2. INVESTIGATION OF PHOTOINDUCED ELECTRON TRANSFER AND CONSECUTIVE REACTIONS BY TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY...........30 min.(2:05)

S. SCHNEIDER and W. HUB, Institut für Physikalische und Theoretische Chemie, Technische Universität München, D 8046 Garching, Federal Republic of Germany.

Intermission

TF3. RESONANCE RAMAN STUDIES OF RADIATION- AND PHOTO-CHEMICAL TRANSIENTS...30 min.(3:00)

G.N.R. TRIPATHI, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana, 46556.

TF4. VIBRATIONAL RAMAN SPECTROSCOPY OF TRANSIENTS IN THE REACTIONS OF VISUAL CHROMOPHORES...30 min.(3:35)

I. GRIEGER, G. RUMBLES, P. KILLOUGH, and G. H. ATKINSON, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

TF5. THE COMPUTATIONAL SIMULATION OF THE X-RAY POWDER SPECTRUM OF ICE Ih...10 min.(4:10)
(Last Minute Addition)

P. W. DEUTSCH, and T. A. STANIK, The Pennsylvania State University at Beaver, Brodhead Road, Monaca, Pennsylvania, 15061.

Thanks to:

Dr. G.N.R. TRIPATHI

FOR BRINGING TOGETHER ALL THE DISTINGUISHED SPEAKERS AND ARRANGING ALL THE DETAILS CONNECTED WITH THIS SEMINAR ON TIME RESOLVED RAMAN SPECTROSCOPY

TUESDAY, JUNE 18, 1985 -- 1:30 P.M.
Room 1005, Physics Laboratory

Chairman Before Intermission: C. E. BLOM, Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, West Germany.

Chairman After Intermission: Y. S. LI, Department of Chemistry, Memphis State University, Memphis, Tennessee, 38152.

TG1. THE PUZZLING MICROWAVE SPECTRUM OF HEXADIENAL..............................10 min.(1:30)

ROBERT K. BOHN, CARL SAHI, and MARK F. GRANVILLE, Department of Chemistry, University of Connecticut, Storrs, Connecticut, 06268.

TG2. THE ROTATIONAL SPECTRUM OF NITRIC ACID IN THE ν_5 EXCITED VIBRATIONAL STATE..15 min.(1:42)

RANDY BOOKER, HENRY EVERITT, FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706; and PAUL HELMINGER, Department of Physics, University of South Alabama, Mobile, Alabama, 36688.

TG3. MILLIMETER/SUBMILLIMETER WAVE SPECTRUM OF METHYL FORMATE IN ITS GROUND TORSIONAL E STATE: APPLICATION OF THE HIGH-BARRIER P.A.M. TO HIGH K........15 min.(1:59)

GRANT M. PLUMMER, ERIC HERBST, FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706; and GEOFFREY A. BLAKE, Department of Chemistry, California Institute of Technology, Pasadena, California, 91125.

TG4. MICROWAVE SPECTRUM, CONFORMATION AND DIPOLE MOMENT OF TRANS-DIFLUOROETHYLENE OZONIDE(F$\overline{\mathrm{CHOOFCHO}}$)..10 min.(2:16)

M. G. SOLTIS, K. W. HILLIG, II, and R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

TG5. MICROWAVE SPECTRUM OF CYCLOHEXYLPHOSPHINE..................................10 min.(2:28)

Y. S. LI, Department of Chemistry, Memphis State University, Memphis, Tennessee, 38152.

TG6. TORSIONAL POTENTIAL FUNCTION OF ETHYLPHOSPHINE.............................15 min.(2:40)

P. GRONER and J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

TG7. MICROWAVE, INFRARED, AND RAMAN SPECTRA, AND CONFORMATIONAL STABILITY OF CHLOROMETHYLPHOSPHONIC DIFLUORIDE...15 min.(2:57)

R. D. JOHNSON, J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208; B. J. VAN DER VEKEN, and P. COPPENS, Rijksuniversitair Centrum Antwerpen, Antwerp 2020, Belgium.

Intermission

TG8. MILLIMETER WAVE SPECTRUM OF HCCCN IN THE EXCITED VIBRATIONAL STATE.........15 min.(3:30)

KOICHI M.T. YAMADA, G. WINNEWISSER, Erstes Physikalisches Institut, Universität zu Köln, 5000 Köln, West Germany; R. A. CRESWELL, and M. WINNEWISSER, Physikalisch-Chemisches Institut, Justus Liebig-Universität, 6300 Giessen, West Germany.

TG9. A REINVESTIGATION OF THE MICROWAVE SPECTRUM OF METHYL PHOSPHONIC DIFLUORIDE...15 min.(3:47)

H. JUSTNES, C. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12180; and T. DIGIUSEPPE, Geo-Centers, Inc., 320 Needham Street, Newton Upper Falls, Massachusetts, 02164.

TG10. THE J=1-2 TRANSITION OF POTASSIUM HYDROXIDE..............................15 min.(4:04)

T. RAW, C. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12180; and T. YAMAMURA, Department of Metallurgy, Tohoku University, Senda, 980, Japan.

TG11. METHYL AND HYDROXYL INTERNAL ROTATION IN METHYL HYDROPEROXIDE..............15 min.(4:21)

M. TYBLEWSKI, A. BAUDER, Laboratorium für Physikalische Chemie, CH-8092 Zürich, Switzerland; and C. E. BLOM, Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, West Germany.

TG12. MICROWAVE SPECTRUM AND QUADRUPOLE COUPLING IN IODOACETONITRILE.............15 min.(4:38)

R. C. CLAYTOR, J. D. GRAYBEAL, Department of Chemistry, Virginia Tech, Blacksburg, Virginia, 24061; and G. M. AULT, Proctor and Gamble Corporation, Cincinnati, Ohio, 45202.

TG13. MICROWAVE SPECTRUM OF PENTAFLUOROSULFANYLIMINOSULFUR DIFLUORIDE............15 min.(4:55)

R. W. WHITE, J. D. GRAYBEAL, Department of Chemistry, Virginia Tech, Blacksburg, Virginia, 24061; S. R. BAILEY, Xerox Corporation, Webster, New York, 14580; and J. S. THRASHER, Department of Chemistry, University of Alabama, University, Alabama, 35486.

WEDNESDAY, JUNE 19, 1985 -- 8:45 A.M.

Auditorium, Independence Hall

CHAIRMEN: K. NARAHARI RAO, Department of Physics,
The Ohio State University, Columbus, Ohio.

RUSSELL M. PITZER, Department of Chemistry,
The Ohio State University, Columbus, Ohio.

Plenary Session

WA1. INFRARED LASER AND MICROWAVE SPECTROSCOPY OF TRANSIENT MOLECULES............................40 min.

EIZI HIROTA, Institute for Molecular
Science, Myodaiji, Okazaki 444, Japan.

WA2. EXCITED STATES -- AN ULTIMATE LIMIT?...........40 min.

D. A. RAMSAY, Herzberg Institute of
Astrophysics, National Research Council
of Canada, Ottawa, Ontario, Canada K1A 0R6.

Intermission

WA3. MANY-BODY STUDIES OF MOLECULAR FORCE CONSTANTS, INFRARED INTENSITIES AND POLARIZABILITIES...............................40 min.

RODNEY J. BARTLETT, Quantum Theory
Project, University of Florida,
Gainesville, Florida, 32611.

WEDNESDAY, JUNE 19, 1985 -- 1:20 P.M. JOHN OVEREND MEMORIAL
Room 1153, Physics Laboratory

Chairman Before Intermission: C. J. WURREY, Department of Chemistry, University of Missouri, Kansas City, Missouri.

Chairman After Intermission: V. F. KALASINSKY, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi.

"JOHN OVEREND".. (1:20)

BRYCE CRAWFORD, JR., Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455.

WE1. INSTRUMENTAL ADVANCES IN RAMAN OPTICAL ACTIVITY (ROA)......................15 min.(1:30)

MARK A. DAVIES, MAX DIEM, Department of Chemistry, City University of New York, Hunter College, New York, New York, 10021; and M. REZA OBOODI, Allied Corporation, Morristown, New Jersey, 07960.

WE2. THEORY OF MAGNETIC VIBRATIONAL CIRCULAR DICHROISM..........................10 min.(1:47)

T. H. WALNUT, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

WE3. VIBRATIONAL CIRCULAR DICHROISM IN TARTARIC ACID ESTERS.....................15 min.(1:59)

P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

WE4. EQUIVALENCE OF THE SEMICLASSICAL MODELS FOR VIBRATIONAL CIRCULAR DICHROISM..10 min.(2:14)

P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

WE5. VIBRATIONAL CIRCULAR DICHROISM, A COIL-HELIX TRANSITION OF POLY-TYROSINE IN NON-AQUEOUS SOLVENTS....................................15 min.(2:26)

S. C. YASUI and T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

WE6. VIBRATIONAL CIRCULAR DICHROISM OF NUCLEIC ACIDS............................15 min.(2:43)

A. ANNAMALAI and T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

Intermission

WE7. VIBRATIONAL CIRCULAR DICHROISM OF β-STRUCTURE FORMING OLIGOPEPTIDES.........15 min.(3:15)

U. NARAYANAN, T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680; C. TONIOLO, and G. M. BONORA, Biopolymer Research Center, C.N.R., Institute of Organic Chemistry, University of Padova, 35121 Padova, Italy.

WE8. VIBRATIONAL CIRCULAR DICHROISM IN BIS(ACETYLACETONATO)(L-ALANINATO) COBALT(III). ISOLATED OCCURRENCES OF THE COUPLED OSCILLATOR AND RING CURRENT INTENSITY MECHANISMS...15 min.(3:32)

D. A. YOUNG, E. D. LIPP, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

WE9. ENHANCED VIBRATIONAL CIRCULAR DICHROISM VIA VIBRATIONALLY GENERATED ELECTRONIC RING CURRENTS..15 min.(3:49)

T. B. FREEDMAN, G. A. BALUKJIAN, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

WE10. EVIDENCE FOR THE RING CURRENT MECHANISM IN THE C-H STRETCHING VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF SUGARS.................................15 min.(4:06)

M. G. PATERLINI and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

WE11. A VALENCE COUPLED OSCILLATOR MODEL FOR THE CALCULATION OF VIBRATIONAL CIRCULAR DICHROISM...15 min.(4:23)

JOHN C. HANSEN and ALBERT MOSCOWITZ, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455.

WE12. VIBRATIONAL CIRCULAR DICHROISM OF (R)-(+)-3-METHYLCYCLOPENTANONE............15 min.(4:38)

LEO LAUX, JOHN C. HANSEN, and ALBERT MOSCOWITZ, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455.
Present address of LEO LAUX: Lockheed, Palo Alto Research Laboratories, 3251 Hanover Street, Palo Alto, California, 94304.

WE13. DETECTION OF PRIMARY AND SECONDARY CHIRAL STRUCTURES IN VIRUSES USING CIDS..15 min.(4:55)

C. W. PATTERSON, S. B. SINGHAM, and G. C. SALZMAN, Los Alamos National Laboratory, University of California, Box 1663, Los Alamos, New Mexico, 87545.

WE14. USE OF A SOLEIL-BABINET COMPENSATOR TO MEASURE RAMAN OPTICAL ACTIVITY SPECTRA..15 min.(5:12)
(Last Minute Addition)

C. G. ZIMBA, S. M. HU, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York.

This paper will be presented instead of WE3 and WE4 which will be canceled because Dr. P. L. Polavarapu telephoned to say that he will be overseas during that time.

WEDNESDAY, JUNE 19, 1985 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman: L. S. ROTHMAN, Air Force Geophysics Laboratory, Optical Physics Division, Hanscom Air Force Base, Massachusetts.

WF1. STANDARD SPECTRA WITH THE IMPROVED FOURIER TRANSFORM SPECTROMETER OF OULU...15 min.(1:30)

V.-M. HORNEMAN and J. KAUPPINEN, Department of Physics, University of Oulu, 90570 Oulu, Finland.

WF2. CAVITY-LOCKED DIODE LASER SPECTROMETER....................................10 min.(1:47)

M. REICH, R. SCHIEDER, H.-J. CLAR, G. WINNEWISSER, KOICHI M.T. YAMADA, Erstes Physikalisches Institut, Universität zu Köln, 5000 Köln 41, West Germany.

WF3. IR SPECTRA OF HIGH TEMPERATURE MOLECULES USING THE BURST OF GAS METHOD......15 min.(1:59)

T. C. DEVORE and T. N. GALLAHER, Department of Chemistry, James Madison University, Harrisonburg, Virginia, 22807.

WF4. VIBRATION-ROTATION SPECTRA OF NH IN THE $\Delta v = 1$ SEQUENCE....................15 min.(2:16)

D. BOUDJAADAR, P. CHOLLET, and G. GUELACHVILI, Laboratoire d'Infrarouge, C.N.R.S., Université de Paris XI, Bat. 350, 91405 Orsay Cedex, France.

WF5. MORE DIODE LASER SPECTRA OF DIATOMIC MOLECULES............................15 min.(2:33)

G. A. THOMPSON, A. G. MAKI, and A. WEBER, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

WF6. FOURIER TRANSFORM RAMAN SPECTROSCOPY OF H_2 AND D_2 IN FLAMES................10 min.(2:50)

D. E. JENNINGS, Planetary Systems Branch, Code 693, NASA/Goddard Space Flight Center, Greenbelt, Maryland, 20771; A. WEBER, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899; and J. W. BRAULT, National Solar Observatory, 950 North Cherry Avenue, Tucson, Arizona, 85726.

Intermission

WF7. THE SPECTRUM OF OCS IN THE 1975-2140 cm^{-1} REGION...........................10 min.(3:15)

N. HUNT, S. C. FOSTER, J.W.C. JOHNS, and A.R.W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

WF8. HIGH RESOLUTION INFRARED SPECTRUM OF CYANOGEN.............................15 min.(3:27)

A. WEBER, W. J. LAFFERTY, and W. B. OLSON, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

WF9. INTENSITIES AND SELF-BROADENINGS IN HF AND HCl............................15 min.(3:44)

A. S. PINE, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899; and A. FRIED, Gas and Particulate Science Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

WF10. HIGH PRECISION INTENSITY AND BROADENING PARAMETER MEASUREMENTS BY A STEP BY STEP F.T. CONTROLLED DIODE LASER..15 min.(4:01)

A. VALENTIN, L. HENRY, CH. NICOLAS, Laboratoire de Spectronomie Moléculaire, Université Pierre et Marie Curie, 75005 Paris, France; and A. MANTZ, Laser Analytics, 25 Wiggins Avenue, Bedford, Massachusetts, 01730.

WF11. LINE STRENGTHS AND WIDTHS IN THE ν_3-FUNDAMENTAL OF N_2O....................10 min.(4:18)

P. VARANASI, Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York, 11794; J. PODOLSKE, M. LOEWENSTEIN, and T. BLACKBURN, Atmospheric Experiments Branch, NASA/Ames Research Center, Moffett Field, California, 94035.

WF12. TDL MEASUREMENTS OF N_2 AND H_2 BROADENING OF C_2H_2..........................10 min.(4:30)

W. L. CHIN and W. E. BLASS, Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee, 37996.

WF13. TUNABLE DIODE LASER MEASUREMENTS OF N_2- AND AIR-BROADENED HALFWIDTHS: LINES OF $^{12}C_2H_2$, H_2O, HDO, AND H_2O_2 IN THE 1250-1380-cm^{-1} REGION...........10 min.(4:42)

V. MALATHY DEVI, D. C. BENNER, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; B. D. SIDNEY, NASA/Langley Research Center, Mail Stop 283, Hampton, Virginia, 23665; C. P. RINSLAND, M.A.H. SMITH, NASA/Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665; and B. FRIDOVICH, NOAA/NESDIS, FOB #4, E/RA22, Washington, D.C., 20233.

WEDNESDAY, JUNE 19, 1985 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chairman Before Intermission:	J. P. CHAMPION, Laboratoire de Spectronomie Moléculaire de l'Université de Dijon, Dijon, France.
Chairman After Intermission:	H. M. PICKETT, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

WG1. GENERATION OF TUNABLE LASER SIDEBANDS IN THE FAR-INFRARED REGION...........15 min.(1:30)

H. M. PICKETT, J. FARHOOMAND, M. A. FRERKING, E. A. COHEN, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California, 91109; and G. A. BLAKE, Department of Chemistry, California Institute of Technology, Pasadena, California, 91125.

WG2. MEASUREMENT OF ABSOLUTE ABSORPTION AND LINESHAPE OF CO AT 115 GHz..........15 min.(1:47)

W. G. READ, E. A. COHEN, H. M. PICKETT, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California, 91109; and K. W. HILLIG, II, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

WG3. DIRECT MEASUREMENT OF THE FUNDAMENTAL ROTATIONAL TRANSITIONS OF THE OH RADICAL AND AMMONIA BY LASER SIDEBAND SPECTROSCOPY........................15 min.(2:04)

G. A. BLAKE, Department of Chemistry, California Institute of Technology, Pasadena, California, 91125; J. FARHOOMAND and H. M. PICKETT, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California, 91109.

WG4. THE EXCITATION MECHANISM OF THE HCN FIR LASER.............................15 min.(2:21)

DAVID D. SKATRUD and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

WG5. SMALL OPTICALLY PUMPED FAR INFRARED LASERS................................15 min.(2:38)

HENRY EVERITT and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

Intermission

WG6. PULSED MICROWAVE FOURIER TRANSFORM SPECTROSCOPY OF SPHERICAL TOPS IN GROUND AND EXCITED VIBRATIONAL STATES.......................................15 min.(3:10)

A. BAUDER, M. OLDANI, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, CH-8092, Zürich, Switzerland; A. G. ROBIETTE, Oxford University Computing Service, 13 Banbury Road, Oxford OX2 6NN, England; M. LOETE, J. P. CHAMPION, G. PIERRE, and J. C. HILICO, Laboratoire de Spectronomie Moléculaire de l'Université de Dijon, F-21000 Dijon, France.

WG7. PURE ROTATIONAL SPECTRA OF ASYMMETRICALLY DEUTERATED BENZENES OBSERVED BY PULSED MICROWAVE FOURIER TRANSFORM SPECTROSCOPY...........................15 min.(3:25)

M. OLDANI, T.-K. HA, and A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, CH-8092 Zürich, Switzerland.

WG8. MICROWAVE SPECTRUM OF METHYL HYDRODISULFIDE................................15 min.(3:40)

M. TYBLEWSKI, T.-K. HA, and A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, CH-8092 Zürich, Switzerland.

WG9. ROTATIONAL ENERGY LEVELS AND PRESSURE BROADENING OF $^{12}CH_3F$ IN ITS GROUND AND ν_3 EXCITED VIBRATIONAL STATES..15 min.(3:58)

RICHARD L. CROWNOVER, DAVID D. SKATRUD, and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

WG10. TIME RESOLVED ROTATIONAL RELAXATION IN $^{13}CH_3F$.............................15 min.(4:15)

RODNEY I. MCCORMICK, DAVID D. SKATRUD, and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

WG11. THE DISTORTION MOMENT ROTATIONAL SPECTRUM OF AsD_3 AND THE ROTATIONAL SPECTRA OF AsH_2D AND AsD_2H..........15 min.(4:32)

G. A. MCRAE, M.C.L. GERRY, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada; M. WONG, and I. OZIER, Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada.
Present address of MCRAE: Jet Propulsion Laboratory, Pasadena, California, 91109; Present address of WONG: Canada Center for Remote Sensing, Ottawa, Ontario, Canada.

WG12. INTERNAL ROTATION IN SIMPLE, UNSATURATED THIOLS AND ALCOHOLS..........10 min.(4:49)

C. PLANT and J.N. MACDONALD, Department of Chemistry, University College of North Wales, Bangor, Gwynedd, North Wales, United Kingdom.

WG13. PRESSURE BROADENING OF MM-WAVE OZONE LINES BY ATMOSPHERIC GASES..........10 min.(5:01)

BRIAN J. CONNOR and H. E. RADFORD, Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts, 02138.

WEDNESDAY, JUNE 19, 1985 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chairman Before Intermission: Y.-N. CHIU, Department of Chemistry, The Catholic University of America, Washington, D.C.

Chairman After Intermission: K. S. VISWANATHAN, Department of Chemistry, Indiana University, Bloomington, Indiana.

WH1. ELECTRONIC ENERGY LEVELS IN LONG POLYENES: $S_2 \rightarrow S_0$ EMISSION IN ALL-TRANS-1,3,5,7,9,11,13-TETRADECAHEPTAENE..............................10 min.(1:30)

R. CHRISTENSEN, L. MCLAUGHLIN, and S. SMITH, Department of Chemistry,
Bowdoin College, Brunswick, Maine, 04011.

WH2. RYDBERG TRANSITIONS IN POLYENES: 1,3,5-HEXATRIENES........................15 min.(1:42)

R. MCDIARMID, Bldg. 2, Room B1-07, National Institutes of Health,
Bethesda, Maryland, 20205; and A. SABLJIC, Institute Rudjer
Boskovic, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia.

WH3. APPLICABILITY OF RESONANT TWO PHOTON IONIZATION IN SUPERSONIC BEAMS TO HALOGENATED AROMATIC HYDROCARBONS..10 min.(1:59)

R. TEMBREULL and D. M. LUBMAN, Department of Chemistry, University of
Michigan, Ann Arbor, Michigan, 48109.

WH4. THE LASER PHOTOELECTRON SPECTRUM OF GAS PHASE p-DIFLUOROBENZENE............15 min.(2:11)

E. SEKRETA, K. S. VISWANATHAN, and J. P. REILLY, Department of
Chemistry, Indiana University, Bloomington, Indiana, 47405.

WH5. HIGH RESOLUTION PULSED LASER OPTOGALVANIC SPECTROSCOPY OF RYDBERG STATES IN XENON IN RF DISCHARGE..15 min.(2:28)

D. KUMAR, L. KLASINC, P. L. CLANCY, R. V. NAUMAN, and S. P. MCGLYNN,
Department of Chemistry, Louisiana State University, Baton Rouge,
Louisiana, 70803.

WH6. PULSED LASER OPTOGALVANIC SPECTROSCOPY OF NITROGEN IN RF DISCHARGE.........10 min.(2:45)

D. KUMAR, L. KLASINC, P. L. CLANCY, R. V. NAUMAN, and S. P. MCGLYNN,
Department of Chemistry, Louisiana State University, Baton Rouge,
Louisiana, 70803.

Intermission

WH7. VERSATILE MULTIPLE MODULATION SCHEME FOR TWO-BEAM LASER SPECTROSCOPY.......10 min.(3:15)

P. ANFINRUD and W. S. STRUVE, Department of Chemistry and Ames
Laboratory - USDOE, Iowa State University, Ames, Iowa, 50011.

WH8. FOUR-PHOTON LINE-STRENGTH AND SELECTION RULES OVER SYMMETRIC-TOP MOLECULES AND TIME-REVERSAL INVARIANCE....................................15 min.(3:27)

Y.-N. CHIU, Department of Chemistry, The Catholic University of
America, Washington, D.C., 20064.

WH9. SOME NEW BANDS OF THE $\tilde{A}\,^2A^1-\tilde{X}\,^2A''$ SYSTEM OF HNCN AND DNCN..................10 min.(3:44)

BARBARA SWEETING, C. WELDON MATHEWS, Department of Chemistry,
Ohio State University, Columbus, Ohio, 43210; and D. A. RAMSAY,
Herzberg Institute of Astrophysics, National Research Council of
Canada, Ottawa, Ontario, Canada, K1A OR6.

WH10. A STUDY OF FLAME SPECIES USING THE COHERENT ANTI-STOKES RAMAN SCATTERING TECHNIQUE...15 min.(3:55)

T. HAN, W. Y. CHEUNG, Geo-Centers Inc., Newton, Massachusetts;
G. C. BAUMANN, NRC Research Associate, c o ARDC, Dover, New Jersey,
07801; D. CHIU, and L. E. HARRIS, ARDC, Dover, New Jersey, 07801.

WH11. LASER SPECTROSCOPY OF SiF_2 AND CHEMILUMINESCENCE IN REACTIONS WITH FLUORINE ATOMS AND MOLECULES.. 5 min.(4:13)

A. C. STANTON, A. FREEDMAN, J. WORMHOUDT, Aerodyne Research, Inc.,
45 Manning Road, Billerica, Massachusetts, 01821; and P. P. GASPAR,
Department of Chemistry, Washington University, St. Louis, Missouri,
83130.

WH12. MOLECULAR GEOMETRY AND PREDISSOCIATION TIMES IN THE $\tilde{A}^1A''$ ELECTRONIC STATE OF HCN AND DCN..........15 min.(4:20)

A. MEENAKSHI and K. K. INNES, Department of Chemistry, State University of New York at Binghamton, Binghamton, New York, 13901.

WH13. DOPPLER-LIMITED DYE LASER EXCITATION SPECTROSCOPY OF HCCl: THE $\tilde{A}\ ^1A''(010)$- $\tilde{X}\ ^1A'(000)$ VIBRONIC BAND..........10 min.(4:37)

J. C. PETERSEN, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

WH14. ASSIGNMENT OF THE SCHUSTER BAND OF AMMONIA.......... 5 min.(4:49)

JAMES K. G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

WH15. ROTATIONAL STRUCTURE OF VIBRATIONAL BANDS IN THE SCHÜLER SYSTEM $3p\,^2F_2 - 3s\,^2A_1$ OF ND_4..........15 min.(4:56)

JAMES K. G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

THURSDAY, JUNE 20, 1985 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairman: R. S. MCDOWELL, University of California, Los Alamos National Laboratory, Los Alamos, New Mexico.

COBLENTZ PRIZE* AND AWARD LECTURES

Award of the Prize by the Coblentz Society............................ (8:30)

RA1. TIME RESOLVED STUDIES OR REACTION DYNAMICS IN SOLUTION...........30 min.(8:40)

G. R. FLEMING and S. H. COURTNEY, Department of Chemistry
and The James Franck Institute, University of Chicago,
Chicago, Illinois, 60637.

RA2 SPECTROSCOPIC STUDIES OF CHAIN EXTENSION IN LONG CHAIN MOLECULES AND POLYMERS.....................................30 min.(9:15)

JOHN F. RABOLT, IBM San Jose Research Laboratory,
San Jose, California, 95193.

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* The Coblentz Prize of $1,000 (plus a travel allowance to present the Award Lecture) is given annually to recognize outstanding young spectroscopists under the age of 36. Nominations for the 1986 Award should be sent to Laurence A. Nafie, Department of Chemistry, Syracuse University, Syracuse, New York, 13210.

THURSDAY, JUNE 20, 1985 -- 10:00 A.M.

Room 1153, Physics Laboratory

Chairman: W. H. WEBER, Department of Physics, Research Staff, Ford Motor Company, Dearborn, Michigan.

RA'1. MAGNETIC FIELD MODULATED INFRARED LASER SPECTROSCOPY OF MOLECULAR IONS......15 min.(10:00)

K. KAWAGUCHI, C. YAMADA, S. SAITO, and E. HIROTA, Institute for Molecular Science, Okazaki, 444, Japan.

RA'2. SUB-DOPPLER SPECTROSCOPY USING A MULTIPLE REFLECTION MIRROR SYSTEM..........15 min.(10:17)

Y. T. CHEN, J. M. FRYE, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

RA'3. OBSERVATION OF THE v=20-17 BAND OF HD^+, EXPERIMENTAL EVIDENCE FOR AN ASYMMETRIC ELECTRON DISTRIBUTION..15 min.(10:34)

ALAN CARRINGTON, Physical Chemistry Laboratory, Oxford University, Oxford, United Kingdom; and RICHARD A. KENNEDY, Department of Chemistry, Ohio State University, Columbus, Ohio, 43210.

RA'4. FLUORESCENCE EXCITATION SPECTROSCOPY OF MOLECULAR IONS IN A FREE JET EXPANSION..15 min.(10:49)

RICHARD A. KENNEDY, YEN-CHU HSU, TERRY A. MILLER, Department of Chemistry, Ohio State University, Columbus, Ohio, 43210; and L. DI MAURO, Department of Physics, Louisiana State University, Baton Rouge, Louisiana, 70803.

RA'5. DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF $HCNH^+$: OBSERVATION OF SEVERAL ISOTOPIC SPECIES AND HOT BANDS...................................12 min.(11:06)

T. AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6; and KEIICHI TANAKA, Department of Chemistry, Kyushu University, Fukuoka 812, Japan.

RA'6. DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF THE ν_1 FUNDAMENTAL BAND OF $HOCO^+$..12 min.(11:18)

T. AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6; and KEIICHI TANAKA, Department of Chemistry, Kyushu University, Fukuoka 812, Japan.

RA'7. DETECTION OF PROTONATED N_2O BY DIFFERENCE FREQUENCY LASER SPECTROSCOPY......12 min.(11:30)

T. AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

RA'8. "TRANSIT" BROADENING OF ION SPECTRA LINES..................................10 min.(11:45)

TAKESHI OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

THURSDAY, JUNE 20, 1985 -- 10:00 A.M.

Room 1009, Physics Laboratory

Chairman: R. J. BARTLETT, Departments of Chemistry and Physics, University of Florida, Gainesville, Florida.

RB1. THE EFFECT OF AN AVOIDED CROSSING ON THE O_2 SCHUMANN-RUNGE PHOTODISSOCIATION CONTINUUM...10 min.(10:00)

BRUCE C. GARRETT, LYNN T. REDMON, and MICHAEL J. REDMON, Chemical Dynamics Corporation, 1550 West Henderson Road, Columbus, Ohio, 43220.

RB2. ELECTRONIC AND GEOMETRIC STRUCTURE OF ScH^+ AND ScH_2^+.........................10 min.(10:12)

AILEEN E. ALVARADO-SWAISGOOD and JAMES F. HARRISON, Department of Chemistry, Michigan State University, E. Lansing, Michigan, 48824.

RB3. ELECTRONIC AND GEOMETRIC STRUCTURES OF THE CHROMIUM CATIONS CrH^+, $CrCH_3^+$ $CrCH_2^+$ AND $CrCH^+$...15 min.(10:24)

AILEEN E. ALVARADO-SWAISGOOD, JOHN ALLISON, and JAMES F. HARRISON, Department of Chemistry, Michigan State University, E. Lansing, Michigan, 48824.

RB4. STRUCTURES AND SPECTROSCOPIC CONSTANTS FOR SOME PROTONATED GROUP VI A MOLECULES...15 min.(10:41)

PAUL G. JASIEN and WALTER J. STEVENS, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RB5. AB INITIO CALCULATIONS ON SMALL Be CLUSTERS...............................15 min.(10:58)

M. M. MARINO and W. C. ERMLER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

RB6. AB INITIO CALCULATIONS ON LARGE Be CLUSTERS...............................15 min.(11:15)

W. C. ERMLER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030; C. W. KERN, National Science Foundation, Washington, D.C., 20550; R. M. PITZER, Department of Chemistry, Ohio State University, Columbus, Ohio, 43210; and N. W. WINTER, Chemistry Division, Lawrence Livermore National Laboratory, Livermore, California, 94550.

RB7. ELECTRONIC STRUCTURE OF POLYHEDRAL ALKANES...............................15 min.(11:32)

CAROL A. SCAMEHORN, SUSAN M. HERMILLER, and R. M. PITZER, Department of Chemistry, Ohio State University, Columbus, Ohio, 43210.

RB8. MOLECULAR PHOTOIONIZATION CROSS SECTIONS BY THE COMPLEX BASIS FUNCTION METHOD...15 min.(11:49)

C. W. MCCURDY, C.-H. YU, and R. M. PITZER, Department of Chemistry, Ohio State University, Columbus, Ohio, 43210.

RB9. THEORETICAL STUDY OF THE N_3 MOLECULE.......................................15 min.(12:06)
(Last Minute Addition)

S. R. LANGHOFF, Mail Stop 230-3, NASA/Ames Research Center, Moffett Field, California, 94035.

THURSDAY, JUNE 20, 1985 -- 10:00 A.M.
Room 1005, Physics Laboratory

Chairman: D. E. JENNINGS, NASA/Goddard Space Flight Center,
Greenbelt, Maryland.

RC1. VIBRATIONS OF A BORON ICOSAHEDRON..15 min.(10:00)

C. L. BECKEL and J. P. VAUGHAN, Department of Physics and Astronomy,
University of New Mexico, Albuquerque, New Mexico, 87131.

RC2. EFFECT OF COLLISIONS ON LINE PROFILES IN THE QUADRUPOLE AND RAMAN
SPECTRA OF MOLECULAR HYDROGEN..20 min.(10:17)

J. D. KELLEY and S. L. BRAGG, McDonnell Douglas Research Laboratories,
P.O. Box 516, St. Louis, Missouri, 63166.

RC3. THE INFRARED SPECTRUM OF LIQUID HD..15 min.(10:39)

M. J. CLOUTER and A.R.W. MCKELLAR, Herzberg Institute of Astrophysics,
National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.
Permanent address of CLOUTER: Department of Physics, Memorial
University of Newfoundland, St. John's, Newfoundland, Canada, A1B 3X7.

RC4. RESONANCE ROTATIONAL RAMAN SCATTERING AS A PROBE OF SUBPICOSECOND
PHOTODISSOCIATION DYNAMICS..15 min.(10:56)

L. D. ZIEGLER, Department of Chemistry, Northeastern University,
Boston, Massachusetts, 02115.

RC5. NEAR-CRITICAL RAMAN SPECTRA OF N_2, CO_2, H_2..15 min.(11:13)

M. J. CLOUTER, H. KIEFTE, and C. G. DEACON, Department of Physics,
Memorial University, St. John's, Newfoundland, Canada, A1B 3X7.
Current address of CLOUTER: Herzberg Institute of Astrophysics,
National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

RC6. CARS SPECTRA OF CO_2 AT DIFFERENT TEMPERATURES. EXPERIMENTAL RESULTS
AT 300, 800, 1200, 1500 K AND THEORETICAL SIMULATION........Arrived Late....15 min.(11:30)

N. PAPINEAU, M. LEFEBVRE, and M. PEALAT, Office National d'Etudes
et de Recherches Aérospatiales, 92322 Chatillon cedex, France.

RC7. OVERTONE STIMULATED RAMAN PUMPING OF H_2 FROM V = 0 TO V = 2 AND SUBSEQUENT
TIME DOMAIN PHOTOACOUSTIC DETECTION OF VIBRATIONAL RELAXATION..............15 min.(11:47)
(Last Minute Addition)

J. GELFAND, R. B. MILES, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New
Jersey, 08544, and T. G. KREUTZ, Department of Chemistry,
Princeton University, Princeton, New Jersey, 08544.

RC8. HIGH-RESOLUTION COHERENT ANTI-STOKES RAMAN SPECTROSCOPY OF H_2..............10 min.(12:04)
(Last Minute Addition)

ANTHONY M. TOICH, DAVID W. MELTON, and WON B. ROH,
Department of Engineering Physics, Air Force Institute
of Technology, Wright-Patterson AFB, Ohio, 45433-6583.

THURSDAY, JUNE 20, 1985 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman Before Intermission:	T. A. MILLER, Department of Chemistry, Ohio State University, Columbus, Ohio.
Chairman After Intermission:	LEWIS DI MAURO, Department of Physics Louisiana State University, Baton Rouge, Louisiana.

RE1. THE USE OF EXTENDED PERMUTATION-INVERSION GROUPS FOR CONSTRUCTING HYPERFINE HAMILTONIANS FOR SYMMETRIC TOP INTERNAL ROTOR MOLECULES LIKE $H_3C\text{-}SiH_3$.......15 min.(1:30)

JON T. HOUGEN, Molecular Spectroscopy Division, National Bureau of
Standards, Gaithersburg, Maryland, 20899.

RE2. NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF $NO^-(N_2O)_1$ AND $NO^-(N_2O)_2$..........15 min.(1:47)

K. H. BOWEN, J. V. COE, J. S. SNODGRASS, C. B. FREIDHOFF, and
K. M. MCHUGH, Department of Chemistry, Johns Hopkins University,
Baltimore, Maryland, 21218.

RE3. NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF $H^-(NH_3)_1$ AND $H^-(NH_3)_2$............15 min.(2:02)

J. T. SNODGRASS, J. V. COE, C. B. FREIDHOFF, K. M. MCHUGH, and
K. H. BOWEN, Department of Chemistry, Johns Hopkins University,
Baltimore, Maryland, 21218.

RE4. NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF $NH_2^-(NH_3)_1$ AND $NH_2^-(NH_3)_2$..........15 min.(2:19)

J. V. COE, J. T. SNODGRASS, K. M. MCHUGH, C. B. FREIDHOFF, and
K. H. BOWEN, Department of Chemistry, Johns Hopkins University,
Baltimore, Maryland, 21218.

RE5. NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF SeO^-............................15 min.(2:36)

J. V. COE, J. T. SNODGRASS, C. B. FREIDHOFF, K. M. MCHUGH, and
K. H. BOWEN, Department of Chemistry, Johns Hopkins University,
Baltimore, Maryland, 21218.

Intermission

RE6. SPECTROSCOPY OF TRYPTOPHAN IN A SUPERSONIC MOLECULAR BEAM..................15 min.(3:15)

THOMAS R. RIZZO, YOUNG D. PARK, LINDA PETEANU, and DONALD H. LEVY,
James Franck Institute and Department of Chemistry,
University of Chicago, Chicago, Illinois, 60637.

RE7. THE ROTATION-INVERSION SPECTRUM OF $(SO_2)_2$..................................10 min.(3:32)

D. D. NELSON, JR., G. T. FRASER, and W. KLEMPERER, Department of
Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

RE8. INFRARED STUDIES OF SEVERAL WEAKLY BOUND COMPLEXES OF NH_3..................20 min.(3:44)

D. D. NELSON, JR., G. T. FRASER, A. CHARO, G. J. GERFEN, and
W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge,
Massachusetts, 02138.

RE9. ROTATIONAL SPECTROSCOPIC STUDIES OF WEAKLY BOUND COMPLEXES OF NH_3..........15 min.(4:06)

G. T. FRASER, D. D. NELSON, JR., G. J. GERFEN, and W. KLEMPERER,
Department of Chemistry, Harvard University, Cambridge, Massachusetts,
02138.

RE10. ROTATIONAL SPECTRA OF WATER-N_2O AND WATER-CO VAN DER WAALS COMPLEXES........15 min.(4:23)

K. I. PETERSON, D. J. YARON, T. A. FISHER, and W. KLEMPERER,
Department of Chemistry, Harvard University, Cambridge, Massachusetts,
02138.

RE11. HCl BF_3, A LEWIS ACID VAN DER WAALS COMPLEX..................ARRIVED LATE...15 min.(4:40)

JAMES M. LOBUE, JANE K. RICE, and STEWART E. NOVICK, Department of
Chemistry, Wesleyan University, Middletown, Connecticut, 06457.

THURSDAY, JUNE 20, 1985 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman Before Intermission: PRABHAKAR MISRA, Department of Physics, Ohio State University, Columbus, Ohio.

Chairman After Intermission: B. J. KROHN, University of California, Los Alamos National Laboratory, Los Alamos, New Mexico.

RF1. SUB-DOPPLER LASER-STARK MEASUREMENTS OF HYPERFINE STRUCTURE IN EXCITED VIBRATIONAL STATES OF NH_3 ....15 min.(1:30)

W. H. WEBER, Department of Physics, Research Staff, Ford Motor Company, Dearborn, Michigan, 48121.

RF2. ROTATIONAL ASSIGNMENT OF OVERTONE BANDS OF NH_3 ....15 min.(1:47)

K. K. LEHMANN, Society of Fellows and Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138; and S. COY, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

RF3. THE $v_2=2,a \leftarrow v_2=1,s$ SPECTRA OF $^{14}NH_3$ AND $^{15}NH_3$ ....15 min.(2:04)

H. SASADA, R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, E. Lansing, Michigan, 48824; G. MAGERL, Institut für Nachrichtentechnik, Technische Universität Wien, A-1040 Vienna, Austria; R. L. POYNTER, and J. S. MARGOLIS, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, California, 91109.

RF4. INFRARED-RADIO-FREQUENCY DOUBLE-RESONANCE SPECTROSCOPY OF CF_3I ....15 min.(2:21)

WAFAA FAWZY and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, E. Lansing, Michigan, 48824.

RF5. INFRARED-MICROWAVE SIDEBAND LASER SPECTROSCOPY OF THE ν_3 AND $2\nu_3 \leftarrow \nu_3$ BANDS OF $^{13}CH_3F$ ....15 min.(2:38)

SANG LEE, R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, E. Lansing, Michigan, 48824; and G. MAGERL, Institut für Nachrichtentechnik, Technische Universität Wien, A-1040 Vienna, Austria.

RF6. FOURIER TRANSFORM SPECTRA OF ν_1 BANDS OF HCN AND $3\nu_2$, $2\nu_2 + \nu_6$ AND $\nu_3 + \nu_5$ BANDS OF H_2CO ....10 min.(2:55)

J. I. CHOE, Department of Chemistry, Chung-Ang University, Seoul, 151, Korea; T. TIPTON, Department of Chemistry, University of Florida, Gainesville, Florida, 32603; R. HUBBARD, Kitt Peak National Observatory, P.O. Box 26732, Tucson, Arizona, 85726; and S. G. KUKOLICH, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

Intermission

RF7. ROTATIONAL ANALYSIS OF VINYLSILANE ....10 min.(3:20)

J. K. MCDONALD, Research Directorate, US Army Missile Laboratory, US Army Missile Command, ATTN: AMSMI-RRD, Redstone Arsenal, Alabama, 35898; J.A.S. SMITH, and V. F. KALASINSKY, Department of Physics, Mississippi State University, Mississippi State, Mississippi, 39762.

RF8. HIGH RESOLUTION INFRARED SPECTRUM OF NITROSYL CHLORIDE ....10 min.(3:32)

J. K. MCDONALD, J. A. MERRITT, Research Directorate, US Army Missile Laboratory, US Army Missile Command, ATTN: AMSMI-RRD, Redstone Arsenal, Alabama, 35898; V. F. KALASINSKY, Department of Physics, Mississippi State University, Mississippi State, Mississippi, 39762; and J. R. DURIG, College of Science and Mathematics, University of South Carolina, Columbia, South Carolina, 29208.

RF9. LOW-FREQUENCY VIBRATIONAL SPECTRA OF THE RING-BENDING AND RING-TWISTING VIBRATIONS OF CYCLOHEXENE ....10 min.(3:44)

V. GAINES and J. LAANE, Department of Chemistry, Texas A&M University, College Station, Texas, 77843.

RF10. FAR-INFRARED SPECTRUM AND RING-PUCKERING VIBRATION OF BICYCLO [3.2.0] HEPT-1-ENE ....10 min.(3:56)

M. TECKLENBURG, J. R. VILLARREAL, and J. LAANE, Department of Chemistry, Texas A&M University, College Station, Texas, 77843.

RF11. τ-DEPENDENCE OF THE VIBRATIONAL ZEROPOINT ENERGY IN THE PARTIALLY DEUTERATED METHYL ALCOHOLS, REVISITED..10 min.(4:08)

T. L. CHANG and C. R. QUADE, Department of Physics, Texas Tech
University, Lubbock, Texas, 79409.

RF12. REDUCTION OF THE VIBRATION-ROTATION-LAM HAMILTONIAN.........................15 min.(4:20)

YUHUA GUAN and RICHARD QUADE, Department of Physics, Texas Tech
University, Lubbock, Texas, 79409.

RF13. ISOMORPHIC HAMILTONIAN OF ACETYLENE WITH EXCITATION IN LOCAL MODES..........10 min.(4:37)

G. A. NATANSON, Joint Institute for Laboratory Astrophysics,
University of Colorado and National Bureau of Standards, Boulder,
Colorado, 80309.

RF14. VARIATIONAL CALCULATIONS OF ROTATIONAL-VIBRATIONAL ENERGY LEVELS OF WATER FOR DIFFERENT FORCE FIELDS AND GEOMETRIES..................ARRIVED LATE....10 min.(4:49)

B. MAESSEN and M. WOLFSBERG, Department of Chemistry, University of
California, Irvine, California, 92717.

RF15. ON THE EQUIVALENCE OF INTRAMOLECULAR POTENTIAL EXPANSIONS IN NORMAL AND VALENCE DISPLACEMENT COORDINATES...........................ARRIVED LATE....10 min.(4:59)

B. MAESSEN, M. WOLFSBERG, Department of Chemistry, University of
California, Irvine, California, 92717; and L. B. HARDING, Technical
Chemistry Group, Chemistry Division, Argonne National Laboratory,
Argonne, Illinois, 60439.

THURSDAY, JUNE 20, 1985 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chairman Before Intermission:	JOHN L. HARDWICK, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana.
Chairman After Intermission	D. L. HUESTIS, Chemical Physics Laboratory, SRI International, Menlo Park, California.

RG1. HYPERFINE SPLITTING OF $2^3\Delta_g$, $3^3\Delta_g$, AND $2^3\Delta_g$-$2^1\Delta_g$ MIXED LEVELS OF Na_2........15 min.(1:30)

LI LI, Qinghai Institute of Salt Lake, Xining, Qinghai, China;
and R. W. FIELD, Department of Chemistry, Massachusetts Institute
of Technology, Cambridge, Massachusetts, 02139.

RG2. STIMULATED EMISSION BASED ON TWO-STEP HYBRID RESONANCE VIA $A^1\Sigma_u^+$ OR $B^1\Pi_u$ STATE OF Na_2..15 min.(1:47)

L.-J. QIN, Z.-G. WANG, K.-C. ZHANG, and I.-S. CHENG, Department of
Physics, East China Normal University, Shanghai 200062, People's
Republic of China.

RG3. TWO-AND THREE-PHOTON ABSORPTION STUDIES OF THE O_2 MOLECULE..................15 min.(2:04)

ABHA SUR, C. V. RAMANA, and STEVEN D. COLSON, Department of
Chemistry, Yale University, New Haven, Connecticut, 06511.

RG4. HIGH RESOLUTION ONE-PHOTON IONIZATION CROSS SECTION OF NO USING THIRD-HARMONIC GENERATION..15 min.(2:21)

PAUL J. MILLER, PETER CHEN, and WILLIAM A. CHUPKA, Department of
Chemistry, Yale University, New Haven, Connecticut, 06511.

RG5. MEASUREMENT OF AUTOIONIZATION RATES IN THE NON-PENETRATING 4F STATE OF NO...15 min.(2:38)

D. T. BIERNACKI, E. E. EYLER, STEVEN D. COLSON, and WILLIAM A. CHUPKA,
Department of Chemistry, Yale University, New Haven, Connecticut, 06511.

Intermission

RG6. RESONANCE ENHANCED MULTIPHOTON IONIZATION OF FREE RADICALS IN A SUPERSONIC EXPANSION. NEW BANDS AND ROTATIONAL ANALYSIS FOR CH AND CH_2.....15 min.(3:15)

PETER CHEN, STEVEN D. COLSON, WILLIAM A. CHUPKA, and JEROME A. BERSON,
Department of Chemistry, Yale University, New Haven, Connecticut,
06511.

RG7. MS-PES MULTIPHOTON IONIZATION STUDIES OF AMMONIA..........................10 min.(3:32)

C. V. RAMANA and STEVEN D. COLSON, Department of Chemistry, Yale
University, New Haven, Connecticut, 06511.

RG8. PICOSECOND PHOTOELECTRON STUDIES OF THE EXCITED ELECTRONIC STATES OF AZAAROMATICS..15 min.(3:44)

J. B. PALLIX and STEVEN D. COLSON, Department of Chemistry, Yale
University, New Haven, Connecticut, 06511.

RG9. CONFIGURATION INTERACTION AND SPIN-ORBIT COUPLING IN THE FOX-HERZBERG SYSTEM OF C_2..15 min.(4:01)

J. L. HARDWICK, Radiation Laboratory, University of Notre Dame,
Notre Dame, Indiana, 46556; and D. H. WINICUR, Department of
Chemistry, University of Notre Dame, Notre Dame, Indiana, 46556.

RG10. ERGODIC BEHAVIOR AND THE ANOMALOUS CONTINUUM FLUORESCENCE OF SMALL MOLECULES..15 min.(4:18)

JOHN L. HARDWICK, Radiation Laboratory, University of Notre Dame,
Notre Dame, Indiana, 46556.

RG11. MICELLAR EFFECTS ON DUAL FLUORESCING COMPOUNDS...........................10 min.(4:35)
(Last Minute Addition)

ATU A. AYUK, Division of Physical & Life Sciences, Fayetteville
State University, Fayetteville, North Carolina, 28301; and
F. S. SADEK, Department of Natural Science, Winston-Salem
State University, Winston-Salem, North Carolina, 27110.

RG12. QUENCHING STUDIES OF DUAL FLUORESCING 1-N,N-DIMETHYLAMINO-4-METHOXY-CARBOXYLIC ACID BENZENE (DMABMCA) BY KI IN 2-PROPANOL/WATER MIXED SOLVENTS..10 min.(4:47)
(Last Minute Addition)

ATU A. AYUK, Division of Physical & Life Sciences, Fayetteville
State University, Fayetteville, North Carolina, 28301.

THURSDAY, JUNE 20, 1985 -- 1:30 P.M.
Room 1008, Evans Chemical Laboratory

Chairman: G.N.R. TRIPATHI, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana.

SEMINAR OF INVITED PAPERS ON TIME RESOLVED RAMAN SPECTROSCOPY

RH1. TIME RESOLVED RESONANCE RAMAN SCATTERING STUDIES OF INTERFACIAL CHEMICAL KINETICS IN MICELLAR AND COLLOIDAL SOLUTIONS.............30 min.(1:30)

LOUIS BRUS, AT&T Bell Laboratories, Murray Hill, New Jersey, 07974.

RH2. NEW TECHNIQUES FOR THE VIBRATIONAL SPECTROSCOPY OF GASES WITH ULTRASHORT LASER PULSES..30 min.(2:05)

A. LAUBEREAU, H. GRAENER, and H.-J. HARTMANN, Physikalisches Institut, University of Bayreuth, 8580 Bayreuth, West Germany.

Intermission

RH3. RESONANCE CARS OF α,ω-DIPHENYLPOLYENES IN THE LOWEST EXCITED SINGLET AND TRIPLET STATES......................................30 min.(3:00)

A. KASAMA, T. KAMISUKI, Y. ADACHI, and S. MAEDA, Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Midori-ku, Yokohama 227, Japan.

RH4. TRIPLET STATE RESONANCE RAMAN SPECTRA OF SMALL POLYENES...........30 min.(3:35)

R. WILBRANDT, F. W. LANGKILDE, and N.-H. JENSEN, Department of Chemistry, Riso National Laboratory, DK-4000 Roskilde, Denmark.

RH5. TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF TRANSIENT SPECIES FORMED DURING THE OXIDATION OF CYTOCHROME OXIDASE BY DIOXYGEN.....30 min.(4:10)

GERALD T. BABCOCK, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824, JOHN M. JEAN, LEAH N. JOHNSTON, WILLIAM H. WOODRUFF, Inorganic and Structural Chemistry Group (INC-4), Isotope and Nuclear Chemistry Division, Los Alamos National Laboratory, University of California, Los Alamos, New Mexico, 87545; and GRAHAM PALMER, Department of Biochemistry, Rice University, P.O.B. 1892, Houston, Texas 77251.

FRIDAY, JUNE 21, 1985 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairman Before Intermission: G. D. CARNEY, Department of Chemistry, Allegheny College, Meadville, Pennsylvania.

Chairman After Intermission: JON MANHEIM, Wright Patterson Air Force Base, Ohio.

FA1. VIBRATIONAL SPECTRA, FORCE CONSTANTS AND Si-O BOND CHARACTERS IN CALCIUM SILICATE CRYSTAL STRUCTURES..10 min.(8:30)

M. HANDKE, Harrick Scientific Corporation, 88 Broadway, Ossining,
New York, 10562. On sabbatical from Institute of Material Science
AGH Cracow, Poland.

FA2. INFRARED OPTICAL AND DIELECTRIC CONSTANTS OF LIQUID ALIPHATIC ALCOHOLS AND THE MAGNITUDE OF THE CHANGE IN MOLECULAR DIPOLE MOMENT DURING THE OH STRETCHING VIBRATION..15 min.(8:42)

J. E. BERTIE, V. BEHNAM, Department of Chemistry, University of
Alberta, Edmonton, Alberta, Canada, T6G 2G2; and H. H. EYSEL,
Anorganisch Chemisches Institut der Universitat Heidelberg,
6900 Heidelberg, West Germany.

FA3. VIBRATIONAL SPECTRA AND CONFORMATIONAL BEHAVIOR OF 1,1-DIETHYLCYCLOPROPANE..10 min.(8:59)

C. J. WURREY, P. M. GREEN, Department of Chemistry, University of
Missouri-Kansas City, Kansas City, Missouri, 64110; and V. F. KALASINSKY,
Department of Chemistry, Mississippi State University, Mississippi
State, Mississippi, 39762.

FA4. VIBRATIONAL SPECTRA OF CYCLOPROPYL CYANIDE AND CYCLOPROPYL CYANIDE-α-d_1..15 min.(9:11)

C. J. WURREY, P. M. GREEN, R. KRISHNAMOORTHI, and Y. Y. YEH,
Department of Chemistry, University of Missouri-Kansas City,
Kansas City, Missouri, 64110.

FA5. VIBRATIONAL SPECTRA OF FLUOROMETHYLCYCLOPROPANE AND BISOXIRANE..............15 min.(9:26)

J. A. SMITH, K. G. WHITEHEAD, C. SAIWAN, and V. F. KALASINSKY,
Department of Chemistry, Mississippi State University, Mississippi
State, Mississippi, 39762.

FA6. FORCE CONSTANTS FOR THE CYCLOPROPENYL CATION..............................10 min.(9:45)

NORMAN C. CRAIG, JULIANTO PRANATA, SARA JAMIE REINGANUM, and
PHILIP S. STEVENS, Department of Chemistry, Oberlin College,
Oberlin, Ohio, 44074.

FA7. VIBRATIONAL SPECTRA OF TRANS-1,2-DIFLUOROETHYLENE OXIDE....................10 min.(9:57)

J. W. AGOPOVICH, C. W. GILLIES, Department of Chemistry, Rensselaer
Polytechnic Institute, Troy, New York, 12181; N. C. CRAIG and
D. J. MCGARVEY, Department of Chemistry, Oberlin College, Oberlin,
Ohio, 44074.

Intermission

FA8. INFRARED AND RAMAN SPECTRA AND CONFORMATIONAL STABILITY OF ETHYLDIMETHYLPHOSPHINE..15 min.(10:20)

T. J. HIZER and J. R. DURIG, Department of Chemistry, University of
South Carolina, Columbia, South Carolina, 29208.

FA9. INFRARED AND RAMAN SPECTRA OF 4-(DIMETHYLAMINO)BENZALDEHYDE AND ITS ZINC COMPLEX..15 min.(10:37)

J. G. ROSENKRANCE and P. W. JAGODZINSKI, Department of Chemistry,
West Virginia University, Morgantown, West Virginia, 26506.

FA10. VIBRATIONAL SPECTRA OF SUPERSOLVENTS: TETRAMETHYLUREA AND HEXAMETHYLPHOSPHORAMIDE..10 min.(10:54)

D. L. McCARTY, R. L. HUNT-KRAMER, and P. W. JAGODZINSKI, Department
of Chemistry, West Virginia University, Morgantown, West Virginia,
26506.

FA11. AN AB INITIO MOLECULAR ORBITAL STUDY OF THE VIBRATIONAL FREQUENCIES OF ONF AND NOF..15 min.(11:05)

L. A. CURTISS and V. A. MARONI, Chemical Technology Division/
Materials Science and Technology Division, Argonne National
Laboratory, Argonne, Illinois, 60439.

FA12. A COMPARISON OF QUANTUM MECHANICAL AND SEMI-CLASSICAL SCF THEORIES FOR H_3^+, H_2O, AND O_3..15 min.(11:23)

G. D. CARNEY, D. LESSESKI, W. REED, and L. PAVLOVICH, Department of
Chemistry, Allegheny, Meadville, Pennsylvania, 16335.

FA13. AB-INITIO QUARTIC FORCE FIELDS IN DIMENSIONLESS NORMAL COORDINATES FOR H_3^+...15 min.(11:38)

G. D. CARNEY and D. LESSESKI, Department of Chemistry, Allegheny
College, Meadville, Pennsylvania, 16335.

FA14. THE ^1L_b STATE OF 1,6:8,13-ETHANO[14]ANNULENE. VIBRATIONAL STRUCTURE AND THE "A BAND"..Arrived Late........15 min.(11:55)

K. A. KLINGENSMITH, J. MICHL, Department of Chemistry, University
of Utah, Salt Lake City, Utah, 84112; and H. J. DEWEY, Los Alamos
National Laboratories, Los Alamos, New Mexico, 87544.

FA15. FAR INFRARED AND RAMAN VAPOR PHASE SPECTROSCOPY OF HETEROCYCLIC COMPOUNDS..15 min.(12:12)
(Last Minute Addition)

W. B. COLLIER and M. M. STRUBE, National Institute for
Petroleum and Energy Research, P.O. Box 2128,
Bartlesville, Oklahoma, 74005.

FA16. OVERTONE SPECTRA AND LOCAL MODE ANALYSIS OF CHLOROTRIFLUOROMETHANE..........10 min.(12:29)
(Last Minute Addition)

A. M. DeSOUZA and D. S. PERRY, Department of Chemistry,
University of Rochester, Rochester, New York, 14627.

FRIDAY, JUNE 21, 1985 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chairman: C. CHACKERIAN, JR., Astrophysical Experiments Branch, NASA/Ames Research Center, Moffett Field, California

FB1. ANALYSIS OF THE ν_3 BAND OF $^{32}SF_6$ FROM SATURATED ABSORPTION SPECTROSCOPY.....10 min.(8:30)

B. BOBIN, Laboratoire de Spectronomie Moléculaire, Université de Dijon, 21100 Dijon, France; CH. BREANT, J. BORDÉ, and CH. BORDÉ, Laboratoire de Physique des Lasers, Université Paris-Nord, 93430 Villetaneuse, France.

FB2. THE ν_3 BANDS OF NATURAL OsO_4 FROM FT-IR SPECTRUM..........................10 min.(8:42)

B. BOBIN, Laboratoire de Spectronomie Moléculaire, Université de Dijon, 21100 Dijon, France; L. HENRY, and A. VALENTIN, Laboratoire de Spectronomie Moléculaire, Université Paris VI, 75005 Paris, France.

FB3. MEASUREMENT OF THE INFRARED-ACTIVE STRETCHING FUNDAMENTAL (ν_3) OF UF_6.......15 min.(8:54)

R. S. McDOWELL, J. P. ALDRIDGE, H. FILIP, H. FLICKER, R. F. HOLLAND, K. C. KIM, W. B. MAIER II, University of California, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545; D. W. MAGNUSON, D. F. SMITH, G. K. WERNER, Union Carbide Corporation, Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tennessee, 37830; and W. B. PERSON, Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

FB4. ANALYSIS OF THE INFRARED-ACTIVE STRETCHING FUNDAMENTAL OF UF_6..............15 min.(9:11)

B. J. KROHN, E. G. BROCK, H. W. GALBRAITH, R. S. McDOWELL, C. W. PATTERSON, University of California, Los Alamos National Laboratory, Los Alamos, New Mexico, 87544; and K. FOX, Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee, 37996-1200.

FB5. LINE WIDTHS AND THEIR TEMPERATURE DEPENDENCE IN THE ν_9-FUNDAMENTAL BAND OF ETHANE...15 min.(9:28)

S. CHUDAMANI, P. VARANASI, Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York, 11794; L. P. GIVER, and F.P.J. VALERO, Astrophysical Experiments Branch, NASA Ames Research Center, Moffett Field, California, 94035.

FB6. SIMULTANEOUS ANALYSIS OF VIBRATIONAL POLYADS IN SYMMETRIC AND SPHERICAL TOPS. THEORETICAL AND NUMERICAL ASPECTS ILLUSTRATED ON CH_4, CD_4 AND CH_3F...15 min.(9:45)

J. P. CHAMPION, Laboratoire de Spectronomie Moléculaire, CNRS, Université de Dijon, 21100 Dijon, France.

Intermission

FB7. FURTHER ANALYSIS OF EFFECTIVE HAMILTONIANS FOR TRIPLY DEGENERATE FUNDAMENTALS OF TETRAHEDRAL MOLECULES. UNAMBIGUOUS FIT OF q^2J^5 AND q^2J^6 TERMS FOR ν_4 OF $^{12}CH_4$...10 min.(10:15)

VI. G. TYUTEREV, V. I. PEREVALOV, Laboratory of Spectroscopy, Institute of Atmospheric Optics, Siberian Branch Acad. Sci. USSR, 634055 Tomsk, USSR; G. PIERRE. J. P. CHAMPION, Laboratoire de Spectronomie Moléculaire, CNRS, Université de Dijon, 21100 Dijon, France; and B. I. ZHILINSKII, Department of Chemistry, Moscow State University, Moscow 117234, USSR.

FB8. MEASUREMENTS OF CH_4 ν_4 HALFWIDTHS USING TWO HIGH-RESOLUTION TECHNIQUES......10 min.(10:27)

V. MALATHY DEVI, D. C. BENNER, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; M.A.H. SMITH, and C. P. RINSLAND, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665.

FB9. LINE STRENGTHS OF METHANE IN THE 2.2 MICRON REGION.........................10 min.(10:39)

J. C. HILICO, M. LOETE, Laboratoire de Spectronomie Moléculaire, Université de Dijon, 21100 Dijon, France; and L. R. BROWN, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, California, 91109.

FB10. DIPOLE MOMENT PARAMETERS OF METHANE....................................15 min.(10:51)

M. LOETE and J. C. HILICO, Laboratoire de Spectronomie Moléculaire, CNRS, Université de Dijon, 21100 Dijon, France.

FB11. HIGH RESOLUTION INFRARED SPECTRUM OF SiH_3D..............................15 min.(11:03)

R. W. LOVEJOY, R. D. SCHAEFFER, Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania, 18015; and W. B. OLSON, National Bureau of Standards, Gaithersburg, Maryland, 20899.

FRIDAY, JUNE 21, 1985 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chairman: C. WELDON MATHEWS, Department of Chemistry, Ohio State University, Columbus, Ohio.

FC1. LASER-INDUCED FLUORESCENCE STUDY OF VIBRATIONAL RELAXATION IN XeF(B)........15 min.(8:30)

G. BLACK, L. E. JUSINSKI, D. C. LORENTS, and D. L. HUESTIS, Chemical Physics Laboratory, SRI International, Menlo Park, California, 94025.

FC2. ABSORPTION LINES IN THE KrCl LASER SPECTRUM AND THE SPONTANEOUS EMISSION OF KrCl..15 min.(8:47)

M. SHIMAUCHI and K. OIKAWA, Department of Physics, Tokyo Gakugei University, Nukui Kitamachi, Koganei-shi, Tokyo 184, Japan.

FC3. CHARGE-TRANSFER SPECTRA OF $(ArKr)^+$ AND $(ArXe)^+$............................15 min.(9:04)

R. H. LIPSON and K. P. HUBER, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

FC4. BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION IN THE LEAST SQUARES FITTING OF SPECTROSCOPIC LINE POSITIONS: THE $X^1\Sigma^+$ STATE OF HYDROGEN CHLORIDE..15 min.(9:21)

J. A. COXON, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3.

FC5. VIBRATIONAL POTENTIAL REPRESENTATION FOR THE X AND A ELECTRONIC STATES OF N_2..15 min.(9:38)

C. L. BECKEL, E. R. NELSON, and D. L. LOVERRO, Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico, 87131.

Intermission

FC6. ANALYSIS OF THE OPTICAL-OPTICAL DOUBLE RESONANCE SPECTRUM OF THE $3^1\Sigma_g^+$ STATE OF Li_2....................................Arrived Late.........15 min.(10:15)

R. A. BERNHEIM, L. P. GOLD, and C. A. TOMCZYK, Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania, 16802.

FC7. ROTATIONAL ANALYSIS OF THE $A^3\Pi_0 \rightarrow X^1\Sigma_0^+$ AND $B^3\Pi_1 \rightarrow X^1\Sigma_0^+$ ..Arrived Late........10 min.(10:32)

W. E. JONES and V. N. SARMA, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3.

FC8. HIGH RESOLUTION STUDY OF THE B $\leftrightarrow$ X SYSTEM OF ISOTOPIC SPECIES OF CO........10 min.(10:44)
(Last Minute Addition)

M. EIDELSBERG, F. LAUNAY, C. LETZELTER, Observatoire de Paris, Département d'Astrophysique Fondamentale (C.N.R.S.) U.A. 812), 92195 Meudon Principal Cédex, France, J.-Y. RONCIN, Eqipe de Spectroscopie (C.N.R.S. U.A. 171), Ecole des Mines, 158 Cours Fauriel, 42023 Saint-Etienne Cédex, France, A. LE FLOCH, Département de Physique, Université de Tours, 37200 Tours, France; and J. ROSTAS, Laboratoire de Photophysique Moléculaire du C.N.R.S., Batiment 213, Université Paris-Sud, 91405 Orsay, France.

FC9. ROTATIONALLY RESOLVED PHOTOELECTRON SPECTRA OF GASE PHASE NO...............10 min.(10:56)
(Last Minute Addition)

K. S. VISWANATHAN, ELLEN SEKRETA, W. G. WILSON, and J. P. REILLY, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

ME1. (1:30)

HIGH RESOLUTION SPECTRUM OF THE C-O STRETCHING BAND OF C-13 METHANOL

I. MUKHOPADHYAY, W. LEWIS-BEVAN, AND R.M. LEES

The high resolution spectrum of the C-O stretching band of $^{13}CH_3OH$ has been obtained in the 950-1100 cm^{-1} region at 0.004 cm^{-1} resolution using a Bomem Fourier transform spectrometer. Many intense P and R branches have been assigned for K values up to 7 and J values up to about 35 in the $v_t=0$ torsional ground state. The strong Q branch region around 1018 cm^{-1} is very crowded, but series of lines can be followed up to reasonable J values. Progress is also anticipated toward assignment of absorption lines in torsionally excited states. The $v_t=0$ assignments were based primarily on ground state combination differences calculated using molecular parameters reported from microwave measurements.

The P and R branch frequencies have been fitted to a simplified model in which the energy levels are expressed as series in powers of J(J+1). The results will be discussed in terms of effective state-dependent molecular parameters. In addition, comments will be made on assignment of far infrared laser lines in the excited C-O stretch state.

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Address of Lewis-Bevan: Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6

ME2. (1.47)

INFRARED AND MILLIMETER SPECTRA OF METHYLAMINE

R.M. LEES, W. LEWIS-BEVAN, K.V.L.N. SASTRY, J.S. PITRE AND T.J. NOBLE

The high resolution spectrum of the C-N stretching band of CH_3NH_2 has been obtained from 900 to 1100 cm^{-1} at 0.004 cm^{-1} resolution using a Bomem Fourier transform spectrometer. In addition, the millimeter wave spectrum of CH_3NH_2 has been investigated in the 60-250 GHz region to fill in gaps in previously reported Q branches and to explore more fully the ground state rotation-torsion-inversion energy level structure at moderate J and K. With accurate ground state combination differences established from the microwave results, it has been possible to assign a number of low K infrared P and R branches for the stronger a-component of the inversion doublets.

It is hoped to identify the weaker s-components of the doublets in order to determine the effects of vibrational excitation on the barriers to inversion and internal rotation, and also to refine and extend the set of molecular parameters describing parallel a-type transitions.

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Address of Lewis-Bevan: Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6.

ME3. (2:04)

ANALYSIS OF THE STIMULATED RAMAN SPECTRUM OF THE $\nu_{16}/\nu_2+\nu_{18}$ FERMI DIAD OF BENZENE

P. ESHERICK, A. OWYOUNG, AND J. PLÍVA

The Raman spectrum of benzene was measured with the aid of the ionization-detected stimulated Raman technique[1] in the region 1580 - 1625 cm^{-1} containing the ν_{16} E_{2g} fundamental band and the $\nu_2+\nu_{18}$ E_{2g} combination band enhanced by close Fermi resonance with the fundamental. With the ~0.007 cm^{-1} resolution attained, the strong ${}^{O}O$ and ${}^{S}S$ branch lines were completely resolved for the higher K values.

Both bands have the regular structure of $\Delta K = \pm 2$, $\Delta l = \pm 1$ transitions, but the lower frequency band exhibits a perturbation localized near $K = 21$, which was ascribed to a $J_{x,y}$-Coriolis interaction with the $\nu_7+\nu_{18}$ E_{1g} state. A Hamiltonian matrix containing the three states and their Fermi, Coriolis, and l-type interactions was used for the treatment of the upper states of the observed bands yielding a set of spectroscopic constants which reproduce the observed spectrum with an over-all standard deviation of 0.0025 cm^{-1}. The unperturbed origins of the ν_{16} and $\nu_2+\nu_{18}$ states are at 1600.966 and 1599.881 cm^{-1} respectively : the identity of the lower lying state as $\nu_2+\nu_{18}$ was established by its constant $C\zeta = +0.05498$ cm^{-1} which is very close to the value reported in the literature for ν_{18}.

[1] P. Esherick and A. Owyoung, Chem. Phys. Letters 103, 235 (1983).

Address of Esherick and Owyoung : Sandia National Laboratories, Albuquerque, N. M. 87185.

Address of Plíva : Department of Physics, Pennsylvania State University, University Park, Pa. 16802.

ME4. (Paper presented by K. BLOM) (2:21)

THE ROTATION-VIBRATION SPECTRUM OF CYANAMIDE AND CARBODIIMIDE

M. Birk and M. Winnewisser

The infrared spectrum of cyanamide, HHNCN, has been recorded from 500 cm^{-1} to 4000 cm^{-1} using a Digilab FTS 20B Fourier transform spectrometer operating with a resolution of 0.09 cm^{-1}. Samples of cyanamide were deposited in the infrared cell which was two meters in length. The entire cell was held at a temperature of 373 K, thus providing enough vapour pressure of cyanamide for the infrared absorption spectra. All fundamental bands of cyanamide including the inversion hot bands except the NCN bending modes have been detected. The rotational structure of the unperturbed part of the 0^+-1^- C-type band, which shows a-type Coriolis interaction for K_a greater than 2, has been assigned and analysed. The band center and the rotational constants of the 1^- state were obtained. Furthermore, three band systems of carbodiimide, HNCNH, were observed under the same experimental conditions. All three bands have previously been observed in the infrared spectra of argon matrix-isolated cyanamide and carbodiimide (1), however, no gas phase spectra were reported. The present results confirm the thermal isomerization of cyanamide. The current state of the analysis of these bands will be reported.

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(1) S. T. King and J. H. Strope, J. Chem. Phys. 54, 1289-1295 (1971).

Address of Birk and Winnewisser: Physikalisch-Chemisches Institut,
Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-6300 Giessen,
Federal Republic of Germany.

ME5. (2:38)

HIGH RESOLUTION INFRARED SPECTRUM OF CH_2NH

L. Halonen and G. Duxbury

The infrared spectrum of methyleneimine, CH_2NH, has been observed in the gas phase with a resolution of 0.0048 cm^{-1} (700 - 1400 cm^{-1}) and of 0.01 cm^{-1} (2800 - 3400 cm^{-1}). CH_2NH was produced by the pyrolysis of CH_3NH_2 at ca. 1000°C. Altogether seven bands, ν_1, ν_2, ν_3, $2\nu_5$, ν_7, ν_8 and ν_9, have been observed and analyzed to yield accurate spectroscopic parameters. The ν_3 and $2\nu_5$ bands were coupled by a high order Coriolis type of resonance and the ν_7, ν_8 and ν_9 fundamentals were strongly coupled by Coriolis interaction. For the latter system more than 2500 transitions were assigned, of which many are "forbidden" transitions, such as ^qQ branches, induced in the ν_9 band by the strong Coriolis interaction between ν_7 and ν_9. The standard deviation of the fit, 0.00075 cm^{-1}, shows clearly the excellent quality of the results. The ν_1, ν_2, ν_3 and $2\nu_5$ bands showed signs of perturbations at high J and K_a quantum numbers and only part of the assigned transitions could be included in the final fits.

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ME6. (3:15)

A GENERALIZED INTERNAL AXIS METHOD FOR HIGH BARRIER TUNNELING PROBLEMS, AS APPLIED TO THE WATER DIMER

JON 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, and is illustrated using 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 of 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. 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.

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Gaithersburg, MD 20899.

ME7. (3:32)

THE TORSIONAL-WAGGING TUNNELING PROBLEM AND TORSIONAL-WAGGING-ROTATIONAL PROBLEM IN HYDRAZINE

NOBUKIMI OHASHI AND JON T. HOUGEN

Results derived previously for the rotational levels of the eight-framework and three-large-amplitude vibrational problem in H_2N-NH_2, using a tunneling formalism based on a treatment of the vibration-rotation problem as a whole, are rederived here 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 in earlier treatments, 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 non-superimposable molecular frameworks that can actually be constructed for H_2N-NH_2.

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ME8. (3:49)

FAR-INFRARED SPECTRUM OF THE TORSIONAL BAND OF HYDRAZINE

N. OHASHI, W. J. LAFFERTY, AND W. B. OLSON

We report here the results of a study of the far-infrared spectrum of hydrazine obtained on the NBS BOMEM DA3.002 Fourier transform spectrometer. The spectrum was recorded in the wavenumber region 200 to 500 cm^{-1} with apodized resolution of 0.011 cm^{-1}. This molecule has two large amplitude motions, a wag and the torsion. The spectrum is complicated because of splittings arising from these motions as well as overlapping with a "hot band" especially below the band origin at 376 cm^{-1}. The assignments were made using polynomial fittings of individual subbands. The B←A, A←B, and E←E transitions were assigned for each subband. The assigned transitions were analyzed through a global fitting procedure with the use of the model Hamiltion of Hougen[1] to obtain molecular parameters in the torsionally excited state. The large-amplitude splitting constants show large changes upon torsional excitation; e. g. the torsional-splitting constant h_{3v} is -892(3) MHz compared to -2.90(2) MHz in the ground state,[2] and the inversion splitting constant h_{5v} is +1931(2) MHz compared to -4010.23(4) MHz in the ground state[2] taking the sign conventions of Refs. 1 and 2.

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[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).

Address of Ohashi: Department of Physics, Faculty of Science, Kanazawa University, Kanazawa 920, Japan.
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ME9. (4:06)

HIGH RESOLUTION SPECTRUM OF THE ν_2 AND ν_3 BANDS OF HOCl

W. J. LAFFERTY AND W. B. OLSON

The ν_2 and ν_3 bands of HOCl have been studied with 0.004 cm^{-1} apodized resolution using the NBS DA3.002 BOMEM Fourier transform spectrometer. The ν_2 band has been studied previously,[1] while the high resolution spectrum of the ν_3 band is reported here for the first time. Although both a- and b-type transitions are permitted for both bands, only a-type transitions were observed. Transitions of both the ^{35}Cl and ^{37}Cl isotopic species were assigned. Results for the ν_2 band are generally in good agreement with the results of Sams and Olson[1]; however, due to the higher resolution avialable in this study, we were able to extend the line assignment to the K=7 transitions. The K=5 levels of the ν_2 band of the ^{35}Cl species were found to be perturbed. This perturbation arises from an X-Y Coriolis resonance with the K=4 levels of the $2\nu_2$ state. The observed transitions were fit using a Watson S-Reduction Hamiltonian including terms through P^8. The molecular constants will be reported.

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[1] R. L. Sams and W. B. Olson, J. of Mol. Spectrosc. 84, 113 (1980).

Address of Lafferty and Olson: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

ME10. (4:23)

VIBRATION ROTATION SPECTRA AND THE HARMONIC FORCE FIELD OF HOCℓ

Catherine M. Deeley[1] and Ian M. Mills[2]

Vibration rotation spectra of HOCℓ have been recorded using the Nicolet 7199 Fourier transform infrared spectrometer at Reading. Measurements were made at a resolution of 0.05 cm^{-1} to determine vibration rotation constants, and the 35-37 Cℓ isotope shifts in the vibration frequencies. The spectrum of DOCℓ has also been recorded, and a preliminary analysis for the band origins has been made.

The vibrational frequency data and centrifugal distortion constants have been used to determine the harmonic force field in a least squares refinement; the force field obtained also gives a good fit to data on the vibrational contributions to the inertial defect. The equilibrium rotational constants of HOCℓ have been obtained, and an equilibrium structure has been estimated.

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[1] C.M. Deeley: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, K1A 0R6

[2] I.M. Mills: Department of Chemistry, The University of Reading, Whiteknights, Reading, Berkshire, England, RG6 2AD

ME11. (4.40)

COLLISION INDUCED ROTATIONAL SPECTRUM OF NONPOLAR HYDROCARBONS AND THEIR MIXTURES WITH ARGON

R. COHEN AND W. PRINGLE

Accurate values of the quadrupole moments of nonpolar hydrocarbons such as allene, ethylene, and ethane have been determined from analysis of the low frequency tail of the CIA rotational spectra of these molecules. Experimental spectra are compared to those calculated by superposition of individual transitions as opposed to spectral moment integrated absorption coefficients. Argon-molecule CIA spectra will be presented and analyzed in terms of the multipole moments and differences in the anisotropies of the molecule-atom versus molecule-molecule collisions.

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ME12 (4:49)

OBSERVATION OF COLLISIONAL LINE MIXING IN A CO$_2$ Q-BRANCH USING A DIODE LASER

L. STROW AND B. GENTRY

Rotationally inelastic collsions can narrow the profile of a Q-branch with increasing pressure. This phenomenon, termed either line mixing or rotational collisional narrowing, has recently been observed in several Raman Q-branches of small molecules at pressures near 1 atm. Recent theoretical calculations by Braun[1] and Armstrong[2] suggest that line mixing should be observable in the CO$_2$ ν_2 Q-branch at 15 µm at pressures of 1 atm or less.

We have observed line mixing in the Q-branch of the $(11^10,03^10)_{II}$ - 00^10 band of CO$_2$ at 1932.47 cm^{-1} using a tunable diode laser. This Q-branch is ideal for studying collisional narrowing because it is largely free from interfering lines due to other vibrational bands. An almost 1 cm^{-1} long spectrum of the Q-branch was recorded at 1 atm pressure of pure CO$_2$. The observed absorption beyond the band head is less than predicted by an isolated line model. Conversely, in the low-J region of the Q-branch the absorption is greater than predicted. This behavior is consistent with the onset of collisional narrowing. The spectrum is interpreted using the line mixing perturbation solution of Rosenkrantz[3] to first order in pressure and a hybrid exponential-power gap fitting law to obtain the inelastic collision rates from the observed linewidths. The implications of this work for the satellite sensing of atmospheric temperature profiles will be discussed.

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[1] C. Braun, J. Mol. Spect., 93, 1 (1982).
[2] R. L. Armstrong, Appl. Opt., 21, 2141 (1982).
[3] P. W. Rosenkranz, IEEE Trans. Antennas Propagat., AP-23, 498 (1975).

Address of Strow: Department of Physics, University of Maryland Baltimore County, Catonsville, Maryland 21228
Address of Gentry: NASA/Goddard Space Flight Center, Code 615.2, Greenbelt, Maryland 20771

MF1. (1:30)

MEASUREMENT OF THE ν_2 PERPENDICULAR BENDING MODE OF Ar-HCl BY INTRACAVITY FAR INFRARED LASER STARK SPECTROSCOPY

D. Ray, R. L. Robinson, D. H. Gwo, and R. J. Saykally

The low frequency ν_2 perpendicular bending fundamental band of the Ar-HCl van der Waals molecule has been measured in direct absorption near 34 cm^{-1} by the new technique of intracavity far infrared laser Stark spectroscopy. Ar-HCl was generated in a free jet expansion of a 2% HCl-in-Argon gas mixture within the cavity of the laser. We have observed $\sim$80 spectral lines on 2 different far infrared laser lines, with excellent signal to noise (10^4). The resolution is sufficient to observe the electric quadrupole hyperfine structure of the transitions. Preliminary analysis of the spectra yields values for the following molecular contants: ν_2, B', D', q, μ', eq_0Q.

This work was supported by the Director, Office of Basic Research, U.S. Department of Energy.

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MF2. (1:47)

INTRACAVITY FAR INFRARED LASER STARK SPECTROSCOPY OF SUPERSONIC MOLECULAR BEAMS

D. Ray, R. L. Robinson, D. H. Gwo, and R. J. Saykally

We have designed and constructed a new intracavity far infrared laser absorption experiment. The spectrometer is similar to a far infrared laser magnetic resonance spectrometer, except we use an electric field instead of a magnetic field to tune the relevant energy level differences into coincidence with the fixed frequency far infrared laser. Spectra of molecules generated in supersonic expansions and in a low pressure gas cell, both within the cavity of the laser, have been obtained. The spectrometer possesses extremely high sensitivity and high resolution (<1 MHz), and will be used to study rotational spectra of radicals and vibration-rotation spectra of weakly-bound molecules, generated and cooled to very low temperatures in supersonic jets.

This work was supported by the Director, Office of Basic Research, U.S. Department of Energy.

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MF3. (2:09)

LASER SPECTROSCOPY OF PHOTOLYTICALLY PRODUCED FREE RADICALS

YEN-CHU HSU, RICHARD A. KENNEDY AND TERRY A. MILLER

The production of free radicals in an expansion of the Campargue type is accomplished by excimer laser photolysis of a suitable precursor seeded into the inert carrier gas. Extensive, and controllable cooling of the free radicals occurs after photolysis through collisions with the carrier gas, and rotational temperatures of <10K can be achieved. The free radicals are characterized by fluorescence excitation spectroscopy. Results for a number of polyatomic free radicals will be described. For these species the rotational cooling leads to a great simplification of the spectra, and considerably assists the assignment of the observed transitions.

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MF4. (2:21)

NEAR-INFRARED SPECTRA OF RARE GAS-HCl COMPLEXES

B. J. HOWARD AND A. S. PINE

High-resolution spectra of the Rg-HCl van der Waals complexes (Rg = Ne, Ar, Kr) have been recorded in the H-Cl stretching region (near 2900 cm^{-1}) using a tunable difference-frequency laser system. The samples were studied under thermal equilibrium conditions (T ≈ 128 K) at low pressures (P_{HCl} = 2 Torr, P_{Rg} = 5-12 Torr) and long path lengths (L = 72-80 m). The Σ-Σ parallel-type H-Cl stretching fundamentals for the Ar and Kr complexes and the Σ-Π perpendicular-type stretch-bend combination for all three complexes have been observed. The lower-order ground-state rotational constants agree with prior molecular-beam electronic-resonance results, but the higher J levels available to these infrared measurements probe the entire van der Waals potential surface up to dissociation. Striking rotational predissociation is observed as the rotational energy approaches and exceeds the van der Waals binding energy plus the centrifugal barrier. The vibrational dependence of the intermolecular potentials is manifest in the observed red shifts of the band centers from free HCl and in the excited-state rotational parameters.

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Address of Pine: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

MF5. (2:38)

ARGON ISOTOPE EFFECT IN THE MICROWAVE SPECTRA OF ArDF

BRIAN L. COUSINS AND JAMES M. LISY

The measurement of rotational transitions[1] in ArHF, involving the less common argon isotopes in natural abundances, has been made possible by modifying the pulsed Fourier-transform Fabry-Perot microwave spectrometer developed by W. H. Flygare and co-workers.[2] We have extended these studies to ArDF by measuring the K = 0 J = 1 → 2 transitions in ^{36}ArDF and ^{38}ArDF at 12,610 and 12,373 MHz, respectively.

The analysis of the rare gas HF binary complexes has traditionally utilized the centrifugal distortion constant, D_J, in determining the equilibrium geometry and well depth. The argon isotopic data permit the determination of the vibration-rotation interaction constant, α_e, (approximately 1000 times larger than D_J) which can be used to improve the determination of the radial potential.

The analysis of the ArDF potential will be discussed with respect to the previous ArHF results.

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[1] B.L. Cousins, S.C. O'Brien and J.M. Lisy, J. Phys. Chem. 88, 5142 (1984).

[2] E.J. Campbell, W. G. Read and J.A. Shea, Chem. Phys. Lett. 94, 69 (1983).

Address of Cousins and Lisy: Department of Chemistry, University of Illinois, 505 S. Mathews, Urbana, IL 61801.

MF6. (2:55)

EVIDENCE FOR A MAGNETIC OCTUPOLE INTERACTION IN THE HYPERFINE SPECTRUM OF NaBr

J. Cederberg, D. Nitz, A. Kolan, T. Rasmusson, K. Hoffman, and S. Tufte

We have used our high resolution molecular beam electric resonance spectrometer to carefully examine the hyperfine spectrum of $Na^{81}Br$ in vibrational states v=0-5 and rotational states J=2-5. A total of 71 transition frequencies have been measured, most with a precision of 1-10 Hz. These can be fit with a reduced chi-square of only 1.23 by using 21 parameters expressing the vibrational and rotational variation of seven interactions including a magnetic octupole interaction for the bromine nucleus. Without inclusion of this interaction the observed frequencies of certain lines in the J=5 spectrum are inconsistent with predictions from other rotational states, with displacements of about 30 Hz. The interactions evaluated in this experiment have the values (all in units of kHz):

$$eQq(Br) = (48026.835\pm.008) + (967.041\pm.012)(v+1/2) - (9.796\pm.005)(v+1/2)^2 + (.0236\pm.0006)(v+1/2)^3 + (.3742\pm.0004)J(J+1) - (.0054\pm.0002)J(J+1)(v+1/2)$$

$$eQq(Na) = -(4932.79\pm.03) + (43.60\pm.03)(v+1/2) - (.177\pm.014)(v+1/2)^2 + (0\pm.002)(v+1/2)^3 + (.017\pm.002)J(J+1) + (.0020\pm.0011)J(J+1)(v+1/2)$$

$$c(Br) = (.3352\pm.0002) + (.00670\pm.00011)(v+1/2)$$

$$c(Na) = (.6799\pm.0007) - (.0058\pm.0003)(v+1/2) \qquad c_4 = (.0905\pm.0009)$$

$$c_3 = (.4220\pm.0007) - (.0041\pm.0002)(v+1/2) \qquad \Omega\omega(\text{for } J=5) = (.0031\pm.0003).$$

Observations consistent with the above have also been made for $Na^{79}Br$.

Work supported by a Northwest Area Foundation Grant of Research Corporation and NSF RUI Grant # PHY-8319293.

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MF7. (3:30)

MICROWAVE SPECTRUM AND STRUCTURE OF THE AR•••ACRYLONITRILE Van der WAALS COMPLEX

R. D. SUENRAM AND F. J. LOVAS

The argon•••acrylonitrile (Ar•••CH_2CHCN) Van der Waals complex has been observed using a pulsed molecular beam Fabry-Perot cavity Fourier transform microwave spectrometer of the Balle-Flygare type.[1] From the large inertial defect that is observed, the argon is located out of the plane formed by the acrylonitrile subunit by approximately 40°.

Two discreet spectra are observed with one being higher in energy than the other by 0.5-1.0 cm^{-1}. The best explanation for the observed spectra is that there is a low barrier to inversion as the acrylonitrile subunit tunnels through a planar configuration of the entire complex. The rotational constants and ^{14}N quadrupole coupling constants for the two states are as follows:

	Ground State	Excited State
A	4857.69 (MHz)	4784.93 (MHz)
B	1602.40 (MHz)	1625.19 (MHz)
C	1225.98 (MHz)	1241.83 (MHz)
χ_{aa}	1.36 (MHz)	1.52
χ_{bb}	-3.25 (MHz)	-3.36
χ_{cc}	1.89 (MHz)	1.83

Details of the analysis and structure elucidation will be presented.

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[1] T. J. Balle and W. H. Flygare, Rev. Sci. Instrum., 52, 33 (1981).

Address of Suenram and Lovas: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

MF8. (3:47)

DIODE LASER SPECTROSCOPY OF VAN DER WAALS COMPLEXES

G. Hayman, J. Hodge, T. Dyke, J. Muenter, and B. Howard

A tunable diode laser has been used to directly observe infrared absorption of van der Waals complexes produced in a pulsed molecular beam source. Ar-OCS, Kr-OCS, and Ar-NNO have been studied in the 5 micron wavelength region with excellent signal to noise ratios and FWHM linewidths of 100 MHz. For Ar-OCS P, Q, and R branches of a perpendicular transition have been analyzed for both $K''=0$ and $K''=1$. Using the known ground state rotational constants, $A'=6690$, $B'=1510$, and $C'=1230$ MHz. The vibrational origin, $\nu_0=2061.74$ cm^{-1}, is 0.46 cm^{-1} red shifted from the C=O stretch of isolated OCS. The excited state geometry is virtually identical to the ground state structure. Preliminary analysis of similar data for Kr-OCS also indicates very little change in geometry, but the vibrational frequency shifts by -0.9 cm^{-1} in this complex. In contrast, the vibrational frequency increases by 0.2 cm^{-1} in Ar-NNO and the distance from Ar to the NNO center of mass increases in the excited state. The observed linewidth arises from Doppler broadening in the uncollimated molecular beam. At this resolution there is no evidence for vibrational predissociation. Experimental details will be given and the results of more complete spectral analysis will be presented.

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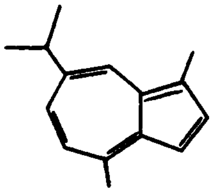
Address of Dyke: Department of Chemistry, University of Oregon, Eugene, OR 97403.
Address of Muenter: Department of Chemistry, University of Rochester, Rochester, NY 14627.

MF9. (4:04)

CONFORMATIONAL ANALYSIS OF GUAIAZULENE IN ITS GROUND AND SECOND EXCITED SINGLET STATE

M.M. CARRABBA, T.M. WOUDENBERG, AND J.E. KENNY

The fluorescence excitation spectrum of jet-cooled guaiazulene (1,4-dimethyl-7-isopropylazulene, I, has been studied in the 0-2200 cm^{-1} region of the $S_2 \leftarrow S_0$ electronic transition. Two spectroscopic origins have been observed at 27483 and 27589 cm^{-1}, corresponding to the two stable conformations of the isopropyl group. The ground-state energy difference for the two rotamers was measured by two different temperature-dependence studies: changing nozzle temperature and changing X/D, the distance between the nozzle and the laser. These two experiments consistently yield a ground-state energy difference of 0.9 ± 0.3 cm^{-1}, and give indirect evidence for a low barrier to internal rotation. The relative stabilities of the two rotamers reverse in the S_2 excited electronic state, and their energy difference is much larger, about 105 cm^{-1}.



I

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MF10. (4:21)

SATURATION STUDIES OF EXCITED-STATE DYNAMICS OF GUAIAZULENE

M.M. CARRABBA, T.M. WOUDENBERG, AND J.E. KENNY

The excited-state dynamics of the vibrationless level of the S_2 electronic state of each of two rotational conformers of guaiazulene were studied in a free jet. The technique used was saturated fluorescence spectroscopy; the data were fit using a three-state kinetic model. Both rotamers showed similar kinetics, dominated by a trapping rate of 1-2 x 10^9 sec^{-1}, which corresponds essentially to internal conversion. Absorption cross-sections of 1Å^2 were obtained for these 0_0^0 transitions. The applicability of various kinetic models and steady-state approximations under our experimental conditions has been examined.

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MF11. (4:38)

FLUORESCENCE QUANTUM YIELDS OF SINGLE VIBRONIC LEVELS OF GUAIAZULENE

T.M. WOUDENBERG AND J.E. KENNY

Several vibronic bands of the S_2 electronic state of 1,4-dimethyl-7-isopropyl azulene were studied using simultaneous measurement of laser absorption and laser induced fluorescence of the chromophore seeded in a pulsed He jet. The relative quantum yields calculated from these measurements will be presented.

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MF12. (Paper Arrived Late) (4:55)

FAR-INFRARED SPECTROSCOPY OF AR-HCL

M. D. MARSHALL, A. CHARO, H. O. LEUNG, AND W. KLEMPERER

We have observed excitation of the low frequency bending mode in Ar-HCl using intracavity molecular beam laser-stark spectroscopy. An optically pumped far-infrared laser oscillating on a transition in CH_3OD near 33.9 cm^{-1} was used to observe several laser-stark resonances in this molecule. Double resonance experiments show these to be transitions to the first excited Π bending state of the complex. In addition, radio frequency electric resonance has allowed the precise characterization of this state giving the following spectroscopic constants:

ν_o - B'	33.92 cm^{-1}
B'	1695.(20) MHz
q_1	-49.583(2) MHz
μ	0.265(3) D
eqQ_{aa}	4.(10) MHz
$eqQ_{bb}-eqQ_{cc}$	-73.927(23) MHz

We discuss the molecular structure in terms of these constants and make comparisons with Ar-HCl potential energy surfaces.

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MG1. (1:30)

DISCRETE TRANSFORM OF MOLECULAR M CHANGING KERNELS BY STARK SUBLEVEL ECHOES

J.M. Liang, L.A. Spinelli, J.E. Thomas, R.R. Dasari and M.S. Feld

We report the investigation of molecular M changing kernels using new Stark sublevel photon echo techniques to obtain, for the first time, the entire distribution of discrete M transfer rates. The method exploits the analogy between velocity space, where inhomogeneous broadening is due to Doppler frequency shifts, and M space where an artificial inhomogeneity can be created with a small Stark field. In the presence of the Stark field, random collision induced coherence transfer between M sublevels of an infrared transition of moderate J leads to Stark field dependant degradation of the molecular macroscopic polarization during the echo dephasing-rephasing process. The effects of inelastic (J changing) collisions and elastic velocity changing collisions which are field independent can be eliminated by measuring the ratio of the echo signals with the field on and off as a function of either echo time delay or Stark field. The nonexponential decay curve which is obtained is related to the M changing collisions kernel by discrete transformation with the frequency components $\nu_s \Delta M$, where ΔM is an integer and ν_s is the Stark shift for unit M.

In the experiment, the (V=0, J=4, K=3) ---> (V_3=1, J=5, K=3) transition in $^{13}CH_3F$ is studied. Acoustooptic (A/0) intensity modulation of 9P32 c.w. CO_2 laser radiation is used for input pulse generation. A novel digital oscillator driver is employed which has no RF leakage, so that A/0 rejected ratios are scattered light limited at ~106:1. Preliminary results yield echo signals with very high signal to background ratio and show completely new nonexponential behavior of the echo decay curve. Applications of both two and three pulse (stimulated) sublevel experiments will be described.

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MG2. (1:47)

ABSORPTION ATTENUATION MEASUREMENT OF ATMOSPHERE FOR 4416A OF He-Cd LASER IN SHANGHAI REGION

CAI PEIPEI, SHANXIONG SHEN, ZHANG HANSHENG, AND I-SHAN CHENG

Absorption attenuation of atmosphere in Shanghai Region was obtained for the first time for 4416A of He-Cd laser. The measurement was made at room temperature through atmosphere simulation in 10-meter long White cell. The results showed that the attenuation coefficient of atmosphere was 3.5 $atm^{-1} km^{-1}$ for 4416A in Shanghai Region.

According to the theoritical analysis, the attenuation of atmosphere for 4480A is 1.0526 km^{-1} where 1.034 km^{-1} is due to aerosols and 0.0186km^{-1} due to gas molecules of atmosphere components.(1)

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(1) R.A. McClatchey, Optical Properties of the Atmosphere , AD-753075.

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MG3. (1:59)

PROPAGATION OF INFRARED RADIATION IN SHANGHAI REGION

SHANXIONG SHEN, YU HAI-PING, I-SHAN CHENG

The features of IR spectroscopy of N_2O in the atmosphere are very important to detect atmospheric temperature , since the detection is based on the inversion evaluation from satellite data of radiance measurement with N_2O transmission in the atmosphere. The measurement and theoritical calculation of absorption spectra of ro-vibrational lines of 10 u bands of N_2O laser by atmospheric N_2O component in Shanghai Region have been obtained as a function of zenith angle, propagating path and wave length.

Results showed that the attenuation became larger with decreasing zenith angle but the effect of propagating path on attenuation was not so high after the laser beam propagated a certain distance. For exemple, the decibel was of $0.259*10^{-5}$ at 5 km under 20^0 zenith angle for P(18) transition but $0.248*10^{-5}$ at the same distance under 50^0 zenith angle, and became almost a constant beyond propagating after 20 kilometers.

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MG4. (2:11)

THE INTERPRETATION OF OVERTONE SPECTRA: MODE-MODE COUPLINGS IN THE TRIHALOMETHANES

W.H. GREEN, W.D. LAWRANCE, J.S. WONG, AND C.B. MOORE

The vibrational spectra of $HCCl_3$, HCF_3, $HCCl_2F$, and $HCClF_2$ have been measured[1] in the vapor from the CH stretching fundamental through to the fifth overtone (i.e. v_1=6), using FTIR and photoacoustic spectrometers. Instead of a single strong band for each CH overtone, several strong bands appear, which are attributable to Fermi resonant combination tones involving the stretch and the CH bend. Some of the observed bands are also markedly broadened by near resonances.

A simple effective spectroscopic Hamiltonian produces good fits to the observed data; a similiar treatment has recently been applied by Quack et. al. to $HCCl_2F$,[2] HCF_3,[3] HCD_3,[4] $HC(CF_3)_3$,[5] and $HCF(CF_3)_2$[2] using primarily FTIR spectra measured up to the third overtone. Strong mode-mode coupling between the CH stretch and bend has also been invoked by Sibert, Reinhardt, and Hynes[6] to explain the overtone spectrum of benzene. Our work confirms the usefulness of considering separately the large stretch-bend off-diagonal term, and clarifies the physical origin of this large, ubiquitous, and practically important coupling.

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[1] J.S. Wong, Ph.D. Thesis, University of California, Berkeley (1981). Some unpublished spectra also measured by C.K. Cheng and J.K. Frisoli.

[2] H.R. Dubal and M. Quack, Mol. Phys. 53, 257 (1984)

[3] H.R. Dubal and M. Quack, J. Chem. Phys. 81, 3779 (1984)

[4] S. Peyerimhoff, M. Lewerenz, & M. Quack, Chem. Phys. Lett. 109, 563 (1984)

[5] J.E. Baggott et. al., J. Chem. Phys. (in press)

[6] E.L. Sibert, W.P. Reinhardt, & J.T. Hynes, J. Chem. Phys. 81, 1115 (1984)

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MG5. (2:28)

INTERACTIONS OF PO RADICALS WITH ATMOSPHERIC GASES[*]

K.N. WONG[**], W.R. ANDERSON, A.J. KOTLAR, M.A. DEWILDE, AND L.J. DECKER

Laser excitation of PO fluorescence in a flow system has been used to study interactions of these radicals with atmospheric gases. The radicals are conveniently excited[1,2] in the (0,0) band of the $B^2\Sigma^+ \leftarrow X^2\Pi$ system (~3250A). Quenching rate constants for the B state by N_2, O_2, CO_2, and H_2O and upper limits thereof for Ar and He gases have been measured. In addition, the reaction of ground state PO with O_2 was briefly studied.

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[*] Supported by the Chemical Research and Development Center.

[**] NAS-NRC Postdoctoral Research Associate.

1. M.A.A. Clyne and M.C. Heaven, Chem. Phys. 58, 145 (1981).

2. W.R. Anderson, S.W. Bunte, and A.J. Kotlar, Chem. Phys. Lett. 110, 145 (1984).

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MG6. (2:45)

THE COLLISIONAL QUENCHING OF ELECTRONICALLY EXCITED NITROGEN

D.H. KATAYAMA

Although numerous experiments have been conducted on the collisional quenching of electronically excited molecules, the quenching process is still poorly understood in terms of deactivation paths, energy gap size and propensity rules. In many cases, the analysis of "purely" electronic deactivation is made difficult because of perturbations between the pertinent electronic states.

A two laser, double resonance technique has been used as a direct probe of collision induced electronic energy transfer from selectively excited states of molecular nitrogen. Because nitrogen is homonuclear the appropriate states have no perturbations between them and "purely" electronic transfer properties can be deduced. In the case of the nitrogen ion, J specificity is observable even for an energy gap of greater than 1500 cm^{-1} with a rate comparable to rotational energy transfer in the initially populated state. In addition, the electronic transfer due to collisions with helium atoms appears to follow optical like propensity rules.

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MG7. (3:15)

TRANSLATIONAL ENERGY DEPENDENCE OF THE ELECTRONIC QUENCHING OF I_2 (B) AND Br_2 (B) BY He

J.P. NICOLAI and M.C. HEAVEN

The van der Waals complexes He–I_2 and He–Br_2 are both known to undergo rapid vibrational predissociation where the halogens are excited to high vibrational levels of the **B** states. The dissociation of the van der Waals bond leads to vibrational relaxation within the **B** state, which may then be detected by spontaneously emitted fluorescence.[1,2] In contrast, both I_2 (B) and Br_2 (B) suffer efficient electronic quenching in collisions with He at room temperature.[3] Quenching is known to occur via collisionally induced predissociation.

These two observations can be reconciled if the quenching cross sections are collision energy dependent. In this talk, we shall present the results of quenching measurements made in a free jet expansion at temperatures around 15 K. For I_2 (B) + He the quenching cross section was found to decrease from its room temperature value of 0.92 $Å^2$ to 0.1 $Å^2$ at 15 K. Measurements on the Br_2 (B) + He quenching are in progress, and the results of both studies will be presented.

Work supported by AFOSR under grant 83–0173.

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(1). D.H. Levy, Ann. Rev. Phys. Chem. **31**, 197 (1980).
(2). L.J. van de Burgt, J.P. Nicolai and M.C. Heaven, J. Chem. Phys. **81**, 5514 (1984).
(3). M.A.A. Clyne, M.C. Heaven and S.J. Davis, J.C.S. Faraday Trans. II **76**, 961 (1980).
(4). G.A. Capelle and H.P. Broida, J. Chem. Phys. **54**, 1220 (1973).

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MG8. (3:32)

ROTATIONAL ENERGY TRANSFER AND ELECTRONIC SELF QUENCHING RATES FOR Br_2 (B)

L.J. VAN DE BURGT and M.C. HEAVEN

The self quenching behavior of selected v′ and J′ states of Br_2 (B) has been investigated in the 0.005–3 torr pressure range. Direct decay lifetime measurements were used to construct Stern-Volmer plots, and for low J′ values a pronounced curvature of these plots was noted at low pressures (<0.5 torr). Br_2 (B) exhibits a strong rotationally dependent predissociation,[1] and the curved Stern-Volmer plots have been interpreted in terms of highly efficient rotational energy transfer to predissociating levels. This process has been simulated using a master equation approach, and approximate rates for electronic quenching (3×10^{-10} cm^3 $molecule^{-1}$ s^{-1}) and rotational energy transfer ($\sum_f k_f = 8 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}) have been extracted from the model. Details of the experiment and computational modeling will be presented, and the compatibility of the rate data with the operating parameters of the Br_2 laser[2] will be discussed.

Work supported by AFOSR under grant 83–0173.

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(1). M.A.A. Clyne, M.C. Heaven and J. Tellinghuisen, J. Chem. Phys. **76**, 5431 (1982).
(2). G. Perram and S.J. Davis, J. Chem. Phys., to be published.

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MG9. (3:49)

LASER EXCITATION AND EMISSION SPECTRA FOR Br_2 IN AN ARGON MATRIX

L.J. VAN DE BURGT, J.P. NICOLAI and M.C. HEAVEN

The emission spectrum of the A′ $^3\Pi(2_u)$—X $^1\Sigma_g^+$ system of Br_2 in an argon matrix is reported. This spectrum has been vibrationally analysed for the first time, and the analysis supports two possible vibrational numberings. These provide estimates for T_e of 12966 ± 8 cm^{-1} and 12679 ± 8 cm^{-1} respectively.

Excitation spectra have been recorded for the A—X and A′—X systems in the region of 490–540 nm. The observed profiles are consistent with direct absorption into the A state continuum. This is at variance with a previous interpretation which indicated that absorption at these wavelengths leads initially to population of the B state, followed by rapid relaxation into the A and A′ states.[1] Further details of the excitation mechanism are being sought in photoselection studies, and the results of these experiments will be presented.

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(1). P.B. Beeken, E.A. Hansen and G.W. Flynn, J. Chem. Phys. **78**, 5892 (1983).

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MG10. (4:06)

VIBRATIONAL LEVEL STRUCTURE AND IVR IN S_1 p-DIFLUOROBENZENE

R.A. Coveleskie, D.A. Dolson, K.W. Holtzclaw, D.B. Moss, and C.S. Parmenter

The chemical timing method for obtaining picosecond time-resolved fluorescence spectra has previously been used to measure IVR parameters in S_1 p-difluorobenzene (pDFB).[1] In this report, the observed parameters for the levels 3^15^1 and $3^15^130^1$ are compared to other results for pDFB and other molecules. Apparent dilemmas arise with regard to the density of the coupled field of vibrational states, the size of the coupling matrix elements, and the coherence width of the excitation. A close examination of the SVL spectroscopy and coupling mechanisms, however, leads to a model that is consistent with the observed spectra and dynamics. Strong, non-resonant couplings (such as Fermi resonance interactions) increase the complexity of the spectral structure by a factor on the order of five, while weak, near-resonant couplings give rise to the congested spectral background and to the observed dynamics. The coherent excitation necessary to observe dynamics is provided by lifetime broadening in the collisionally perturbed system. Simulated fluorescence spectra and comparisons between room temperature and supersonically cooled samples have also been used to provide support for the proposed level structure.

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1. R.A. Coveleskie, D.A. Dolson, and C.S. Parmenter, J. Phys. Chem. (in press).

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MG11. (4:23)

VIBRATIONAL PREDISSOCIATION AND IVR FROM THE VAN DER WAALS COMPLEX OF PARA-DIFLUOROBENZENE AND Ar

D.L. Catlett, Jr., D. Krajnovich, and C.S. Parmenter

The van der Waals complex, pDFB···Ar, as observed in a supersonic expansion is characterized by well depths of 348 cm^{-1} and 378 cm^{-1} in S_0 and S_1 states, respectively. Dispersed emission spectra obtained after pumping each of five absorption bands ranging to 1250 cm^{-1} of vibrational energy in the electronically excited complex are comprised of $S_1 \rightarrow S_0$ fluorescence from the complex and $S_1 \rightarrow S_0$ fluorescence from the uncomplexed pDFB indicating that predissociation lifetimes are competative with the 10 nsec fluorescence lifetimes. The identification of vibrational product states of the uncomplexed pDFB show that few of the energetically available channels are used when the complex predissociates. The observed competition among possible predissociation channels is compared to a predictive model for collision-induced vibrational energy flow in S_1 pDFB.

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MG12. (4:40)

VIBRATIONAL ENERGY TRANSFER IN S_1 PARA-DIFLUOROBENZENE BY COLLISIONS WITH Ar

D.L. Catlett, Jr. and C.S. Parmenter

State-to-state vibrational energy flow by collisions with Ar atoms has been mapped out for 7 levels with up to 818 cm^{-1} of vibrational energy in S_1 para-difluorobenzene. The most efficient pathways for energy transfer involve changes in the lowest frequency mode, ν_{30} (this is also a promoting mode for collision-free IVR). The energy flow is modelled well by propensity rules similar to those for benzene. Rate constants for energy flow into the entire vibrational field were measured for levels up to 2500 cm^{-1} where the state density is 200 states/cm^{-1}. The rules model these rate constants well for initial levels below 1100 cm^{-1}. The modelling fails for the higher levels possibly on account of extensive level mixing and IVR.

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MG13. (4:57)

CIS - TRANS ISOMERIZATION OF GLYOXAL IN A SUPERSONIC EXPANSION

J.R. Johnson, D. Krajnovich, K.W. Butz, and C.S. Parmenter

Both the trans and cis forms of glyoxal have long been observed in 300 K spectroscopic studies, where the cis:trans population ratio is ~ 10^{-3}. We are using $S_1 \rightarrow S_0$ fluorescence to explore the extent to which this population is frozen when the 300 K trans/cis mixture is expanded in a supersonic jet. The cis-trans isomerization during the expansion can be modelled with the method of Felder and Gunthard (Chem. Phys. 71 9 (1982)). With barriers to the cis-trans internal rotation between 330 and 590 cm^{-1}, as derived from theoretical treatments, this model predicts frozen cis/trans population ratios corresponding to temperatures as high as 200 K. Experiments are characterizing this isomerization under a variety of beam conditions.

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TA1. (8:30)

THE ν_3 AND ν_1 BANDS OF THE $^{16}O\,^{16}O\,^{18}O$ AND $^{16}O\,^{18}O\,^{16}O$ ISOTOPIC SPECIES OF OZONE

J.-M. FLAUD, C. CAMY-PEYRET, A. PERRIN, V. MALATHY DEVI, C.P. RINSLAND and M.A.H. SMITH

Spectra of ^{18}O-enriched ozone samples have been recorded around 10 µm with a resolution of 0.005 cm^{-1} using the McMath Fourier transform interferometer. Different isotopic mixtures have been used to facilitate the assignment of the spectra : with an excess of oxygen 16, the main absorbing species are $^{16}O_3$, $^{16}O\,^{16}O\,^{18}O$ (noted 668) and $^{16}O\,^{18}O\,^{16}O$ (noted 686) whereas with an excess of oxygen 18 the main absorbers are $^{18}O_3$, $^{18}O\,^{18}O\,^{16}O$ and $^{18}O\,^{16}O\,^{18}O$. The spectrum of normal ozone being now well known, we have concentrated our attention on the study of the spectra of the two isotopic species 668 and 686. The 686 molecule belongs to the C_{2v} point group and consequently the structure of the observed bands (i.e. ν_3 and ν_1) is the same as for $^{16}O_3$. On the contrary 668 belongs to the C_s point group and ν_3 and ν_1 are hybrid bands having A-and B-type components. Due to the number of isotopic species, it was rather difficult to start the analysis. In fact, we managed to begin the analysis using both series of lines and ground state combination differences. Then, with the help of the ground state rotational constants known from microwave studies, we have obtained upper levels which were introduced in a least-squares fit leading to the determination of a first set of rotational and coupling constants which then were used to calculate extrapolated line positions allowing new assignments. This process was repeated until all the lines were assigned. For both molecules the ν_3 A-type band is the stronger and the easiest to assign. For 686 it has been possible to locate lines of the much weaker ν_1 band (B-type). For 668 the ν_1 band is mainly of A-type (the B-type ν_1 band is hardly visible). This ν_1 A-type band has a strong and narrow Q branch around 1090 cm^{-1} resulting from the superposition of more than 200 single lines. This Q branch is clearly visible in spectra of the earth's atmosphere. For 686 the rotational energy levels of the (001) and (100) states were reproduced within their experimental error (0.0005 cm^{-1}) taking into account the Coriolis interaction. For 668, both Fermi and Coriolis type interactions were necessary to reproduce correctly the experimental levels. Several line intensities of both isotopic species were measured leading to the determination of the transition moment operators of the observed bands.

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TA2. (8:47)

IDENTIFICATION OF ^{18}O-ISOTOPIC LINES OF OZONE IN INFRARED GROUND-BASED SOLAR ABSORPTION SPECTRA

C. P. RINSLAND, V. MALATHY DEVI, J.-M. FLAUD, C. CAMY-PEYRET, M. A. H. SMITH, and G. M. STOKES

There has been some controversy concerning the isotopic composition of ozone in the upper stratosphere. Calculations have been reported[1] which indicate that above 40 km, the photodissociation rate of $^{16}O^{18}O$ should be considerably larger than for $^{16}O^{16}O$. As a consequence, an enrichment in $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$ might occur. Although nighttime mass spectroscopic measurements show a peak heavy ozone enhancement of over 40%,[2] recent calculations indicate that exchange reactions[3] and a lower $^{16}O^{18}O$ photodissociation rate[4] should prevent any enhancement. To attempt to resolve the discrepancies among these results, we recorded 0.005 cm^{-1} resolution laboratory spectra of pure $^{16}O_3$, natural ozone, and ^{18}O-enriched ozone with the McMath interferometer on Kitt Peak. The data cover 600-1300 cm^{-1}. Based on the spectroscopic parameters derived from the analysis of these laboratory spectra,[5] a number of relatively well isolated lines of the ν_3 bands of $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$ have been identified in solar absorption spectra recorded with the same interferometer.

The analysis of the solar absorption spectra shows a marginally statistically significant enhancement in heavy ozone. Relative to the concentrations in a natural sample of ozone, isotopic abundances of 1.05 ± 0.07 and 1.11 ± 0.11 in the total column of atmospheric ozone are derived for $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$, respectively. A more sensitive test for heavy ozone enhancement in the upper stratosphere should be possible from high-resolution measurements of the same lines with balloon-borne and satellite-borne instruments.

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[1] R. J. Cicerone and J. L. McCrumb, Geophys. Res. Lett. 7 251 (1980).
[2] K. Mauersberger, Geophys. Res. Lett. 8, 935 (1981).
[3] J. A. Kaye and D. F. Strobel, J. Geophys. Res. 88, 8447 (1983).
[4] A. J. Blake, S. T. Gibson, and D. G. McCoy, J. Geophys. Res. 89, 7277 (1984).
[5] J. M. Flaud et al., preceding abstract.

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TA3. (8:59)

TEMPERATURE DEPENDENCE OF N_2-BROADENED HALFWIDTHS OF OZONE

R. R. GAMACHE AND L. S. ROTHMAN

We have calculated nitrogen-broadened halfwidths of ozone over a temperature range from 200 to 350 K. The calculations were done using the QFT-ID method[1] which has been shown to give halfwidths to better than 10%. The temperature dependence of the broadening coefficient has been evaluated for a wide range of transitions that cover J from 1 to 35, the full manifold of Ka for particular J values and for some transitions of stratospheric importance. The temperature dependence is given in terms of the temperature exponent, n, from the expression $\gamma(T)/\gamma(T_0) = (T_0/T)^n$, for the 126 transitions studied. The results indicate an average temperature exponent of n = 0.77 for N_2-broadening of ozone. The results are not strongly dependent on the rotational quantum number J but do show some dependence on Ka. Comparison is made with experimentally determined temperature coefficients[2,3] and other theoretical calculations.[4,5]

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1. R. R. Gamache and R. W. Davies, J. Mol. Spec. 109, 283-299 (1985).
2. J. M. Colmont and N. Monnanteuil, J. Mol. Spec. 104, 122-128 (1984).
3. B. J. Connor and H. E. Radford, Center for Astrophysics, Smithsonian Astrophysical Observatory, Cambridge, MA, private communications.
4. G. D. T. Tejwani and E. S. Yeung, J. Chem. Phys. 63, 1513-1517 (1975).
5. J.-Y. Mandin, J.-M. Flaud and C. Camy-Peyret, Laboratoire de Physique Moléculaire d'Optique Atmosphérique, CNRS, Orsay, France, private communications.

This work was supported by the Air Force Office of Scientific Research through AFGL Task 2310G1.

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TA4. (9:11)

BALLOON-BORNE ATMOSPHERIC INFRARED EMISSION SPECTRA OBTAINED WITH THE SCRIBE INTERFEROMETER

L.S. ROTHMAN, G.A. VANASSE, F.H. MURCRAY, F.J. MURCRAY, and D.G. MURCRAY

Balloon-borne measurements were made using the Stratospheric Cryogenic Interferometer Balloon Experiment (SCRIBE) interferometer from Holloman AFB on October 1983 and July 1984. The instrument obtained 0.06 cm^{-1} resolution data with good S/N in the spectral region of 600 to 1400 cm^{-1} with an interferometer scan time of 25 seconds. Representative spectra will be shown which demonstrate the capability of the SCRIBE interferometer for atmospheric emission measurements. Spectra obtained from the October 1983 flight in the 750 to 1000 cm^{-1} region will be shown; these include data taken at a float altitude of 30 km and at several viewing angles including nadir. Emission spectra of trace gas species easily identified will be presented; these include HNO_3, $CFCl_3$ (F11), and CF_2Cl_2 (F12). Downlooking spectra at four different altitudes representing upwelling atmospheric radiation in the 15-μm CO_2 band will also be presented. Comparisons of several of the observed spectra with simulated high-resolution spectral calculations will be presented. Of particular interest is a FASCODE run of HNO_3 and its comparison with laboratory absorption measurements and the balloon observations at float altitude looking down towards a tangent height of maximum nitric acid concentration.

This work was supported by the Air Force Office of Scientific Research.

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TA5. (9:28)

CALCULATED ENERGY LEVELS AND INTENSITIES FOR THE ν_1 AND $2\nu_2$ BANDS OF HDO

A. PERRIN, J.-M. FLAUD and C. CAMY-PEYRET

A Hamiltonian taking explicitly into account both Fermi and Coriolis interactions has been set up for triatomic molecules of symmetry C_s and used to reproduce very satisfactorily the available rotational energy levels[1,2] of the $\{(1\,0\,0),(0\,2\,0)\}$ interacting states of HDO, providing us with realistic wavefunctions as well as precise rotational constants and vibrational energies. Then, to calculate line intensities, these wavefunctions were used together with suitably chosen transition moment operators expanded up to degree 2 in $\vec{J}$ and having the correct symmetry in the C_s group, leading to hybrid bands of both A- and B- type. Using this formalism, it has been possible to determine, from the fit of the existing experimental intensities[1], the coefficients appearing in the expansions of the transition moments operators of the $2\nu_2$ and ν_1 bands of HDO. In this way, we have improved upon the F-factor formalism which needs much more parameters to reproduce the line intensities with the same precision. Finally, using the transition moments as well as the wavefunctions and energy levels deduced from the diagonalization of the Hamiltonian matrix, we have calculated the whole spectrum of the ν_1 and $2\nu_2$ bands of HDO.

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[1] R.A. Toth, V.D. Gupta and J.W. Brault, Appl. Opt. 21, 3337 (1982).

[2] N. Papineau, C. Camy-Peyret, J.-M. Flaud and G. Guelachvili, J. Mol. Spectrosc. 92, 451 (1982)

Address of Perrin, Flaud and Camy-Peyret : Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, Bât. 221 Campus d'Orsay, 91405 Orsay Cedex, France.

TA6. (9:40)

THE SECOND TRIAD OF INTERACTING STATES OF $H_2{}^{18}O$. LINE POSITIONS AND INTENSITIES FOR THE $3\nu_2$, $\nu_1+\nu_2$ AND $\nu_2+\nu_3$ BANDS

J.-P. CHEVILLARD, J.-Y. MANDIN, J.-M. FLAUD AND C. CAMY-PEYRET

The spectrum of oxygen-18 enriched water vapor, was recorded between 4 400 and 6 100 cm^{-1} with the aid of a Fourier transform spectrometer[1]. Its analysis allowed to determine 60 energy levels of the $(0\,3\,0)$ vibrational state of $H_2{}^{18}O$, and to improve the knowledge of the energy levels belonging to the $(1\,1\,0)$ and $(0\,1\,1)$ vibrational states of this molecule. A fit of 330 rotational levels of the $(0\,3\,0)$, $(1\,1\,0)$ and $(0\,1\,1)$ states was performed using 54 effective constants and taking into account the Coriolis-type and Fermi-type interactions. Moreover, 853 line intensities belonging to the $3\nu_2$, $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands were measured. The constants involved in the rotational expansion of the transformed transition moment operator corresponding to these bands were determined through a fit of these line intensities. The constants obtained were then used to compute the whole spectrum of the $3\nu_2$, $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands of $H_2{}^{18}O$. This spectrum should be of interest for atmospheric studies.

---

[1] J.W. Brault, Proceedings of JOSO Workshop (1978). In Osservatori e memorie dell' Osservatorio Astrophysico di Arcetri 106, 33 (1979).

Address of Chevillard, Mandin, Flaud and Camy-Peyret : Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, Bât.221 Campus d'Orsay, 91405 Orsay Cedex, France.

TA7. (10:10)

ATMOSPHERIC WATER VAPOR ABSORPTION AT 1.3 μm*

S. L. BRAGG AND J. D. KELLEY

Absorption spectra of water vapor and water vapor broadened by air have been measured at the frequency of the atomic iodine transition at 1.3 μm (7603.14 cm^{-1}). The absolute absorption cross section at 7603.14 cm^{-1} has been determined for each spectrum. The absorption cross section for 2 kPa of water vapor in 100 kPa air is 1.1 (±0.2) x 10^{-24} cm^2 at 7603.14 cm^{-1}. All absorption at this frequency is attributed to the wings of nearby water vapor lines.

A theoretical model, based on pressure broadening coefficients determined in this study, yields a simple expression for the absorption cross section at 7603.14 cm^{-1}.

$$\sigma = 5.0 \times 10^{-26} (p_{H_2O} + 0.25\, p_{air})$$

with p the pressure in kPa, and the cross section σ in cm^2.

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*This work was supported by Air Force Weapons Laboratory Contract F29601-82-C-0019.

Address of Bragg and Kelley: McDonnell Douglas Research Laboratories, P.O. Box 516, St. Louis, Missouri, 63166.

TA8. (10:27)

ANALYSIS OF ν_2 OF D_2S

JAMES R. GILLIS, RONALD D. BLATHERWICK, AND FRANCIS S. BONOMO

We have recorded and analyzed the high resolution spectrum of the ν_2 band of D_2S from 740 to 1100 cm^{-1}. Approximately 670 transitions from $D_2{}^{32}S$ and 130 transitions from $D_2{}^{34}S$ have been assigned. The spectrum was fitted using Watson's A - form Hamiltonian evaluated in the I-R representation. Ground state constants for $D_2{}^{32}S$ were obtained from a simultaneous least squares fit of microwave lines[1] and our ground state combination differences. Upper state constants were obtained from a least squares fit of the spectral transitions, keeping the ground state constants fixed. Because there were not enough $D_2{}^{34}S$ transitions to form ground state combination differences capable of yielding ground state constants, the $D_2{}^{34}S$ transitions were fitted using isotopic mass adjustment terms[2] for upper and lower state A, B, and C and for ν_0.

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[1] R.L. Cook, F.C. DeLucia, and P. Helminger, J. Mol. Spectrosc. 41, 123-136 (1972).

[2] W.C. Lane, T.H. Edwards, J.R. Gillis, F.S. Bonomo, and F.J. Murcray, J. Mol. Spectrosc. 95, 365-380 (1982).

Address of authors: Physics Department, University of Denver, Denver, CO 80208

TA9. (10:44)

ENERGY LEVELS AND BAND STRENGTHS OF CARBON DIOXIDE CALCULATED BY DIRECT NUMERICAL DIAGONALIZATION

RICHARD B. WATTSON and LAURENCE S. ROTHMAN

The Direct Numerical Diagonalization technique[1] has been applied to the two principal symmetric species of carbon dioxide. Incorporating recent new high resolution measurements made at the McMath Solar Facility at Kitt Peak National Observatory by Rinsland et al[2] and the 2-meter path difference Fourier transform spectrometer at AFGL, new values for the potential function and dipolar coefficients have been calculated. The results are compared with the potential functions calculated by earlier Direct Numerical Diagonalization efforts as well as the contact transformation approach. The results are also discussed in terms of the effects of truncation errors and completeness of basis sets.

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1. R.B. Wattson and L.S. Rothman, paper MF16, Thirty-ninth Symposium on Molecular Spectroscopy, Ohio State University (1984).
2. C.P. Rinsland, D.C. Benner, V. Malathy Devi, P.S. Ferry, C.H. Sutton, and D.J. Richardson, Appl. Opt. 23, 2051 (1984).

This work was supported by the Air Force Office of Scientific Research, through AFGL task 2310G1.

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Burlington, MA 01803
Address of Rothman: Optics Division, Air Force Geophysics Laboratory
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TA10. (10:56)

INTENSITY AND PRESSURE BROADENING MEASUREMENTS IN THE ν_3 FUNDAMENTAL OF CO_2

J. W. C. JOHNS

New measurements of the absolute intensities and pressure broadening coefficients (both self and N_2) of individual CO_2 lines near 4.3 μm have been made using a Bomem DA3.002 spectrophotometer. Care has been taken in all the measurements in order to try and limit errors to the order of 1%. The extent to which this aim has been achieved will be discussed.

Address: Herzberg Institute of Astrophysics, 100 Sussex Drive, Ottawa,
Ontario, K1A 0R6, CANADA

TA11. (11:08)

MOLECULAR PARAMETERS FOR CARBON DIOXIDE BANDS IN THE 2.86 - 3.18 μm SPECTRAL REGION

D. CHRIS BENNER, V. MALATHY DEVI AND C. P. RINSLAND

Line positions and intensities of carbon dioxide transitions in the 3140-3500 cm^{-1} spectral interval have been determined from long-path, low-pressure absorption spectra recorded at 0.01-cm^{-1} resolution and at room temperature using the Fourier transform spectrometer in the McMath solar telescope complex at the National Solar Observatory. More than thirty bands belonging to the ${}^{12}C^{16}O_2$, ${}^{13}C^{16}O_2$, ${}^{16}O^{12}C^{18}O$, ${}^{16}O^{13}C^{18}O$ and ${}^{16}O^{13}C^{17}O$ molecular species have been identified and unambiguous assignments have been made for about 2000 lines. Some of the upper vibrational levels are involved in crossing perturbations.

For the more than 15 bands wholly contained in this spectral interval, absolute intensities have been derived for unblended lines using a nonlinear least squares spectral fitting technique. For these measurements, the gas pressures ranged from 1 to 10 Torr in a 24 to 384 m absorption path. The measured intensities have been analyzed to determine vibrational band intensities and F-factor coefficients for the bands.

Address of Benner and Malathy Devi: Department of Physics, College of William and Mary, Williamsburg, VA 23185.

Address of Rinsland: NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665.

TA12. (11:20)

LINE POSITION MEASUREMENTS OF ${}^{13}C^{16}O_2$ AND ${}^{13}C^{16}O^{18}O$ AT ELEVATED TEMPERATURES IN THE 2.8 μm REGION

Mark P. Esplin and John P. Mycroft

The AFGL High Resolution Interferometer has been used to measure spectra of a CO_2 sample enriched with ${}^{13}C$. The sample, consisting of 88% ${}^{13}C^{16}O_2$ and 11% ${}^{13}C^{16}O^{18}O$, was placed in a high temperature absorption cell with an optical path length of 3.5 meters. Spectra were taken at several pressures and at three temperatures: 300 K, 500 K, and 800 K. Line positional information from the different spectra were combined into a single data set. A least-squares-fit was then used to obtain new rotation-vibration constants.

This work was supported by the Air Force Office of Scientific Research as part of AFGL Task 2310G1.

Address of Esplin: Stewart Radiance Laboratory, Utah State University, 139 The Gread Rd., Bedford, Massachusetts 01730.

Address of Mycroft: Geophysics Scholar, Optical Physics Division, U.S. Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts 01731.

TA13. (11:32)

CO_2 BAND INTENSITIES IN THE 9.4 AND 10.4 μm REGIONS

M. S. ABUBAKAR and J. H. SHAW

CO_2 lines in the region 900 - 1110 cm^{-1} have been analyzed by the nonlinear, least-squares method of whole band analysis. The spectrum of a natural sample of CO_2 at room temperature and a pressure of 177 torr with a 474 m path-length was recorded with a Fourier Transform spectrometer. The intensities of the bands at 960.959 cm^{-1} and 1063.734 cm^{-1} and of several weaker overlapping bands agree within a factor of two with the AFGL[1] values.

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[1] L. S. Rothman and L. D. G. Young, J. Quant. Spectros. Radiat Transfer 25, 505 (1981).

Address of Abubakar and Shaw: Department of Physics, The Ohio State University, Columbus, Ohio, 43210

TA14. (11:44)

A CHARGE FLOW MODEL FOR THE HIGHER DERIVATIVES OF THE MOLECULAR DIPOLE MOMENT

JEFFREY L. HYLDEN AND JOHN OVEREND

This model uses the effective charge concept advanced by Decius[1] to model higher derivatives of the molecular dipole moment. The effective charge is expanded in terms of internal coordinates and the charge flow parameters are empirically fit to data from infrared intensities and average dipole moments. The advantages of this model are that: 1) the signs of the higher derivatives can be predicted from knowledge of the signs of the fundamentals, 2) linear parameters that cannot be determined from fundamental data can be determined from combination band data, and 3) the parameters generated are more chemically intuitive than those of other models. Applications to small molecules will be discussed.

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[1] J. Decius, J. Mol. Spec. 57 348

Address of Hylden: Naval Research Laboratory, Code 6833, Washington, DC 20375-5000.
Address of Overend: Deceased November 28, 1984.

Work done at Chemistry Department, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455.

TA15. (Last Minute Addition) (12:01)

OXYGEN-BROADENED LINEWIDTHS OF CARBON DIOXIDE

E. ARIE, N. LACOME ,P. ARCAS and A. LEVY

The widths of oxygen-broadened carbon dioxide lines in the 10.6 μm transition have been measured by using a stabilized single-line CO_2 laser as a source [1]. The measurements were carried out at 296°K and for lower temperatures. The observed values are compared to the theoretical results obtained on the basis of the atom-atom model previously applied in the case of N_2O [2] . At room temperature the agreement is better than 5 percent.

[1] E. ARIE, N. LACOME and C. ROSSETTI, Can J. Phys. 50, 1800 (1972)
[2] N. LACOME, A. LEVY and C. BOULET, J. Mol. Spectrosc. 97, 139 (1983)

Address : Laboratoire d'Infrarouge, associé au C.N.R.S., Université de Paris XI, Bâtiment 350, 91405 ORSAY CEDEX (France).

TB1. (8:30)

INFRARED MATRIX ISOLATION INVESTIGATION OF THE MOLECULAR COMPLEXES OF SILICON AND GERMANIUM TETRAFLUORIDES WITH WEAK LEWIS BASES, Bruce S. Ault

The matrix isolation technique has been applied for the study of the intermediate, 1:1 complexes of the Lewis acids SiF_4 and GeF_4 with weak Lewis bases, including CH_3CN and HCN, as well as the stronger base pyridine. All three are characterized by distinct, shifted vibrational modes of both the acid and base subunits; these shifts suggest that the complexes are bound through the nitrogen atom of the base to the silicon or germanium center. The pyridine complexes showed by far the greatest shifts, as well as the highest product yield. The HCN complexes were unusual, in that the HCN act as a Lewis base in this system, contrary to its usual chemical behavior. All of the vibrational modes of the coordinated HCN subunit were observed in the GeF_4 complex; the C-H stretch shifted 15 cm^{-1} to lower energy, the C-N stretch 40 cm^{-1} to higher energy, and the bending mode roughly 30 cm^{-1} to higher energy. This latter mode did not split upon coordination, suggesting a linear arrangement for the H-C-N-Ge linkage. Additional complexes with weak bases are under investigation, and will be discussed.

Address of Ault: Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

TB2. (8:47)

INFRARED MATRIX ISOLATION STUDIES OF THE COMPLEXES OF THE HYDROGEN HALIDES WITH SUBSTITUTED CYCLOPROPANES, Candace E. Truscott and Bruce S. Ault

The complexes formed between the hydrogen halides and a variety of substituted cyclopropanes have been isolated and characterized in inert matrices. The complexes may be divided into two classes, those in which the cyclopropane ring bears an electron-withdrawing group as a substituent and those in which the substituent is an electron donor. Methyl-substituted cyclopropanes fall into the latter group. These complexes were characterized by an intense hydrogen halide stretching mode that was shifted to lower energies by up to 100 cm^{-1} from that of the uncomplexed position. In addition, perturbed vibrational modes of the methyl-substituted cyclopropane ring were observed. These results are analogous to those obtained for the the H-X-cyclopropane complexes and suggest that the complexes are similar in structure. The results for cyclopropyl bromide and cyanide were very different. An intense hydrogen halide stretching mode could be observed, but the only perturbed modes of the substituted cyclopropane corresponded to a perturbed C-Br or C-C-N vibrational mode. These results suggest that the complex formed between cyclopropanes containing electron withdrawing groups as substituents and the hydrogen halides are structurally different than the HX-cyclopropane complexes. These studies are being continued and a wider variety of substituted cyclopropanes are being examined.

Address of Truscott and Ault: Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

TB3. (9:04)

INFRARED SPECTROSCOPIC STUDIES OF MATRIX ISOLATED COMPLEXES OF ClF WITH SELECTED LEWIS BASES, Nicholas P. Machara and Bruce S. Ault

The matrix isolation technique has been successfully used to stabilize complexes formed between ClF and a variety of Lewis bases. Twin jet deposition was employed in these studies, and argon and nitrogen were used as the matrix materials. For those Lewis bases which contained an oxygen atom, product bands were located near parent bands which had been assigned to vibrations involving the oxygen atom. These results indicate that the ClF molecule is bound to the oxygen atom in the complex. Perturbed ClF vibrations were shifted to lower energies up to 100 cm^{-1} and often revealed FCl^{35}/FCl^{37} isotopic splitting. Studies are underway with nitrogen-containing Lewis bases, and will be discussed.

Address of Machara and Ault: Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

TB4. (9:21)

VIBRATIONAL SPECTRA OF FREE RADICALS FORMED IN THE PRIMARY REACTION OF F ATOMS WITH THE METHYL HALIDES

MARILYN E. JACOX

When F atoms produced in a microwave discharge are codeposited with CH_3X (X = Cl, Br, I) in an argon matrix at 14 K, the products of two primary reaction channels are isolated, yielding heretofore inaccessible information regarding the reaction mechanism. A prominent infrared absorption can be assigned to the X-F stretching fundamental of the CH_3XF free radical reaction intermediate in each of these three systems. F-atom attack of the methyl group leads to the formation of a very weakly bound $F\cdots HCH_2X$ complex, for which spectroscopic evidence is presented. This complex decomposes either spontaneously or upon excitation with visible radiation, producing the H_2CX free radical hydrogen-bonded to HF.

Address: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Md. 20899.

TB5. (9.38)

FTIR SPECTRUM OF CARBON-13 SUBSTITUTED SiC_2 TRAPPED IN ARGON AT 8 K

RICHARD A. SHEPHERD AND W.R.M. GRAHAM

The products from vaporizing silicon carbide at 2900 K and quenching in argon at 8 K have been studied using Fourier transform infrared spectroscopy. Two absorptions at 1741.1 and 824.4 cm^{-1} have been identified as vibrations of SiC_2. The appearance of four additional bands at 1708.2, 1674.2, 814.7, and 805.3 cm^{-1} upon single and double isotopic substitution with carbon-13 shows conclusively that SiC_2 possesses C_{2v} symmetry rather than the long assumed $C_{\infty v}$. This result is in agreement with recent results from the rotational analysis of the 498 nm transition.[1] Furthermore, the mixed isotopic spectra indicate that the 1741 and 824 cm^{-1} frequencies should be assigned to the ν_1 and ν_2 vibrations, respectively. Force constants derived in the present study suggest that this molecule is best understood as a silicon atom singly bonded to two doubly bonded carbon atoms. Implications for upper state vibrational assignments are discussed.

Supported by The Robert A. Welch Foundation, Grant P-786.

[1] D.L. Michalopoulos, M.E. Geusic, P.R.R. Langridge-Smith, R.E. Smalley, J. Chem. Phys. 80, 3556 (1984).

Address of Shepherd and Graham: Department of Physics, Texas Christian University, Fort Worth, Texas 76129

TB6. (10:10)

ESR SPECTRA OF Ag_3 ($^2A_1$) IN AN N_2 MATRIX

K. KERNISANT, G. A THOMPSON AND D. M. LINDSAY

ESR spectra assigned to Ag_3 molecules have been produced by codepositing atomic silver with excess nitrogen at temperatures close to 4.2 K. The spectra are characterized by an axially symmetric spin Hamiltonian having $g_{//}$ = 1.9933(3) and $g_{\perp}$ = 1.9558(3) and, for $^{107}Ag_3$, $A_{//}(1)$ = 310.8(6) G with $A_{\perp}(1)$ = 310.1(6) G and $A_{//}(2)$ = 76.0(2) G with $A_{\perp}(2)$ = 72.6(2) G for the apical(1) and basal(2) nuclei, respectively. The axial symmetry of the spectra is believed to imply that the trimer is rotating about one axis. There is no evidence for a pseudorotating trimer spectrum. The isotropic spin populations are $\rho_{5s}(1) = 0.51$ and $\rho_{5s}(2) = 0.12$ implying an acute angled geometry with ground state symmetry $^2A_1$. This is in sharp contrast to the obtuse angled isomer ($^2B_2$ ground state) found for Ag_3 in a C_6D_6 matrix. For $Ag_3(^2A_1)$ there is little p-character on the apical atom but a 10-15% p-hybridization on each of the two basal nuclei.

Address of Kernisant, Thompson and Lindsay: Department of Chemistry, City University of New York, The City College, Convent Ave. at 138th St., N.Y. N.Y. 10031.

TB7. (10:27)

ESR OF HSiO AND Si_2 MOLECULES AT 4°K

R. J. VAN ZEE AND W. WELTNER, JR.

Vaporization of quartz or surface oxidized silicon produced the ^1HSiO molecule (containing 5% natural abundance of $^1H^{29}SiO$) trapped as an impurity in solid neon and argon at 4°K. Signals near g = 2.0 in X-band ESR spectra exhibited hyperfine (hf) splittings due to ^1H(160 G) and ^{29}Si(220 G). The spectra of HSiO are similar to those of HCO and indicate that it is also a bent doublet molecule.[1]

From vaporized silicon metal an ESR signal is obtained in argon matrices at 10,200 G which is attributed to $X^3\Sigma$ Si_2 (as Douglas proposed[2]) based on the observed ^{29}Si hf pattern. The position of this signal establishes the zero-field splitting |D| = 2.5 cm^{-1}.

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[1] G. Herzberg and D. A. Ramsay, Proc. Roy. Soc. (London) A233, 34; F. J. Adrian, E. L. Cochran, and V. A. Bowers, J. Chem. Phys. 36, 1661 (1962).
[2] A. E. Douglas, Can. J. Phys. 33, 801 (1955).

Address of Van Zee and Weltner: Chemical Physics Center and Department of Chemistry, University of Florida, Gainesville, Florida, 32611

TB8. (10:39)

ESR of $V(CO)_n$ (n = 1 to 3) MOLECULES AT 4°K

R. J. VAN ZEE, S. B. H. BACH, AND W. WELTNER, JR.

Vanadium carbonyls were produced by trapping vaporized vanadium metal in neon and argon matrices doped with small amounts of ^{12}CO and ^{13}CO. Analyses of the X-band ESR spectra indicate that VCO has a $^6\Sigma$ ground state with a broad, relatively flat, potential. This is evidenced by two distinctly different sets of ^{51}V hyperfine splittings (hfs) and zero-field splittings (|D|) in argon matrices. Only one of these molecules is trapped in neon. ^{13}C hfs is 6 G in both matrices. $V(CO)_2$ has a $^4\Sigma$ ground state with |D| = 0.30 cm^{-1}; the ^{13}C hfs is unresolved. A signal near g = 2 (S = $\frac{1}{2}$) is assigned to $V(CO)_3$ with D_{3h} or C_{3v} symmetry. The trend among the three carbonyls is for $A_{iso}(^{51}V)$, i.e., the unpaired s character, to decrease as n increases.

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TB9. (10:56)

ELECTRONIC STATES OF MATRIX-ISOLATED NI ATOMS: A MAGNETIC CIRCULAR AND LINEAR DICHROISM STUDY

JAN PYKA, MARTIN VALA, MARC EYRING, JEAN-CLAUDE RIVOAL AND CHRISTIAN GRISOLIA

The absorption, magnetic circular dichroism (MCD) and magnetic linear dichroism (MLD) spectra of Ni atoms isolated in an argon matrix (4.2 K) have been measured. By utilizing the complementarity of the predicted MCD and MLD signals for transitions to states of different J values, together with the known gas phase positions and relative intensities, an assignment for all observed bands has been made. All bands in the region 360-270nm originate from atoms in sites whose ground state is $^3D_3$, whereas bands in the ~240-230nm region arise from atoms whose matrix ground state is $^3F_4$.

Saturation studies (MLD and MCD) reveal an important quenching of the $^3D_3$ ground state angular momentum. Calculations including full ground state Zeeman and crystal field (octahedral) interactions provide an excellent fit to the observed curves. The crystal field splitting is much larger than heretofore suspected.

Address of Pyka, Vala and Eyring: Department of Chemistry, University of Florida, Gainesville, FL 32611.
Address of Rivoal and Grisolia: Laboratoire d'Optique Physique, ESPCI, 10 Rue Vanquelin, Paris 75231, France.

TB10. (11:13)

HYBRID EXCITED ELECTRONIC STATES IN SEMICONDUCTOR CRYSTALLITES OF DIAMETER ≈15-50Å, LOUIS BRUS

The electronic properties of metals and semiconductors result from extensive delocalization of the atomic valence electrons. These properties develop only gradually with cluster size. We synthesize and structurally characterize (via the electron microscope) crystalline clusters of the semiconductors ZnS, CdS, and PbS. The clusters are excised fragments of the bulk lattice. However, the lowest excited electronic state lies above the bulk bandgap energy; the excited states are hybrids between the molecular and solid state regimes. We discuss molecular orbital theory for these large "molecules".

Address: AT&T Bell Laboratories, Murray Hill, New Jersey 07974, USA

TB11. (11:30)

A SPECTROSCOPIC STUDY OF THE SPIN DIPOLAR INTERACTIONS OF THE EXCITED TRIPLET STATE OF DIPHENYLMETHYLENE

DANIEL J. GRAHAM

Diphenylmethylene (DPM) is an organic biradical which possesses triplet spin multiplicity in the ground electronic state. This ground state has been thoroughly examined using EPR spectroscopy. However, little is known about the paramagnetic aspects of the excited triplet state.

We have dispersed DPM in benzophenone single crystals. We have examined the laser-induced fluorescence of the guest and the magnetic field effects thereupon at low temperature. We have investigated both the sensitized and non-sensitized fluorescence in order to gain information about the spin dipolar interactions of DPM's excited triplet state.

Address: Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506.

TB12. (11:47)

ELECTRONIC SPECTRA OF Re^{4+} AND Ir^{4+} DOPED IN THE DISTORTED OCTAHEDRAL HOSTS

R.K. Yoo, B.A. Kozikowski and T.A. Keiderling

Single-crystal absorption and excitation spectra of Re^{4+} and Ir^{4+} doped in the distorted-octahedral hosts of K_2SnX_6(X=Cl, Br) and the pure K_2ReCl_6 at liquid He temperature have been obtained in the near-ir and visible regions. The analysis of these data will be discussed in conjunction with the previously observed Os^{4+} in the similar environments.

Address of Yoo and Keiderling: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, Illinois 60680, USA.

TC1. (8:30)

PHOTOIONIZATION SPECTRUM OF TRIPLET RYDBERG STATES OF H_2

R. D. KNIGHT AND LIANG-GUO WANG

Photoionization of highly-excited triplet states of H_2 has been studied for the first time. A thermal beam of metastable $c^3\Pi_u$ molecules is excited by a frequency-doubled pulsed dye laser (λ~340 nm) to autoionizing nd Rydberg states ($n \simeq 10$-20) converging to a variety of rovibrational levels of the H_2^+ core. Any ions produced are accelerated into a particle detector. We have observed a rich, wide-spread spectrum exhibiting no obvious order. The Hund's case d model of Eyler and Pipkin[1] can be used to make tentative identifications of many lines, but strong channel interactions will necessitate a multichannel quantum defect analysis. Our narrow laser bandwidth ($\lesssim 0.5$ cm^{-1}) provides a significant increase in resolution over that previously achieved in studies of the singlet autoionizing states.

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[1] E. E. Eyler and F. M. Pipkin, Phys. Rev. A 27, 2462 (1983).

Address: Department of Physics, Ohio State University, Columbus, Ohio 43210

TC2. (8:42)

OBSERVATION OF THE AUTOIONIZING GERADE TRIPLET RYDBERG SERIES IN H_2

R. KACHRU AND H. HELM (PRESENTED BY D. L. HUESTIS)

We have observed the autoionizing gerade Rydberg ns and nd series in molecular hydrogen. A frequency doubled tunable YAG-pumped dye laser beam is used to excite the fast beam of H_2 ($c\ ^3\Pi_u$) to the ns, nd Rydberg states. Excitation to the Rydberg states is detected by separating the autoionization product, i.e., H_2^+, from the neutral beam and counting it. The observed autoionization has a large number of closly spaced lines since four gerade electronic series are accesible from 16 vibrational levels of the c state. We have scanned the dye laser with a linewidth of 0.6 cm^{-1} from 3360 to 3580 Å covering the Rydberg series from n=10 to the continuum for $\Delta v=0$ transitions. A smaller portion of the spectrum at the dye laser linewidth of 0.1 cm^{-1} reveals the fine structure of the c state. A preliminary analysis of the term energies indicates that lines with n as high as 34 are discernable in the spectra. We are at present attempting a detailed assignment using MQDT.

Supported by the National Science Foundation

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TC3. (8:59)

Probing Excited States of NO involved in Multistate Interactions using the OODR-MPI Technique

W.Y.Cheung, W.A.Chupka, S.D.Colson, D.Gauyacq, Ph.Avouris and J.J.Wynne

Many new transitions from the (3sσ)$A^2\Sigma^+$ state to higher Rydberg and valence states in $^{14}N^{16}O$ have been observed by the technique of optical-optical double resonance multiphoton ionization (OODR-MPI). Upper states include members from the np, nd, nf Rydberg states (n= 3 to 6) and several vibrational levels of the $B^2\Pi$ and $L^2\Pi$ valence states. The spectral simplification aspect of the double resonance technique allows for the observation of these spectra without appreciable band overlap. Analysis of our data leads to the identification of several previously unobserved mixed Rydberg-valence vibrational levels. Discussions of the Rydberg-valence interactions in the 68600-71200 cm^{-1} energy region of $^{14}N^{16}O$ are presented in light of these results.

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TC4. (9:16)

DETECTION OF THE $L'^2\Phi$ STATE OF NO

M. R. TAHERIAN AND T. G. SLANGER (PRESENTED BY D. L. HUESTIS)

By using the techniques of stimulated emission pumping combined with fluorescence dip spectroscopy it has been possible to characterize the metastable NO($L'^2\Phi$) state. The spectroscopic parameters are:

$T_e = 53740.81 \pm 0.20\ cm^{-1}$

$\omega_e = 999.36 \pm 0.18\ cm^{-1}$

$B_e = 1.1189 \pm 0.0029\ cm^{-1}$

$A = -42.480 \pm 0.032 - 0.310 \pm 0.035(v+1/2)\ cm^{-1}$

$r_e = 1.4204 \pm 0.0037$ Å

$\omega_e x_e = 9.92 \pm 0.03\ cm^{-1}$

$\alpha_e = 0.0199 \pm 0.0027\ cm^{-1}$

The state is produced by initially populating NO($B'^2\Delta_{5/2}$, v=3, J=7.5) with 157.630 nm radiation from an F_2 laser. While observing the B'-X fluorescence emission, a Raman-shifted dye laser is tuned through the appropriate spectral regions (950-1300 nm), and intensity decreases are observed at the positions of the J = 6.5, 7.5, and 8.5 rotational levels of the $^2\Phi$ state (as well as other states). The first four vibrational levels have been detected in this manner, with the numbering being confirmed by the recent matrix isolation detection of v=0 by Chergui *et al.*[1] Perturbations in the v=1 level of the $B'^2\Delta$ state, postulated by Huber[2] as being due to the $L'^2\Phi$ state, are shown to involve the v=9 level.

Supported by the National Science Foundation

[1] M. Chergui, V. Chandrasekharan, W. Bohmer, R. Haensel, H. Wilcke, and N. Schwentner, Chem. Phys. Lett. 105, 386 (1984).

[2] M. Huber, Helv. Phys. Acta, 37, 329 (1964).

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TC5. (9:33)

ABSORPTION CROSS SECTION MEASUREMENTS OF OXYGEN IN THE WAVELENGTH REGION 195-241 nm OF THE HERZBERG CONTINUUM

A.S.C. CHEUNG, K. YOSHINO, W.H. PARKINSON, AND D.E. FREEMAN

The continuum cross section of oxygen at 296-300 K has been measured with a resolution of 0.13 nm throughout the wavelength region 205-241 nm with oxygen pressures from 5 to 760 torr and optical lengths from 13.3 to 133 m. The three processes contributing to the observed cross section are absorption into two continua, viz., the Herzberg continuum of O_2 and a pressure-dependent continuum involving two molecules of O_2, and Rayleigh scattering. Extrapolation of the observed cross section to zero pressure yields the continuum cross section of O_2, from which the calculated Rayleigh scattering is subtracted to give the Herzberg continuum absorption cross section of O_2. Our previous Herzberg continuum cross sections[1] obtained from studies at high resolution (0.0013 nm) between the Schumann-Runge absorption lines in the region 194-204 nm, are combined with the present results to give the Herzberg continuum cross section at 1 nm intervals throughout the region 195-241 nm. Comparison between different laboratory measurements and in situ stratospheric studies will also be presented.

This work is supported by the Fluorocarbon Program Panel of the Chemical Manufacturers Association under Agreements FC 82-412 and FC 83-486 with Harvard College.

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[1] A.S.C. Cheung, K. Yoshino, W.H. Parkinson and D.E. Freeman, Can. J. Phys. 62, 1752 (1984).

Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138

TC6. (10:05)

SCHUMANN-RANGE ABSORPTION BANDS OF $^{18}O_2$

K. YOSHINO, D. E. FREEMAN, A. S. C. CHEUNG, AND W. H. PARKINSON

The absorption spectrum of the Schumann-Range bands of isotopic oxygen, $^{18}O_2$, has been investigated with a 6.65 m vacuum spectrograph in the wavelength region 175-198 mm. The absorption cell, 50 cm in length, can be cooled with liquid nitrogen. Most of bands are as diffuse as those of ordinary oxygen, $^{16}O_2$. For the higher upper state vibrational levels, $v'>12$, the bands of $^{16}O_2$ become sharp and the triplet components have been separated. The analogous bands of $^{18}O_2$ remain diffuse, and the triplet components can be resolved only for lines with high rotational quantum numbers. Rotational analyses have been completed except for the bands near the dissociation limits. In particular, the 13 bands, (2,0)-(19,0), with $v''=0$ and the 13 weaker bands, (6,1)-(18,1), with $v'=1$ have been analyzed rotationally.

This work was supported by NASA grant NSG 5176 to Harvard College and NASA grant NAG 5-484 to Smithsonian Astrophysical Observatory.

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TC7. (10:22)

Perturbations in the B state of S_2

K. Raghuveer, and A. Smith

Though the B - X system of S_2 has been studied by many people, the upper $B^3\Sigma_u^-$ state, being highly perturbed, still presents a few anomalies. Line intensities and line position anomalies in high resolution CW laser absorption measurements of the [8,1] band of the B - X system are explained in terms of $B^3\Sigma_u^-$ - $B''^3\Pi_u$ perturbations, using recent results of Matsumi et al.[1] Approaches to deriving deperturbed constants for the B and B" states of of S_2 will be discussed.

[1] Y. Matsumi, T. Munakata, and T. Kasuya, J. Chem. Phys. 81, 1108, (1984).

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Philadelphia, Pennsylvania 19104.

TC8. (10:39)

AN EXTENSION OF THE ROTATIONAL ANALYSIS OF THE a $^3\Pi$ - X $^1\Sigma^+$ TRANSITION OF BCl

LISA HAMILTON AND C. WELDON MATHEWS

Additional data will be presented on the rotational structure of the 0-0 band of the $^3\Pi$ - X $^1\Sigma^+$ transition of BCl, initially reported by Lebreton, Marsigny and Ferran[1], at 4940 Å. The present studies also have resulted in the new observation of the 1-0 band of the same system.

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[1] J. Lebreton, L. Marsigny, and J. Ferran, Compte Rendus 272, 1094-1097.

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18th Avenue, Columbus, Ohio 43210.

TC9. (10:51)

LASER SPECTROSCOPY OF RARE EARTH OXIDES; RECENT RESULTS

C. LINTON, D.M. GAUDET, A. HOCQUET, P. CARETTE, H. SCHALL and M. DULICK

Over the past few years, we have studied the spectra of several rare-earth oxide molecules and have explained their spectra using Ligand Field Theory. This paper will survey the most recent results of this investigation.

We shall discuss the laser induced fluorescence spectra of several molecules. Resolved fluorescence spectra have been used to provide energy linkages between low lying states. High resolution excitation spectra were used for the rotational analysis, Ω assignments, examination of isotope spectra and, where possible, analysis of hyperfine structure. The experimental results will be discussed and compared with the Ligand Field Theory predictions.

Among the oxides to be discussed are those of Dysprosium (DyO), Samarium (SmO) and Neodymium (NdO).

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Address of Dulick: Ionospheric Physics Division, Air Force Geophysics Laboratory/LID, Hanscom Air Force Base, Bedford, Massachusetts, 01731.

TC10. (11:08)

DIPOLE MOMENTS OF THE GROUND AND FIRST EXCITED VIBRATIONAL STATES OF ^{35}ClO

D. J. YARON, K. I. PETERSON AND W. KLEMPERER

The analysis of atmospheric infrared absorption by ClO requires accurately determined band intensities. For the fundamental band, theoretical intensity calculations[1] give a result which is twice as large as experimental results[2]. In view of this discrepancy, it is important to independently check the calculated dipole moment function with experimentally measured dipole moments. The v=0 and v=1 dipole moments of ClO were obtained using the molecular beam electric resonance technique. ClO is formed in a supersonically expanded discharge of 10-20% O_2 and 3-4% Cl_2 in an Ar buffer gas. Transitions within the $^2\pi_{3/2}$, J=3/2 state of ^{35}ClO were monitored as a function of electric field up to 1600 V/cm. At zero field, this state is split into eight levels by the magnetic hyperfine structure and lambda doubling. Because the lambda doubling (~100 kHz) is much smaller than the hyperfine splitting (~100 MHz), the Stark effect is difficult to analyze. Observations of a large number of transitions were necessary for a definitive assignment. The tentative nature of the v=1 dipole moment arises from this difficulty. The dipole moments obtained were 1.2980 (12) D for the v=0 state and 1.2779 (19) for the v=1 state (tentative). The difference between these two measured values is 0.0201 D which is significantly lower than the theoretically predicted result of 0.028 D[1].

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[1] S. R. Langhoff, J. P. Dix, J. O. Arnold, R. W. Nicholls and L. L. Danylewych, J. Chem. Phys. 67,4306 (1977).

[2] J. R. Gillis and A. Goldman, J. Quant. Spectrosc. Radiat. Transfer 26, 23 (1981).

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TC11. (11:25)

LINE STRENGTH OF THE ATOMIC CHLORINE $^2P_{1/2} \leftarrow {}^2P_{3/2}$ SPIN ORBIT TRANSITION

A.C. STANTON AND J. WORMHOUDT

Direct absorption or emission measurements of the ground state spin-orbit transitions in the halogen atoms ($^2P_{1/2} \leftrightarrow {}^2P_{3/2}$ magnetic dipole transitions) have been reported for iodine, bromine, chlorine, and fluorine.[1,2] In the case of atomic fluorine, tunable diode laser absorption measurements have established an accurate value for the radiative lifetime,[1] in good agreement with a calculation. As noted in Ref. 1, the only other measurement of this forbidden transition in a halogen has been for iodine, where there is also reasonable agreement with calculations.

We present the measurement by diode laser absorption of the radiative lifetime for the analogous transition in atomic chlorine, together with a comparison with theoretical calculations. Since chlorine atoms are the principal active species in plasma etching of semiconductors and metals using chlorine-containing gases,[3] diode laser absorption has the potential of being a very useful diagnostic of these important microelectronics fabrication processes.

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[1] A.C. Stanton and C.E. Kolb, J. Chem. Phys. 72, 6637 (1980).

[2] A.C. Stanton, J.C. Wormhoudt, and J.W. Duff, in Spectral Line Shapes, Vol. 2, Walter de Gruyter, New York, 1983, p. 515.

[3] D.L. Flamm and V.M. Donnelly, Plasma Chemistry and Plasma Processing 1, 317 (1981).

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TC12. (Formerly FC6) (11:32)

HYPERFINE STRUCTURE OF BaI $X^2\Sigma^+$

W.E. ERNST, J. KÄNDLER and J. LÜDTKE

Among the alkaline earth monohalide radicals BaI presents a particular challenge to the spectroscopist because of the extremely congested optical spectra. Recently Johnson et al.[1)] succeeded in rotationally analyzing the $C^2\Pi - X^2\Sigma^+$ (0,0) band system around 550 nm. For the correct identification of the observed hyperfine structure, however, an independent measurement of the X state hyperfine structure was required.
Using the molecular beam laser-microwave double-resonance method we studied rotational transitions in the electronic ground state. At linewidths of about 10 kHz the hyperfine structure from the weakly coupled iodine nucleus ($I = 5/2$) was well resolved. Including the rotational constants of $X^2\Sigma^+$ from Törring and Doebl[2)] in a fit procedure we determined his parameters (3σ errors in parentheses):

BaI	$X^2\Sigma^+$	$v = 0$	$b = 93.14(7)$ MHz
			$c = 52.2\ (1)$ MHz
			$eqQ = -33.3\ (5)$ MHz

1) M.A. Johnson, C. Noda, J.S. McKillop, and R.N. Zare, Can.J.Phys., in press.

2) T. Törring and K. Doebl, Chem.Phys.Lett., in press.

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TC13. (Formerly FC7) (11:49)

HIGH RESOLUTION SPECTROSCOPY OF $Sr^{79}Br$ AND $Sr^{81}Br$: $B^2\Sigma^+ - X^2\Sigma^+$ ROTATIONAL ANALYSIS AND HYPERFINE STRUCTURE

W.E. ERNST AND J.O. SCHRÖDER

The $B^2\Sigma^+ - X^2\Sigma^+$ system of strontium monobromide produced in a gas phase reaction was investigated by using Doppler free laser polarization spectroscopy. The extremely dense spectra could only be assigned with the help of microwave polarization labeling$^{1)}$ and additional band selective detection of the laser induced fluorescence. About 1500 lines from the (0,0),(1,1), and (2,2) bands were identified and fitted together with the results of independent microwave measurements of the $X^2\Sigma^+$ state in a weighted least squares fit. Local perturbations were found in all vibrational states of both isotopic species and attributed to the interaction of $B^2\Sigma^+$, v_B with $A^2\Pi_{1/2}$, $v_A=v_B+3$. Band head positions of $\Delta v=\pm 1$ bands were used for the vibrational analysis.

Applying microwave optical polarization spectroscopy (MOPS)$^{2)}$ we were able to resolve the hyperfine structure in the $X^2\Sigma^+$ state and determine ground state hfs parameters of $Sr^{79}Br$ and $Sr^{81}Br$. This way the hfs in the sub-Doppler optical spectra of the B-X system could be interpreted and hfs parameters for the $B^2\Sigma^+$ state be derived.

1) W.E. Ernst, Opt. Commun. 46, 18 (1983).
2) W.E. Ernst and T. Törring, Phys.Rev.A 27, 875 (1983).

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TE1. (1:30)

THE EQUILIBRIUM STRUCTURE OF PROTONATED NITROGEN DETERMINED FROM HIGH RESOLUTION INFRARED SPECTROSCOPY

J. C. Owrutsky, C. S. Gudeman, C. C. Martner, N. H. Rosenbaum, L. M. Tack and R. J. Saykally

The $(11^10) \leftarrow (01^10)$ hot band of protonated nitrogen (N_2H^+) has been measured using a color center laser and the technique of velocity modulation. High-J (up to J=40) lines, in addition to those previously reported (1), have also been measured in the ν_1 vibration. This data was combined with the relevant published work to enable an equilibrium structure to be calculated. Rotational transitions have been reported by Szanto et al. (2), Van den Heuval and Dymanus (3) and Sastry et al. (4). The ν_2 bands of N_2H^+ and N_2D^+ have been observed by Sears.(5,6). The ν_3 of N_2H^+ and N_2D^+ have been measured by Foster and McKellar (7) while the ν_1 and $(11^10) \leftarrow (01^10)$ hot band have been observed by Nesbitt et al. (8). These data have been combined in a weighted least squares analysis to yield rotational constants, centrifugal distortion constants and l-type doubling constants. Using this information, we have calculated the equilibrium structure of protonated nitrogen.

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1. C.G. Gudeman, M.H. Begemann, J.Pfaff and R.J. Saykally, J. Chem. Phys. 78, 5837 (1983).
2. P.G. Szanto, T.G. Anderson, R.J. Saykally, N.D. Piltch, J.A. Dixon, and R.C. Woods, J. Chem. Phys. 75, 4261 (1981).
3. T.C. Van der Heuval and A. Dymanus, Chem. Phys. Lett. 92, 219 (1982).
4. K.V.L.N. Sastry, P. Helminger, E. Herbst and F.C. Delucia, Chem. Phys. Lett. 84, 286 (1981).
5. T.J. Sears, J. Opt. Soc. Amer. B. 2, XX (1985).
6. T.J. Sears, preprint.
7. S.C. Foster and A.R. W. McKellar, J. Chem. Phys. 81, 3423 (1984).
8. D.J. Nesbitt, H. Petek, C.S. Gudeman, C.B. Moore and R.J. Saykally, J. Chem. Phys. 81, 5281 (1984).

This work was supported by the National Science Foundation, Structure and Thermodynamics Program.

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TE2. (1:47)

MEASUREMENT OF THE ROTATIONAL SPECTRUM OF H_2O^+ BY LASER MAGNETIC RESONANCE SPECTROSCOPY

S. E. Strahan, R. P. Müller, and R. J. Saykally

We report here the first study of the rotational spectrum of an open-shell polyatomic ion. H_2O^+ is produced in an intracavity A.C. discharge using 1 torr of helium and a trace of water vapor. Fifty-five hyperfine-Zeeman lines have been measured from three different rotational transitions, revealing both singlet and triplet hyperfine structures from the protons. An analysis is underway employing a Watson S-reduced Hamiltonian with electron spin, hyperfine, and Zeeman interaction terms. The LMR data is supplemented by optical combination differences in a weighted least-squares fit. Results of the fit provide information on the electron distribution in the ion and ultimately will yield a precise molecular structure.

H_2O^+ is a molecule of both astrophysical and atmospheric interest, and has been observed in the tails of comets. This high resolution study by LMR will yield molecular constants necessary for the prediction of accurate rest frequencies to be used in searches for H_2O^+ in these environments.

This work was supported by the Director, Office of Basic Research, U.S. Department of Energy.

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TE3. (2:04)

MEASUREMENT OF THE ROTATIONAL SPECTRUM OF OH^+ AND OD^+ BY LASER MAGNETIC RESONANCE

M. Gruebele, Rene P. Müller and Richard J. Saykally

Rotational fine structure transitions have been observed for the OH^+ and OD^+ molecular ions V=0 in the $X^3\Sigma^-$ ground state by far-infrared laser magnetic resonance spectroscopy. The ions were generated in an intracavity discharge using 1 torr of helium and 30 mT of H_2O/D_2O. Measurements of $N=1\leftarrow0$, $N=2\leftarrow1$ and $N=3\leftarrow2$ have been made up to 17 kG for both species, with resolution of the OH^+ hyperfine structures. The data is being analyzed using a modified Tinkham-Strandberg Hamiltonian for $^3\Sigma$ states. Results of this analysis will be used to accurately predict astrophysically accessible rotational transitions.

This work was supported by the Director, Office of Basic Research, U.S. Department of Energy.

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TE4. (2:21)

OBSERVATION OF OH+ AND H2O+ INFRARED FUNDAMENTAL BANDS

M.W. CROFTON, R.S. ALTMAN, M.-F. JAGOD, B.D. REHFUSS, AND T. OKA

Infrared spectra of the fundamental band of OH+ and the ν_3 band of H_2O+ have been observed in an a.c. glow discharge of a $He/H_2/O_2$ (100:1:1) gas mixture. A laser difference frequency spectrometer and velocity modulation were used for the detection. The intensity of the transitions indicates OH+ and H_2O+ concentrations of ~5 x 10^8 cm-3, with an H_3O+ abundance of the same order.

The observed spectrum of OH+ has enabled us to improve the accuracy of the molecular constants reported by Merer et. al.[1] For the ν_3 band of H_2O+, eight pairs of combination differences in the ground state were used together with the previous data of Lew[2] to determine improved ground state constants. The molecular constants in the (0,0,1) state were determined for the first time.

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[1] A.J. Merer, D.N. Malm, R.W. Martin, M. Horani, and J. Rostas, Can. J. Phys., 53, 251(1975)

[2] H. Lew, Can. J. Phys., 54, 2028(1976)

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TE5. (2:38)

EXPERIMENTAL DETERMINATION OF THE H_3O^+ GROUND STATE INVERSION SPLITTING

DI-JIA LIU and TAKESHI OKA

High resolution infrared spectra of the $1^- - 0^+$ (10μm), $1^+ - 0^-$ (20 μm) and $1^- - 1^+$ (27μm) ν_2 vibration-inversion bands of H_3O^+ have been observed in an ac glow discharge by using tunable diode lasers and velocity modulation technique. The three band origins were found to be at 954.4003(25) cm^{-1}, 525.8237(13) cm^{-1} and 373.2304(47) cm^{-1}, respectively. The rotational and centrifugal distortion constants of these three bands were also obtained from the least-squares fitting of observed transitions. From the molecular constants obtained above, we have determined the ground state inversion splitting of H_3O^+ molecular ion to be 55.3462(55) cm^{-1} and predicted the ground state inversion spectrum in the far IR region and the inversion-rotation spectrum in the millimeter wave region. These predictions may be used to detect this fundamental molecular ion in interstellar space.

A comparison has been made between our experimental molecular constants and the relative strength of these three bands with those ab-initio theoretical predictions for this long-standing problem.

The discharge chemistry of H_3O^+ is discussed with reference to the observed line strength - gas composition relation and known ion-molecule reactions.

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TE6. (3:10)

SPECTACULARLY INTENSE INFRARED VIBRATIONAL TRANSITIONS IN SPATIALLY DEGENERATE ELECTRONIC STATES

B. SCHARF AND TERRY A. MILLER

High symmetry for molecules in non-degenerate electronic states tends to reduce or eliminate the possibilities for electric dipole transitions in polyatomic molecules. However if the electronic state is degenerate, Child and Longuet-Higgins showed 25 years ago, that new transitions can occur in both the microwave and IR region. We have extended this early work and found various types of spectacularly intense vibrational transitions, with oscillator strengths comparable to fully allowed electronic transitions. The close connection between the intensity of these enhanced vibrational transitions and the existence of an anomalous permanent dipole moment, with its implications for microwave spectra and the Stark effect, is elucidated. These results are of special interest for experiments aimed at detecting the spectra of small, symmetrical polyatomic ions and radicals.

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TE7. (3:27)

IMPROVEMENTS IN THE VIBRATION INTERVAL PREDICTIONS FOR H_3^+

G. D. CARNEY AND S. ADLER-GOLDEN

This study reports an excellent least squares curve fit of Dykstra and Swope's ab-initio H_3^+ potential energy surface.[1] The curve fit function is a sixth degree symmetry adapted polynominal expressed in the variables $\rho_i = (R_i - R_{eq})/R_i$ with equilibrium bond length R_{eq} and instantaneous bond lengths R_i. Vibration energies[1] are determined using variational methods, and the theoretical and available experimental excitation energies for H_3^+, D_3^+, H_2D^+, and D_2H^+ agree to within 2 cm^{-1}.

---

[1] C. E. Dykstra and W. C. Swope, J. Chem. Phys. 70, 1 (1979).

Address of Carney: Department of Chemistry, Allegheny College, Meadville, PA 16335
Address of Adler-Golden: Spectral Science Incorp., 111 South Bedford Street, Burlington, MA 01803

TE8. (3:44)

INFRARED EMISSION SPECTRA OF H_2, H_3 AND H_3^+ FROM A HYDROGEN DISCHARGE AT VARIOUS PRESSURES

W. A. MAJEWSKI, J. K. G. WATSON, AND J. W. C. JOHNS

A new hollow-cathode emission tube operating in the pressure range 0.2 to 100 torr has been constructed and used to record the infrared spectrum of a hydrogen discharge at various pressures with a Bomem Fourier transform spectrometer. The different pressure-dependences of the production and deexcitation rates of different species make it possible to use the pressure-dependences of the intensities in order to discriminate between the valence and Rydberg transitions of H_2, *the Rydberg transitions of* H_3, and the vibration-rotation transitions of H_3^+.[2] This H_3^+ emission spectrum complements and extends to higher J-values the previous absorption spectrum. New lines of the other species have also been observed, and their assignments will be discussed.

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TE9. (4:01)

THE ν_2 AND ν_3 BANDS OF H_2D^+ AND D_2H^+

S.C. FOSTER, A.R.W. McKELLAR, AND J.K.G. WATSON

Extensive diode laser spectra of H_2D^+ in the 2000-2500 cm^{-1} region and of D_2H^+ in the 1800-2300 cm^{-1} region have been recorded. These data are supplemented by difference-frequency laser measurements on H_2D^+ by Crofton and Oka, and by ion beam measurements on D_2H^+ by Shy and Wing.[1] For both isotopes the ν_2 and ν_3 vibrations are strongly coupled by a Coriolis interaction, and the bands must be analyzed simultaneously; these analyses have now been accomplished. Previous studies[2] of the ν_1 bands were very helpful in providing ground state combination differences to confirm our assignments. For H_2D^+, over 60 transitions have been assigned and fitted with a standard deviation of about 0.008 cm^{-1}, and for D_2H^+ the numbers are similar. The resulting molecular parameters are in good general agreement with ab initio calculations.[3]

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[1] J.-T. Shy, Ph.D. Thesis, University of Arizona (1982); J.-T. Shy, J.W. Farley, and W.H. Wing, Phys. Rev. A 24, 1146 (1981).

[2] T. Amano and J.K.G. Watson, J. Chem. Phys. 81, 2869 (1984); K.G. Lubic and T. Amano, Can. J. Phys. 62, 1886 (1984).

[3] For example: G.D. Carney, Can. J. Phys. 62, 1871 (1984).

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TE10. (4:18)

ASTRONOMICAL DETECTION OF THE $1_{10} \rightarrow 1_{11}$ TRANSITION OF H_2D^+

T. G. PHILLIPS, G. A. BLAKE, J. KEENE, R. C. WOODS, AND E. CHURCHWELL

An emission line has been observed in the giant molecular cloud NGC 2264 at the frequency expected for the $1_{10} \rightarrow 1_{11}$ transition of H_2D^+, while a similar search in the dark cloud TMC 1 produced a negative result. These observations were made using the Kuiper Airborne Observatory to avoid the severe attenuation at 372 GHz by atmospheric water vapor. The strength of the observed line is in approximate agreement with the H_2D^+ abundance anticipated from models of interstellar chemistry. The failure to observe emission in TMC 1, where the H_2D^+ abundance is expected to be large, is inferred to result from the low degree of excitation of the 1_{10} level in this very cold object and can be related to the extent of equilibration between ortho and para H_2 in the interstellar medium.

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TE11. (4:35)

THE MICROWAVE SPECTRUM OF SO^+

H. E. WARNER, N. CARBALLO, AND R. C. WOODS

Several transitions in the rotational spectrum of the $X^2\Pi$ (v =0) state of the SO^+ ion have been observed. Discharges in Ar-SO_2, Ar-O_2-H_2S, or pure SO_2 were employed to produce this species successfully. The very characteristic slow Zeeman effect of the $^2\Pi_{1/2}$ state was used to unambiguously identify the SO^+ lines, even though many stronger interfering lines of other species, both paramagnetic and diamagnetic, were present in the spectrum. The new spectroscopic constants agree well with previous values from optical spectroscopy.

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TE12. (4:52)

A STUDY OF MOLECULAR ION DISTRIBUTION IN THE POSITIVE COLUMN OF D.C. GLOW DISCHARGES BY DIODE LASER SPECTROSCOPY

Fu-Shih Pan and Takeshi Oka

The high spatial resolution of laser infrared ion spectroscopy enables us to monitor the distribution of molecular ions *in situ* in the discharges. We observed the radial distribution of ion densities in the positive column of glow discharges using strong absorption lines of ArH^+ and H_3^+. The results show a remarkable depletion of ion densities in the center of plasma for the high current density (400mA/cm) and/or high pressure (10 torr) regime. The very high abundance of ArH^+ allows us to measure also the translational, rotational and vibrational temperatures. Together with our previous study of ion mobility,[1] this method provides us with a powerful means of plasma diagnostics which is sensitive to quantum state.

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[1] N.N. Haese, F.S. Pan, and T. Oka, Phys. Rev. Lett., 50, 1575 (1983).

Address: Department of Chemistry and Department of Astronomy, and Astrophysics, The University of Chicago.

TF1. (1:30)

TIME-RESOLVED RESONANCE RAMAN OF PHOTOTRANSIENTS

M. A. El-Sayed

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In the absence of time-resolved structural studies with x-ray techniques on the short time scale at the moment, time-resolved vibrational spectroscopy becomes one of the most effective tools used to understand the mechanisms of physical and chemical changes. Due to large resonance Raman enhancements, high laser photon flux and short laser pulses, the Raman (vibration) spectra, and thus the inferred molecular structures, of short-lived transients are now determined in the subpicosecond to the second time scale. This led to a more accurate description of the mechanisms involved in a number of photochemical, photophysical and photobiological processes.

Some of the time-resolved resonance Raman techniques developed in our as well as in other laboratories using both c.w. and pulsed lasers will first be described. A few examples of the kinds of problems that have been studied with time-resolved resonance Raman techniques will then be discussed.

TF2. (2:05)

INVESTIGATION OF PHOTOINDUCED ELECTRON TRANSFER AND CONSECUTIVE REACTIONS BY TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY

S. SCHNEIDER AND W. HUB

The apparatus used to record Resonance Raman Spectra of photoinduced transients with nanosecond time resolution is described.

The value of information on the vibrational quanta of intermediates for the elucidation of reaction mechanisms is demonstrated by various examples. In view of the fact that photoinduced reactions of excited stilbenes are among the most intensively studied model reactions, the electron transfer between stilbenes and various electron donors and acceptors, respectively, are discussed in more detail /1-3/.

In an attempt to make an assignment of the observed vibrational frequencies of both the stilbene anion and cation, various deuterium substituted stilbenes are included in the study.

1/ W. Hub et al., J. Amer. Chem. Soc. 106, 701 (1984)
2/ W. Hub et al., J. Amer. Chem. Soc. 106, 708 (1984)
3/ W. Hub et al., J. Phys. Chem. 88, 2308 (1984)

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TF3. (3:00)

RESONANCE RAMAN STUDIES OF RADIATION- AND PHOTO-CHEMICAL TRANSIENTS

G.N.R. TRIPATHI

Time-resolved techniques are applied to examine the resonance Raman spectra, structures, and kinetic behavior of transient intermediates in a number of radiation- and photo-chemical reactions. The following systems will be discussed:

(1) Dihalide radical anions (Cl_2^-, Br_2^-, I_2^-) in aqueous solution. Bond dissociation energies (1.6, 1.3, 0.9 eV respectively) have been evaluated.

(2) Transient species in the pulse radiolytic reactions of aqueous aniline. The Raman spectra of anilino, aniline radical cation and benzidine radical cation have been observed.

(3) Photoexcited triplet (T_1) states of N-heterocyclic molecules and their reactions.

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TF4. (3:35)

Vibrational Raman Spectroscopy of Transients in the Reactions of Visual Chromophores

I. Grieger, G. Rumbles, P. Killough, and G. H. Atkinson

Time-resolved resonance Raman (TR^3) spectroscopy has been used to record the vibrational spectra and to monitor the dynamical properties of transient intermediates found in the reactions of visual chromophores. The experimental approach derives from pump-probe configurations using two independently tunable dye lasers with time resolution extending to <10 ps.

Results will be presented on the excited and ground-state mechanisms for isomerization and conformational changes in retinals and in the bacteriorhodopsin photocycle. The vibrational Raman spectra of the conformational and structural intermediates found during these reactions also will be described. These data lead to clear distinctions between the reaction pathways that proceed along either excited or ground state potential surfaces. The availability of TR^3 spectra for these intermediates permits these mechanistic routes to be viewed in terms of the structural changes occurring in the retinal chromophore. These experiments also comment on the photolytic interruption of retinal isomerization occurring on ground-state potential surface by the high laser intensities used to initiate and probe the reactions.

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TF5. (Last Minute Addition) (4:10)

THE COMPUTATIONAL SIMULATION OF THE X-RAY POWDER SPECTRUM OF ICE Ih

P. W. DEUTSCH AND T. A. STANIK

Metropolis Monte Carlo calculations have been performed on a 192 water molecule periodic unit cell. The cell has been set up initially to possess a zero point dipole moment, and it has been subjected to a static energy minimization. The unit cell has been run and equilibrated at a variety of input temperatures ranging from a very low 20K to a temperature high enough to melt the system (300K).[1] Structure factors for the oxygen sublattice have been obtained in sufficient quantity to form an oxygen powder spectrum at various temperatures. The oxygen structure factors used are averages over at least 10^6 Monte Carlo steps. Oxygen form factors have been obtained from the literature [2], and they have been employed in combination with the structure factors to form x-ray powder spectra. The results are compared with values in the literature.[3]

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[1] B. N. Hale et. al.: J. Chem. Phys. 78 , 5103 (1983) ; J. Phys. Chem. 87, 4309 (1983).

[2] L. R. M. Morin , J. Phys. Chem. Ref. Data 11 , 1091 (1982); B. D. Cullity, Elements of X-ray Diffraction , (Reading, Mass.: Addison Wesley, 1978) , 520.

[3] L. G. Dowell and A. P. Rinfret, Nature 188, 1144 (1960).

Address of Deutsch and Stanik: The Pennsylvania State University at Beaver,
Brodhead Rd., Monaca, Pennsylvania 15061.

(1:30)

TG1.

THE PUZZLING MICROWAVE SPECTRUM OF HEXADIENAL

ROBERT K. BOHN, CARL SAHI and MARK F. GRANVILLE

The microwave spectrum of trans,trans-2,4-hexadienal can be assigned to the species with anti-periplanar conformations about the C-C single bonds(1). Hexadienal is a nearly symmetric top (kappa = -0.997, calc'd) whose a-type R-branch pileups form narrow (5 MHz FWHM) bands whose K components are unresolved but the bands from each vibrational species are resolved from each other. The spectrum reveals a complex array of vibrational satellite bands extending upward in frequency from the ground state band (B+C = 1592.5 MHz). Assuming the torsional modes about the two central C-C single bonds are the molecule's lowest frequency vibrational modes, that torsional potential functions from acrolein and butadiene are transferable to hexadienal, and that the operator for B+C is represented by the geometrically calculated B+C as a function of the two torsional angles, much of the vibrational satellite structure of the spectrum can be simulated.

This model describes the microwave spectrum with one glaring deficiency: the intense, broad absorption bands displaced to slightly higher frequencies (B+C = 1604.0 MHz) from the ground state and the discrete vibrationally excited species are not explained. Various models for this intense band series will be discussed.

(1) W. E. Steinmetz, J. E. Pollard, J. M. Blaney, B. K. Winker, I. K. Mun, F. J. Hickernell and S. J. Hollenberg, J. Phys. Chem. 83, 1540 (1979).

Address: Department of Chemistry, University of Connecticut, Storrs, CT 06268

(1:42)

TG2.

THE ROTATIONAL SPECTRUM OF NITRIC ACID IN THE ν5 EXCITED VIBRATIONAL STATE

RANDY BOOKER, PAUL HELMINGER, HENRY EVERITT, AND FRANK C. DE LUCIA

Extensive measurements of the rotational spectrum of nitric acid (HNO_3) in its ν5 excited vibrational state have been carried out in the millimeter and submillimeter wave spectral region. The assignment of this spectrum was significantly aided by the recent infrared work of Maki and Wells[1]. Much of the data was obtained on a new broadband millimeter and submillimeter spectrometer which is based on traveling wave tube and harmonic generator technology. The long, continuous survey sweeps allowed by this system greatly aided the assignment of the relatively weak excited state features from the very dense background spectra of the ground and lower lying excited states.

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[1] A.G. Maki and J.S. Wells, J. Mol. Spectrosc. 108, 17 (1984).

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TG3. (1:59)

MILLIMETER/SUBMILLIMETER WAVE SPECTRUM OF METHYL FORMATE IN ITS GROUND TORSIONAL E STATE: APPLICATION OF THE HIGH-BARRIER P.A.M. TO HIGH K

GRANT M. PLUMMER, GEOFFREY A. BLAKE, ERIC HERBST AND FRANK C. DE LUCIA

We report the measurement of over one hundred new rotational transitions of the internal rotor $HCOOCH_3$ in its E symmetry state. The principal axis method has been used to analyze these and all previously collected data. For relatively high barriers, such as that in methyl formate, the A and E states can be treated as distinct asymmetric tops: only the latter showing explicit perturbations due to the internal rotation. The splitting of the E levels has been calculated using successive Van Vleck transformations and two-by-two diagonalizations, simplified by the evaluation of the perturbation matrix elements in the symmetric top basis.

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TG4. (2:16)

MICROWAVE SPECTRUM, CONFORMATION AND DIPOLE MOMENT OF TRANS-DIFLUOROETHYLENE OZONIDE(F$\overline{\text{CHOOFCHO}}$)

M. G. SOLTIS, K. W. HILLIG II, AND R. L. KUCZKOWSKI

The rotational spectra of five isotopic species of trans-difluoroethylene ozonide (trans-3,5-difluoro-1,2,4-trioxolane) were assigned in the region 18.0 - 40.0 GHz. These included the parent species, both single- and double-substituted deuterium species, the double $^{18}O_p$ and triple ^{18}O species.

The spectrum consisted of b-type transitions with a 10:6 intensity alternation consistent with a C_2 axis of symmetry. The ground state rotational constants for the normal species are: A = 6093.333(3) MHz, B = 2287.188(1) MHz, and C = 2001.709(1) MHz. The electric dipole moment was determined from Stark effect measurements to be: μ_b = 0.994(5) Debye.

These results indicate an O_p-O_p twist conformation with diaxial fluorine substituents. The following selected bond lengths (Å) and angles (deg) were obtained using both Kraitchman calculations and the method of predicate observables (diagnostic least-squares).

$r(O_p\text{-}O_p) = 1.459(10)$
$r(C\text{-}O_p) = 1.368(15)$
$r(C\text{-}O_e) = 1.396(20)$
$r(C\text{-}F) = 1.370(15)$

$<(O\text{-}C\text{-}O) = 107.0(10)$
$<(C\text{-}O\text{-}O) = 101.4(10)$
$<(C\text{-}O\text{-}C) = 105.0(10)$

$\tau(C\text{-}O\text{-}O\text{-}C) = 41.5(10)$
$\tau(F\text{-}C\text{-}O\text{-}O) = 84.5(10)$

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TG5. (2:28)

MICROWAVE SPECTRUM OF CYCLOHEXYLPHOSPHINE

Y. S. Li

The microwave spectrum of cylcohexylphosphine has been observed in the frequency region from 18.0 to 26.5 GHz. Rotational assignments have been made for the normal isotopic species as well as the $C_6H_{11}PD_2$ isotopic species. From the experimental data, the assigned spectrum may be identified to result from the *gauch* conformer which exists in the chair form with the phosphino group in the equatorial position.

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TG6. (2:40)

TORSIONAL POTENTIAL FUNCTION OF ETHYLPHOSPHINE

P. GRONER AND J. R. DURIG

Microwave spectra of new isotopic species of ethylphosphine $CH_3CH_2PH_2$ were assigned to derive an improved molecular structure.[1] FTIR spectroscopy in the torsional region with higher resolution than used previously[1] provided new data from which improved potential functions of both the PF_2 and CH_3 torsions were derived. The possibility of coupling of both torsions is tested using a two-dimensional model.[2]

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[1] J. R. Durig and A. W. Cox, J. Chem. Phys., 63, 2303 (1975); 64, 1930 (1976).
[2] R. Meyer, J. Mol. Spectrosc., 76, 266 (1979).

Address: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208

TG7. (2:57)

MICROWAVE, INFRARED, AND RAMAN SPECTRA, AND CONFORMATIONAL STABILITY OF CHLOROMETHYLPHOSPHONIC DIFLUORIDE

R. D. JOHNSON, J. R. DURIG, B. J. VAN DER VEKEN, AND P. COPPENS

The microwave spectrum of chloromethylphosphonic difluoride, $ClCH_2POF_2$, has been investigated in the region from 26.5 to 30 GHz. The a-type R-branch transitions have been assigned for both the ^{35}Cl and ^{37}Cl isotopic species for the trans conformer on the basis of the rigid rotor model. For the ground vibrational state the rotational constants for the ^{35}Cl isotope were found to be A = 4392.4 ± 2.3, B = 1543.36 ± 0.01 and C = 1512.30 ± 0.01 MHz and for the ^{37}Cl isotope: A = 4395.3 ± 2.7, B = 1502.04 ± 0.01 and C = 1472.54 ± 0.01 MHz. With reasonably assumed structural parameters for the C-H and P=O distances as well as the HCH angle, a diagnostic least-squares adjustment was utilized to obtain the other six structural parameters. The infrared and Raman spectra have been recorded, and both the trans and gauche conformers have been identified in the vibrational spectra of the fluid phases. From a temperature study of the Raman spectrum of the liquid phase the enthalpy between the trans and gauche conformers was determined to be 370 ± 50 cm^{-1} (1.06 kcal/mol) with the trans conformer being thermodynamically preferred. Band contour simulation of the infrared gas phase bands also shows that the trans conformer is more stable in this phase. Upon crystallization only the trans conformer remains in the solid state. The asymmetric torsion for the trans conformer was observed as a series of closely spaced Q branches beginning at 82.5 cm^{-1} and falling to lower frequency and the corresponding transitions for the gauche conformer begin at 72.9 cm^{-1}. *These transitions have been used to obtain the potential constants for the asymmetric rotation.*

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TG8. (3:30)

MILLIMETER WAVE SPECTRUM OF HCCCN IN THE EXCITED VIBRATIONAL STATE

Koichi M.T. Yamada, G. Winnewisser, R.A. Creswell, and M. Winnewisser

The pure rotational spectrum of cyanoacetylene, HCCCN, in the vibrationally excited states has been measured in the frequency region from 8 to 210 GHz at Giessen. All vibrational satellites arising from the states lower than 1000 cm^{-1} have been identified and analyzed. The states $(v_4,v_5,v_6,v_7)=(0,0,0,1)$, $(0,0,0,2)$, $(0,0,1,0)$, $(0,0,1,1)$, and $(0,0,1,2)$ are found to be unperturbed and were analyzed using a newly proposed effective Hamiltonian[1].

A weak anharmonic resonance has been detected between the (0,0,0,3) and (0,1,0,0) states which are almost exactly degenerate. The analysis of these states was carried out by diagonalizing the energy matrix based on 6 wavefunctions (3 for each symmetric and antisymmetric sub-matrix). The first excited state of the C-C streching vibration, (1,0,0,0), perturbs strongly the (0,0,2,0) state by a Fermi resonance, and also perturbs the (0,1,0,1) and the (0,0,0,4) states. In addition a weak anharmonic resonance was found between the (0,0,0,4) and the (0,1,0,1) state. In this case, an 8x8 matrix was diagonalized for the symmetric states, and a 5x5 for the antisymmetric states. Thus out of seven normal modes, we could determine accurately for four modes the unperturbed rotational constants of the first excited states.

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[1] K.M.T. Yamada, F.W. Birss, and M.R. Aliev, to apear

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TG9. (3:47)

A REINVESTIGATION OF THE MICROWAVE SPECTRUM OF METHYL PHOSPHONIC DIFLUORIDE

H. JUSTNES, C. GILLIES, AND T. DIGIUSEPPE

The microwave spectrum of methyl phosphonic difluoride, $CH_3(F_2)$ PO, was reinvestigated in the region of 26,500 to 36000 MHz. It is found that previous reports on the microwave spectrum of this compound contain errors in the measured transition frequencies for the ground vibrational state.[1,2] Revised rigid rotor rotational constants (MHz) for the ground state are

$$A = 4495.814(7), \quad B = 4271.851(5) \text{ and } C = 4125.899(5).$$

Previous microwave assignment of two vibrational satellites are shown to be erroneous.[1,2] Three sets of excited vibrational state lines have been identified and fit well to rigid rotor theory. Relative intensity measurements permit tentative vibrational assignments of the states to first excitations of the CH_3 torsion, CPO bend and PF_2 deformation by comparison to the vibrational work.[1] The three excited states exhibited no resolvable microwave transition splitting. The implications of these results to previous estimates of the methyl torsional barrier will be discussed.

---

[1] J.R. Durig, K.S. Kalasinsky and V.F. Kalasinsky, J. Mol. Strut., 34, 9 (1976).

[2] J.R. Durig, A.E. Stanley and Y.S. Li, J. Mol. Strut., 78, 247 (1982).

Address of Justnes and Gillies: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180 Address of DiGiuseppe: Geo-Centers, Inc., 320 Needham St., Newton Upper Falls, MA 02164.

TG10. (4:04)

THE J=1-2 TRANSITION OF POTASSIUM HYDROXIDE

T. RAW, T. YAMAMURA, AND C. GILLIES

A high temperature microwave spectrometer has been developed for the detection of KOH monomer in the vapor above alkali carbonate eutectics in fuel cell atmospheres. The microwave spectrum of KOH was investigated in the J=1-2 region around 32GHz at 580 C employing Stark modulation. Radio frequency-microwave double resonance techniques confirmed the assignment of the l-doublet vibrational states. A nonlinear least-squares fit of the partially resolved quadrupole hyperfine structure to a Lorentzian line shape yielded ν_0 = 32834.33(5)MHz and eQq= -7.19(8)MHz for the ground vibrational state. These data are consistent with the higher J data and lead to a smaller uncertainty in eQq.[1-3] Results for excited vibrational states will be discussed, as well as design features which have resulted in high spectrometer sensitivity for the detection of KOH.

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[1] P. Kuijpers, T. Torring, A. Dymanus Z. Naturforsch. 30a, 1256 (1975).
[2] E.F. Pearson, B.P. Winnewisser, M.B. Trueblood Z. Naturforsch. 31a, 1259 (1976).
[3] P. Kuijpers, T. Torring, A. Dymanus Z. Naturforsch, 32a, 930 (1975).

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TG11. (4:21)

METHYL AND HYDROXYL INTERNAL ROTATION IN METHYL HYDROPEROXIDE

M. Tyblewski, A. Bauder and C.E. Blom

Recently, preliminary investigations on the microwave and millimeterwave spectra of methyl hydroperoxide (CH_3OOH) have been reported (1). The two lowest OH-torsional states 0^+ and 0^- are coupled by strong Coriolis interactions. "Forbidden" transitions ($0^+ \rightarrow 0^-$ with $\Delta K_c = 1$) have been observed when asymmetry splitting and CH_3-rotational splitting are comparable in magnitude. In the present contribution an accurate Hamiltonian is presented, which describes the 0^+ and 0^- states. A 22-term Hamiltonian was adjusted to 160 experimental data; the average difference between observed and calculated transition frequencies was 140 kHz. The energy difference between the rotational ground state levels of 0^+ and 0^- was determined to be 448760.3(1) MHz. CH_3-rotational splittings have been analysed and were treated using perturbation theory.

---

(1) 8th Colloquium on High Resolution Mol. Spectrosc., Tours, 1983, paper H13.
39th Symposium on Molecular Spectroscopy, Columbus OH, 1984, paper MG5.

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TG12. (4:38)

MICROWAVE SPECTRUM AND QUADRUPOLE COUPLING IN IODOACETONITRILE

R. C. CLAYTOR, G. M. AULT, AND J. D. GRAYBEAL*

The high resolution microwave spectrum of iodoacetonitrile, $^{127}ICH_2CN$, has been observed in the region from 12.5-40 GHz. Separate fits of a series of ^{b}Q-branch transitions using an analytical version of the conventional A-C vs K plot technique and the Kirchhoff NBS fitting program[1] for a combination of ^{b}R- and ^{b}Q type transitions gave rotational constants (in MHz) of A=20037(3), B=1747.9(4) and C=1622.8(4).

Using second order quadrupole theory the analysis of the hyperfine structure of 7 separate transitions yielded nuclear quadrupole coupling parameters (in MHz) of χ_{aa}=-1276, χ_{bb}=233, χ_{cc}=1043 and χ_{ab}=1370. The nuclear quadrupole coupling constants (in MHz) in the principle axis system of the electric field gradient tensor are χ_{zz}= -2086 and $\chi_{xx}=\chi_{yy}$=1043. A comparison of χ_{zz} with values for related compounds and with analogous compounds of other halogens indicates a higher degree of covalency for the C-I bond as would be expected. Analysis of the spectral fit and the nature of the quadrupole coupling will be presented.

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[1] W. H. Kirchhoff, J. Mol. Spectrosc. 41, 333 (1972).

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TG13. (4.55)

MICROWAVE SPECTRUM OF PENTAFLUOROSULFANYLIMINOSULFUR DIFLUORIDE

R. W. WHITE, S. R. BAILEY, J. S. THRASHER, AND J. D. GRAYBEAL*

The low resolution spectrum of the most abundant isotopic species of pentafluorosulfanyliminosulfur difluoride, $F_2{}^{32}S{=}N^{32}SF_5$, in the region of 12.5-26.5 GHz consists of an intense series of ^{a}R-type bands and a weak series of ^{c}Q-type bands. Analysis of this low resolution spectrum gave parameters of B+C = 1538 MHz and 2A-B-C = 2389 MHz. These parameters indicate that the sketal structure of the molecule is one having the sulfur and nitrogen lone pair electrons cis to the S=N bond.

The high resolution spectra for three isotopic species, all in natural abundance, have been measured and assigned. The rotational constants (in MHz) determined by use of the Kirchhoff NBS fitting program[1] are: $F_2{}^{32}S{=}N^{32}SF_5$ (100 transitions), A=1964.90(2), B=784.93(1), C=754.00(1); $F_2{}^{34}S{=}N^{32}SF_5$ (25 transitions), A=1959.83(3), B=774.01(1), C=744.66(1); $F_2{}^{32}S{=}N^{34}SF_5$ (35 transitions), A=1964.72(2), B=782.69(1), C=751.98(1). A preliminary structural fit of these constants indicates that the bond lengths are close to the values obtained for similar compounds but the SNS angle is considerably larger than the SNC angle in $F_2S{=}NCOF$ and $F_2S{=}NCF_3$. Details regarding the assignments and the structural parameters obtained will be discussed.

---

[1] W. H. Kirchhoff, J. Mol. Spectrosc. 41, 333 (1972).

*Work supported by NASA Langley

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WE1. (1:30)

INSTRUMENTAL ADVANCES IN RAMAN OPTICAL ACTIVITY (ROA)

Mark A. Davies, M. Reza Oboodi and Max Diem

The observation of ROA, the differential, inelastic scattering of left and right circularly polarized photons by chiral media, has been plagued by the presence of polarization artifacts, the magnitude of which may exceed the desired effect. The spurious signals can be minimized by maximizing the circularity of the exciting laser beam, modulated via an electro optic modulator (EOM), and by cancelling polarization artifacts via a dual beam light collection system, pioneered by Hug[1].

The former method involves alignment of the EOM to minimize η, the ellipticity of the exciting radiation, and adjusting θ, the azimuth of any residual ellipticity, such that the major axis of the polarization ellipse is at 45° with respect to the scattering plane. Four intensity measurements of the laser beam allow the determination of the term $\cos 2\eta \cos 2\theta$, which determines the magnitude of the artifacts[2]. In the ROA unit now operational at Hunter College, this term is computed in real time by the instrument control processor during optical alignment, and can be reduced to about 1/1000. Similarily, software was developed to allow the precise balancing of the light levels in both collection arms such that remaining artifacts will cancel.

The above alignment procedure permits artifact levels to be reduced such that the total ROA, observed without a polarization analyzer in the scattered light, may be collected, thus allowing a detailed comparison of total, polarized and depolarized ROA components in a number of samples.

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1. W.Hug, Applied Spectrosc., 35, 115 (1981)
2. L.A.Barron and J.Vrbancich, J.Raman Spectrosc., 15, 47 (1984)

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WE2. (1:47)

THEORY OF MAGNETIC VIBRATIONAL CIRCULAR DICHROISM

T.H. WALNUT

Semiquantitatine theories of both type A and type B magnetic vibrational circular dichroism (MVCD) have been applied to the spectra observed by Devine and Keiderling[1,2].

The distinctive part of the theory is the detailed perturbation analysis of the part of the electronic momentum that is caused by nuclear motion. The treatment required going beyond the Born-Oppenheimer approximation.

The theory accounts in a simple way for the sign and approximate magnitude of the dichroism in the fundamental vibrations of ammonia, methyl halides, and 1,3,5 tri-substituted benzenes.

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[1] T.R. Devine and T.A. Keiderling J. Chem. Phys. 79 5776 (1983).
[2] T.R. Devine and T.A. Keiderling J. Phys. Chem. 88 390 (1984).

Address of Walnut: Department of Chemistry, Syracuse University, Syracuse, New York, 13210 USA

WE3. (1:59)

VIBRATIONAL CIRCULAR DICHROISM IN TARTARIC ACID ESTERS

P. L. POLAVARAPU

Vibrational circular dichroism spectra in 1800-900 cm^{-1} region were measured for both enantiomers of Tartaric acid, Dimethyl tartrate, Diethyl tartrate and Diisopropyl tartrate in CCl_4 and D_2O (or DMSO-d_6) solvents. The observed spectral correlations will be explained in terms of intermolecular (or intramolecular) hydrogen bonding and a single rotamer conformation.

Address of Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, TN 37235 USA.

WE4. (2:14)

EQUIVALENCE OF THE SEMICLASSICAL MODELS FOR VIBRATIONAL CIRCULAR DICHROISM

P. L. POLAVARAPU

The bond moment model for VCD is reformulated to eliminate an existing inconsistancy and it is shown that the reformulated bond moment model, charge flow model and bond current model are all equivalent in the final expression for VCD intensity.

Address of Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, TN 37235 USA.

WE5. (2:26)

VIBRATIONAL CIRCULAR DICHROISM, A COIL-HELIX TRANSITION OF POLY-TYROSINE IN NON-AQUEOUS SOLVENTS

S.C. Yasui and T.A. Keiderling

This work demonstrated the application of VCD to clarify the controversial conformations of poly-tyrosine in non-aqueous solvents. The VCD of poly-tyrosine in the Amide I and II regions in dimethyl sulfoxide (DMSO); DMSO-d_6; 80:20 mixtures of DMSO or DMSO-d_6 with dichloroacetic acid (DCA), trifluoroacetic acid (TFA), trifluoroethanol (TFE); and 50:50 mixture with trimethyl phosphate (TMP) have been measured. In pure DMSO an oppositely signed VCD was seen as compared to the mixtures. The latter were characteristic in sign pattern and shape of right-handed helices for poly-L-Tyrosine (PLT). Similar results were obtained in the Amide A region. The pure PLT:DMSO results in the Amide I region are similar to poly-lysine: D_2O and may be characteristic of random-coil VCD.

Address of Keiderling and Yasui: Department of Chemistry, University of Illinois, P.O. Box 4348, Chicago, Illinois 60680.

WE6. (2:43)

VIBRATIONAL CIRCULAR DISCHROISM OF NUCLEIC ACIDS

A. ANNAMALAI AND T.A. KEIDERLING

This preliminary work reports the vibrational circular dichroism for several homo-poly-ribonucleic acids, DNA's and RNA's measured for the C=O, C=C and P=O stretching modes under different conditions. A qualitative comparison of the results is made in light of single and double strands of these molecules. The results obtained for the homo-poly-ribonucleic acids are in agreement with the ordered or random structure nature of these molecules as indicated by other studies.

Address of Keiderling and Annamalai: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, Illinois 60680, USA.

WE7. (3:15)

VIBRATIONAL CIRCULAR DICHROISM OF β-STRUCTURE FORMING OLIGOPEPTIDES

U. Narayanan, T.A. Keiderling, C. Toniolo, and G.M. Bonora

We have obtained vibrational circular dichroism spectra (VCD) for series of films of BOC -(L-X)$_n$ - OMe homo-oligo-peptides where X = Ala, Val, Leu, Nva and n = 3-7 in the Amide I and A regions. These compounds are known to form a β-structure from ir and CD studies. Our measurements indicate a series of changes with increasing chain length that may result from the formation of hydrogen bonds correlating to the onset of [illegible]-type bonding and then the formation of an extended β-structure. Solution VCD spectra were also measured for (Val)$_7$, (Ala)$_6$ and (Ala)$_7$ as a function of temperature and solvent variation and then correlated to the film results.

Address of U. Narayanan and T.A. Keiderling: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, IL 60680, USA.

Address of C. Toniola and G.M. Bonora: Biopolymer Research Center, C.N.R., Institute of Organic Chemistry, University of Padova, 35121 Padova, Italy.

WE8. (3:32)

VIBRATIONAL CIRCULAR DICHROISM IN BIS(ACETYLACETONATO)(L-ALANINATO)COBALT(III). ISOLATED OCCURRENCES OF THE COUPLED OSCILLATOR AND RING CURRENT INTENSITY MECHANISMS

D. A. Young, E. D. Lipp and L. A. Nafie

Vibrational circular dichroism spectra have been obtained for Δ-and Λ-bis(acetylacetonato)(L-alaninato)cobalt(III) in the hydrogen stretching region between 3400 and 2800 cm^{-1} and the mid-infrared region between 1600 and 1180 cm^{-1}. The bisignate VCD spectrum centered at 1522 cm^{-1}, due to the doubly degenerate antisymmetric CC stretching mode of the acetylacetonato rings, is interpreted on the basis of the coupled oscillator intensity mechanism. Remaining VCD features are explained primarily in terms of vibrational currents in rings formed by an intramolecular hydrogen bond or transition metal ligation. It is shown, based on the appearance of a large negative VCD band in the NH stretching region of the Δ-complex, which does not appear in the Λ-complex, that an intramolecular hydrogen bond forms between the L-alaninato ligand and one of the acetylacetonato ligands in the Δ-complex, but forms only weakly if at all in the Λ-complex.

Address: Department of Chemistry, Syracuse University, Syracuse, New York 13210.

WE9. (3:49)

ENHANCED VIBRATIONAL CIRCULAR DICHROISM VIA VIBRATIONALLY GENERATED ELECTRONIC RING CURRENTS

T. B. Freedman, G. A. Balukjian and L. A. Nafie

The enhanced vibrational circular dichroism (VCD) observed for some CH and OH stretching vibrations is interpreted in terms of a vibrationally generated ring current mechanism. The molecules investigated include phenylethane derivatives, α-hydroxy acids and esters, and amino acids. The large methine CH stretching VCD in molecules containing an adjacent ring closed by hydrogen bonding or π-π interaction is not observed in molecules where these rings do not form. For the closed ring, an oscillating magnetic moment can arise from oscillating electronic current produced by the methine vibration, and is responsible for the large VCD. Enhancement of methyl stretching VCD when through space interaction between the methyl group and π orbitals is present, and enhancement of OH stretching VCD for a hydroxyl group involved in an intramolecular ring provide further examples of vibrationally generated ring currents in VCD. General rules governing the sense of electronic current flow for a given phase of the nuclear motion are proposed which are consistent with all the spectra thus far obtained.

Address: Department of Chemistry, Syracuse University, Syracuse, New York 13210.

WE10. (4:06)

EVIDENCE FOR THE RING CURRENT MECHANISM IN THE C-H STRETCHING VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF SUGARS

M. G. Paterlini and L. A. Nafie

An interpretation of the CH stretching VCD in sugars has been developed in terms of electronic currents generated by the C(2)H, C(3)H and C(4)H methine stretching vibrations in adjacent intramolecularly hydrogen bonded rings. A comparison of the VCD spectra of D-mannose, D-glucose and D-glucose-2-d_1 will be presented which illustrate the model. The cancellation of ring current contributions which result in nearly zero VCD in glucose, are prevented in D-glucose-2-d_1 by deuteration and in D-mannose by altering the configuration at C(2); in such a way, a large monosignate negative CH stretching VCD is observed for these two sugars. The model is also shown to be consistent with VCD spectra of additional sugars surveyed previously(1).

---

[1] H. A. Havel, P.D. Thesis, University of Minnesota, 1981.

Address: Department of Chemistry, Syracuse University, Syracuse, New York 13210

WE11. (4:23)

A VALENCE COUPLED OSCILLATOR MODEL FOR THE CALCULATION OF VIBRATIONAL CIRCULAR DICHROISM

JOHN C. HANSEN AND ALBERT MOSCOWITZ

The coupled-oscillator model is appropriate in a number of situations that arise in connection with vibrational circular dichroism (VCD). One such situation is where the normal modes of interest may be adequately described in terms of a set of isolated degenerate (or quasidegenerate) oscillators which couple principally among themselves. Frequently, the coupling mechanism is not specified and the interaction terms in the secular equation are taken as empirical parameters. In this work we show how they may be estimated from a valence force field. A particular case of interest is where the oscillators interact only indirectly by G and/or F matrix coupling to other coordinates. These indirect second-order interactions can be transformed so as to appear as direct couplings among the oscillators via a Van Vleck transformation. Dipole and rotational strengths may then be calculated from the resulting eigenvectors in conjunction with the local transition diploes and their relative geometry.

Address: Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

WE12. (4:38)

VIBRATIONAL CIRCULAR DICHROISM OF (R)-(+)-3-METHYLCYCLOPENTANONE

LEO LAUX, JOHN C. HANSEN, AND ALBERT MOSCOWITZ

The vibrational circular dichroism (VCD) spectra of (R)-(+)-3-methylcyclopentanone and its 2,2,5,5-d_4 derivative in CCl_4 solution have been measured in the C-H and C-D stretching regions. The deuterated species shows a large ($|R| \sim 70 \times 10^{-45}$ esu^2 cm^2) bisignate VCD spectrum in the C-D stretching region. Attempts to account for these data by coupling among only four erstwhile degenerate C-D stretching modes fails. The data are better accounted for by more complex descriptions of the nuclear motions and attendant electronic charge flows that involve additional moieties, e.g. the carbonyl group.

Address: Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455
Present address of Laux: Lockheed, Palo Alto Research Laboratories, 3251 Hanover St., Palo Alto, California 94304

WE13. (4:55)

DETECTION OF PRIMARY AND SECONDARY CHIRAL STRUCTURES IN VIRUSES USING CIDS

C. W. PATTERSON, S. B. SINGHAM, AND G. C. SALZMAN

We demonstrate that the angular distribution of circular intensity difference scattering (CIDS) has a superposition principle for scattering arising from primary and secondary helical structure in macromolecules. We use this principle to analyze the CIDS signal from viruses.

Address of Patterson, Singham, and Salzman: Los Alamos National Laboratory, University of California, Box 1663, Los Alamos, NM 87545.

WE14. (Last Minute Addition) (5:12)

USE OF A SOLEIL-BABINET COMPENSATOR TO MEASURE RAMAN OPTICAL ACTIVITY SPECTRA

C. G. Zimba, X. M. Hu, and L. A. Nafie

A problem in measuring Raman optical activity (ROA) spectra has been the elimination of scattering artifacts which are present when the incident light is not perfectly circularly polarized. It has been shown that both the direction and the magnitude of the linearly polarized component should be nearly identical for both the left and the right senses of nearly circularly polarized light [1].

In the past, an electro-optic modulator (EOM) has been used to modulate the laser radiation between left and right circularly polarized states. Typically, this approach has involved a difficult and tedious allignment involving seven non-independent variables.

In an effort to circumvent that procedure, we have recently used a Soleil-Babinet compensator to generate the circularly polarized light. The compensator, which behaves essentially as a variable quarter-wave plate, has two independent adjustments: rotation about the laser beam and translation of a crystalline quartz wedge across the laser beam. As the wedge is translated, the thickness of quartz through which the laser beam passes changes and thus alters the retardation. The compensator can be alligned in ten minutes to produce better circular polarization, with more direct control over the slight linear residual, than the EOM.

Spectra measured with a diode array detector will be presented.

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[1] L.D. Barron and J. Vrbancich, J. Raman Spectroscopy, 15, 47 (1984).

Address: Department of Chemistry, Syracuse University, Syracuse, NY 13210

WF1. (1:30)

STANDARD SPECTRA WITH THE IMPROVED FOURIER TRANSFORM SPECTROMETER OF OULU

V.-M. HORNEMAN AND J. KAUPPINEN

The infrared standard spectra and about 2500 wavenumbers of lines between 500 cm^{-1} and 900 cm^{-1} have been produced with our modified Fourier transform spectrometer system. These spectra of H_2O, N_2O, CO_2 and OCS and the wavenumbers of lines will be presented in "Handbook of Infrared Standards with Spectral Maps and Molecular Parameters" by G. Guclachvili and K. Narahari Rao.

The spectra were the first true measurements with our new cube corner interferometer built at our laboratory. The maximum optical path difference of the interferometer is now 8 m providing a theoretical resolution of 0.0009 cm^{-1}. In these measurements the spectral resolution was between 0.002 cm^{-1} and 0.003 cm^{-1}. This is more than twice better than in our earlier measurements with the flat mirror interferometer. However, the signal to noise ratio is even better than before using the same source (Globar) and detector (Golay). This means, that the cube corner interferometer works in practice clearly better than older one. The absorption path length was 1 m. The pressures in the measurements were H_2O: 2 Torr, N_2O: 0.5 and 1.5 Torr, CO_2: 0.06 and 0.2 Torr and OCS: 0.5 Torr.

Although the spectra were first ones with the new system the results were quite good. Especially the accuracy of the wavenumbers inside the spectral bands was high. In the best conditions it was $\pm 13 \cdot 10^{-6}$ cm^{-1} ($\pm$ 0.39 MHz) defined as a standard deviation. It is limited only by the signal to noise ratio. The absolute accuracy is more difficult to calculate, because there may be several source of systematic errors: the precision of the reference lines[1], pressure shifts and phase errors. We have estimated it to be about $\pm 60 \cdot 10^{-6}$ cm^{-1} ($\pm$ 1.8 MHz).

---

[1] J.S. Wells, F.R. Petersen, A.G. Maki, and D.J. Sukle, Appl. Opt. 20, 1676 (1981).

Address of the authors: Department of Physics, University of Oulu, 90570 Oulu, Finland.

WF2. (1:47)

CAVITY-LOCKED DIODE LASER SPECTROMETER

M. Keich, R. Schieder, H.-J. Clar, G. Winnewisser, Koichi M.T. Yamada

Diode lasers have been used for high resolution molecular spectroscopy because of its relative ease of handling. However the accuracy of the measurement and the sensitivity of the diode laser spectrometer are limited by the frequency instabiltiy of the free-running diode. Therefore, in the present work we locked the diode laser to a fringe of a Fabry-Perot interferometer(FPI). By tuning the optical path length of the FPI, now the fringe-locked diode laser can be scanned. Since the frequency jitter of the laser can almost be removed, the obtained spectra are practcally free from noise, which implies that the usual noise observed in unlocked diode laser spectra are caused essentially by the frequency instability of the diode. The detail of the method and applications, which are now in progress, will be presented.

Address. Erstes Physikalisches Institut, Universität zu Köln, 5000 Köln 41, West Germany.

WF3. (1:59)

IR SPECTRA OF HIGH TEMPERATURE MOLECULES USING THE BURST OF GAS METHOD

T. C. DeVore and T. N. Gallaher

The infrared spectra of several molecules which are stable only at high temperatures, have been observed using a family of related techniques which are collectively known as the burst of gas method. Two methods were used to generate these gas bursts. In the first, a burst of reactant gas is passed over a hot sample surface. The molecule of interest is formed by chemical reactions between the gas and the surface. The spectra of Al_2Cl_6, W_nO_{3n} (n= 1 - 3), and TiF_4 will be used to illustrate this method. In the second procedure, a precursor solid is rapidly heated to a very high temperature to generate the gas burst. The spectra of KOCN monomer and dimer, and the C_2F_2 will be used to illustrate this method. In all cases, the spectra of the gas bursts have been obtained with a Nicolet MX-1 FT-IR.

Address: Department of Chemistry, James Madison University,
Harrisonburg, Virginia, 22807.

WF4. (2:16)

VIBRATION-ROTATION SPECTRA OF NH IN THE Δv = 1 SEQUENCE

D. BOUDJAADAR, P. CHOLLET, and G. GUELACHVILI

The emission of a cold plasma of a mixture of H_2 and N_2 flowing through a reactor and excited by a R.F. discharge has been recorded from 2000 cm^{-1} to 4000 cm^{-1} under Doppler-limited resolution with the High Information Fourier transform spectrometer of Laboratoire d'Infrarouge.

The observation of the rotation-vibration bands 1-0, 2-1, 3-2, 4-3, 5-4 of ^{14}NH in its X^3 fundamental electronic state is reported.

Address: Laboratoire d'Infrarouge, Laboratoire Associe au C.N.R.S., Universite
de Paris XI, Batiment 350, 91405 Orsay Cedex (France).

WF5. (2:33)

MORE DIODE LASER SPECTRA OF DIATOMIC MOLECULES

G. A. THOMPSON, A. G. MAKI, AND A. WEBER

We have been using a tunable infrared diode laser in attempts to measure the spectra of diatomic molecules in the gas phase. The Δv=2 transitions of LiI have been measured from v=2-0 to v=9-7 at a temperature of about 800°C. The spectra have been fit, along with microwave measurements taken from the literature, to a set of Dunham coefficients. We find ω_e = 496.84 cm^{-1}. Measurements and/or attempts to measure other molecules such as MgO will also be described.

Address of Thompson, Maki, and Weber: Molecular Spectroscopy Division,
National Bureau of Standards, Gaithersburg, MD 20899.

AD-A160 415 SSYMPOSIUM ON MOLECULAR SPECTROSCOPY (40TH) HELD AT COLUMBUS OHIO ON 17-21 JUNE 1985(U) OHIO STATE UNIV COLUMBUS DEPT OF CHEMISTRY I N RAO 21 JUN 85 2/2

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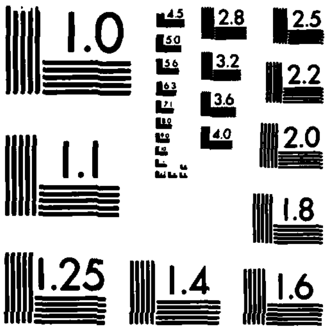

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WF6. (2:50)

FOURIER TRANSFORM RAMAN SPECTROSCOPY OF H_2 AND D_2 IN FLAMES

D. E. JENNINGS, A. WEBER, AND J. W. BRAULT

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 lengths 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 cell.[2] Raman scattering of argon-ion laser light was observed with the 1-m Fourier transform spectrometer at Kitt Peak.[3] The observed pure-rotation spectra of H_2 and D_2, and the vibration-rotation spectra of H_2, contain transitions with higher rotational energy than had been possible to observe previously at room temperature. The transitions in H_2 extended to J=9-7 and those in D_2 extended to J=12-10. The rotation-vibration coefficients will be re-examined taking the new transitions into account.

---

[1] R. F. Knacke and E. T. Young, Ap. J. (Letters) 249, L65 (1981).

[2] Cell provided by R. A. Hill. See R. A. Hill, A. J. Mulac, and C. E. Hackett, Appl. Opt. 16, 2004 (1977).

[3] The 1-m FTS is a facility of the National Solar Observatory, National Optical Astronomy Observatories, operated by the Association of Universities for Research in Astronomy, Inc. under a grant from the National Science Foundation.

Address of Jennings: Planetary Systems Branch, Code 693, NASA/Goddard Space Flight Center, Greenbelt, MD 20771.
Address of Weber: National Bureau of Standards, Washington, DC 20234.
Address of Brault: National Solar Observatory, 950 North Cherry Avenue, P.O. Box 26732, Tucson, AZ 85726.

WF7. (3:15)

THE SPECTRUM OF OCS IN THE 1975-2140 cm^{-1} REGION

N. HUNT, S.C. FOSTER, J.W.C. JOHNS, AND A.R.W. McKELLAR

We have recorded the spectrum of carbonyl sulphide in the region of the ν_1 band with near Doppler-limited resolution (0.0024 cm^{-1} unapodized) using a Bomem DA3.002 spectrometer. The OCS sample had natural isotopic abundances, and a 15 cm absorption path was used. Sixteen bands were analyzed, including the following five bands for the first time at high resolution:

$^{16}O^{13}C^{32}S$	10^00-00^00	2009.2285 cm^{-1}
$^{16}O^{13}C^{32}S$	11^10-01^10	2002.4274 cm^{-1}
$^{18}O^{12}C^{32}S$	10^00-00^00	2026.1470 cm^{-1}
$^{16}O^{12}C^{32}S$	04^00-00^00	2104.8280 cm^{-1}
$^{16}O^{12}C^{32}S$	05^10-01^10	2115.1689 cm^{-1}

As pointed out previously,[1] OCS is an excellent calibrant for tunable infrared lasers because it is relatively easy to obtain and handle, it exhibits strong regularly spaced lines with abundant weaker structure to aid in location, it does not exhibit hyperfine structure, and each band can be well-represented by relatively few parameters. Our results should be helpful for diode laser calibration in the 5 μm region.

---

[1] J.S. Wells, F.R. Petersen, and A.G. Maki, Appl. Opt. 18, 3567 (1979).

Address of Hunt, Foster, Johns and McKellar: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

WF8. (3:27)

HIGH RESOLUTION INFRARED SPECTRUM OF CYANOGEN

A. WEBER, W. J. LAFFERTY, AND W. B. OLSON

New measurements of the IR spectrum of C_2N_2 were obtained with the NBS BOMEM DA3.002 Fourier transform spectrometer equipped with a 20m White cell. The spectra of the $\nu_1+\nu_5^1$, $\nu_3+\nu_4^1$, and $\nu_1-\nu_5^1$ combination and difference bands were recorded 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 accompained by numerous hot bands which complicate the assignment process. The ν_3 band system was also recorded yielding new measurements superceding those reported earlier [1]. The ν_3 band of the $^{13}C^{12}CN_2$ isotope, present in the gas in natural abundance, was also observed. Results of the analysis of the $\nu_1-\nu_5^1$ band system will be presented.

---

[1] A. Weber, W. J. Lafferty, and W. B. Olson, paper RE5, Thirty Ninth Symposium on Molecular Spectroscopy, The Ohio State University, June 1984.

Address of Weber, Lafferty, and Olson: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899

WF9. (3:44)

INTENSITIES AND SELF-BROADENINGS IN HF AND HCl

A. S. PINE AND A. FRIED

Precision linestrengths and self-broadened lineshapes in the fundamental bands of HF and HCl at T=295 K have been measured with a high-resolution difference-frequency laser spectrometer. The intensity measurements were carried out under low-pressure, Doppler-limited conditions with high-purity samples yielding accurate integrated band strengths (S_v^I = 390(4), 118(1), 38(1) cm^{-2} atm^{-1}), transition moments ($|\langle\mu_v\rangle|$ = 0.0998(5), 0.0730(5), 0.0731(5) Debye), and linear Herman-Wallis factors (c_1 = -0.0521(2), -0.0256(1), -0.0253(2)) for HF, $H^{35}Cl$ and $H^{37}Cl$ respectively. The self-broadening measurements were made for pressures less than ~200 Torr to minimize polymerization. Lineshape profiles incorporating collisional narrowing effects were least-squares fit to the data in order to extract the broadening coefficients and diffusion constants for these gases.

Address of Pine: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.
Address of Fried: Gas and Particulate Science Division, National Bureau of Standards, Gaithersburg, MD 20899.

WF10. (4:01)

HIGH PRECISION INTENSITY AND BROADENING PARAMETER MEASUREMENTS BY A STEP BY STEP F. T. CONTROLLED DIODE LASER

A. VALENTIN, HENRY, Ch. NICOLAS, A. MANTZ

High signal to noise ratios in the monochromatic emission for a diode laser generally permit rather precise measurements of line intensities. Line width determinations and broadening parameter measurements with diodes require very precise knowledge of the laser frequency. Significant improvements in measurement of width and broadening parameters can be realized by frequency locking the diode laser emission frequency to several points within the profile of the spectral line being measured.

In this work a portion of the diode laser beam is sent through the Paris Longpath Fourier transform interferometer where the diode emission is locked to the Fourier transform lamb dip stabilized fringe system by controlling the polarization current through the diode. As the interferometer steps through optical path differences the diode laser emission frequency is tuned also.

Elementary step sizes in these experiments correspond to a path difference $\lambda/8 = 632.8/8$ or 79.1 nm which allows for several tens of sample points over a line profile. Each sample point has a frequency precision better than 10^{-5} in wavenumber units.

With such precision the "Doppler - Fizeau Width" of a line is known with a precision better than 10^{-2}. Results in N_2O ν_3 and $\nu_2 + \nu_3 - \nu_3$ bands will be given as an illustration of the method described here.

Address of Valentin, Henry and Nicolas: Laboratoire de Spectronomie Moléculaire - Université Pierre et Marie Curie - Tour 13 - 4 Place Jussieu - 75005 Paris, France

Address of Mantz: Laser Analytics - 25 Wiggins Avenue - Bedford, MA. 01730 U.S.A.

WF11. (4:18)

LINE STRENGTHS AND WIDTHS IN THE ν_3-FUNDAMENTAL OF N_2O

P. VARANASI, J. PODOLSKE, M. LOEWENSTEIN, AND T. BLACKBURN

Using a tunable diode laser spectrometer and the sweep integration technique, we have measured the strengths and N_2-broadened half-widths of a few lines in the P-branch of the ν_3 fundamental of N_2O. The strength measurements at 297K are consistent with the value 1198 cm^{-2} atm^{-1} for the strength of the ν_3-fundamental and 1338 cm^{-2} atm^{-1} for the combined strength of the fundamental and the "hot bands". Our line width data are in excellent agreement with the recently reported FTS data of Lacome et al[1].

---

[1] N. Lacome, A. Levy and G. Guelachvili, Appl. Optics, 23, 425 (1984)

Address of Varanasi: Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York 11794-2300
Address of Podolske, Loewenstein and Blackburn: Atmospheric Experiments Branch, NASA Ames Research Center, Moffett Field, California 94035

WF12. (4:30)

TDL MEASUREMENTS OF N_2 AND H_2 BROADENING OF C_2H_2

W. L. CHIN AND W. E. BLASS

Measurements of nitrogen and hydrogen broadening of acetylene in the 14μm, region have been carried out using our swept frequency TDL system. Observations have been made for a number of hot bands as well as $\nu_4 + \nu_5$. In addition, preliminary intensity measurements have been carried out for a number of C_2H_2 transitions.

Typical sweep rates are on the order of 6 cm^{-1}/sec at an 100Hz repetition rate. Our synchronized 100 Hz aperature modulation system will be described.

Address of Chin and Blass: Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200

WF13. (4:42)

TUNABLE DIODE LASER MEASUREMENTS OF N_2- AND AIR-BROADENED HALFWIDTHS: LINES OF $^{12}C_2H_2$, H_2O, HDO, AND H_2O_2 IN THE 1250-1380-cm^{-1} REGION

V. MALATHY DEVI, B. D. SIDNEY, C. P. RINSLAND, M. A. H. SMITH, D. C. BENNER, AND B. FRIDOVICH

Two tunable diode lasers have been used to measure room temperature Lorentz halfwidths for a number of lines of $^{12}C_2H_2$, H_2O, HDO, and H_2O_2 in the 1250-1380-cm^{-1} region. Both N_2- and air-broadened halfwidths have been determined for 29 lines in the P and R branches of the $(\nu_4 + \nu_5)^0$ combination band of $^{12}C_2H_2$. The measured N_2-broadened widths agree within 3% with values obtained previously for a few lines using the same technique.[1] The air-broadened halfwidths are observed to always be less than the N_2 widths and, on average, we find $\gamma_0(\text{air}) = 0.97\ \gamma_0(N_2)$. N_2- and air-broadened halfwidths have also been derived for a number of lines in the ν_2 bands of H_2O and HDO. These values will be compared with previously published results. Dry air has been added to a 50% pure sample of H_2O_2 to determine air-broadened widths for a number of lines in the ν_6 band.

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[1] J. R. Podolske, M. Loewenstein, and P. Varanasi, J. Mol. Spectrosc. 107, 241-249 (1984).

Address of Malathy Devi and Benner: Physics Department, College of William & Mary, Williamsburg VA 23185.
Address of Sidney: NASA Langley Research Center, Mail Stop 283, Hampton, VA 23665
Address of Rinsland and Smith: NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665.
Address of Fridovich: NOAA/NESDIS, FOB #4, E/RA 22, Washington, DC 20233.

WG1. (1:30)

GENERATION OF TUNABLE LASER SIDEBANDS IN THE FAR-INFRARED REGION

H. M. PICKETT, J. FARHOOMAND, G. A. BLAKE, M. A. FRERKING AND E. A. COHEN

Continuously tunable laser sidebands have been generated by mixing radiation from an optically pumped far infrared (FIR) molecular laser beyond 3000 GHz with that from millimeter-wave klystrons in a Schottky-barrier diode. An enhancement in conversion efficiency over similar systems reported previously is obtained by using a Michelson interferometer to separate the sidebands from the carrier and by placing the Schottky diode in an open structure corner cube mount. With 4 mW of laser power at 693 and 762 GHz the sideband power was measured to be 10μW. This is at least an order of magnitude better than the previously reported results. At higher frequencies, 22 mW of 1627 GHz laser power produced about 7.5μW of sideband output while 3mW of 1839 GHz laser power generated about 200 nW of sideband radiation. The lower efficiency at the higher frequencies is due primarily to the mismatch between the laser radiation and the fixed-length diode antenna. Spectral lines have been observed up to 3200 GHz. The molecular absorbtion signals are easily seen using either video or lock-in detection techniques. The combination of various lines from FIR lasers, the continuous tunability of klystrons, and the high efficiency of this system promises nearly complete coverage of the entire submillimeter and far-infrared regime, and provides a powerful tool for spectroscopic measurements. Some of these recent measurements to provide frequency calibration throughout the region will be described.

Address for Pickett, Cohen, Farhoomand and Frerking: Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109 USA
Address for Blake: Department of Chemistry, California Institute of Technology, Pasadena, California 91125 USA

WG2. (1:47)

MEASUREMENT OF ABSOLUTE ABSORPTION AND LINESHAPE OF CO AT 115 GHz

W. G. READ, K. W. HILLIG II, E. A. COHEN AND H. M. PICKETT

The self broadened lineshape of CO was measured using a microwave spectrometer incorporating a Fabry-Perot cavity as the absorption cell. To a high degree of approximation the absolute absorption is proportional to the change in cavity $\underline{Q}$ between an empty and a pressurized cell. Preliminary results for CO measured at 29.2 torr at 295K yield a self-broadening coefficient of 3.57(7) MHz/torr, peak absorption coefficient of $2.91(7)\times10^{-4}$ cm^{-1}, and an integrated intensity of $1.02(1)\times10^{-5}$ nm^2 MHz. This is in good agreement with the theoretical value of 1.016×10^{-5} nm^2 MHz. Results for H_2O broadened by nitrogen and O_2 self-broadening will be discussed.

Address for Read, Cohen and Pickett: Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109 USA
Address for Hillig: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109 USA

WG3. (2:04)

DIRECT MEASUREMENT OF THE FUNDAMENTAL ROTATIONAL TRANSITIONS OF THE OH RADICAL AND AMMONIA BY LASER SIDEBAND SPECTROSCOPY

G. A. BLAKE, J. FARHOOMAND, AND H. M. PICKETT

We report for the first time the direct (zero-field) spectra of rotational transitions of the OH radical in its $\Omega = 3/2$ and $1/2$ states at 3036, 2509.9 and 1834.7 GHz using a recently developed far-infrared laser sideband spectrometer. These measurements have verified and refined the predictions of previous LMR work, thereby confirming the far-infrared detection of interstellar OH. We have also measured several lines of ammonia in the region from 1 to 3 THz. Comparison will be made between the experimental frequencies and predictions based on high resolution infrared spectra. The increased accuracy of these direct measurements will be useful to future astronomical and atmospheric studies of these important transitions.

Address of Blake: Department of Chemistry, California Institute of Technology Pasadena, California 91125, USA
Address of Farhoomand and Pickett: Jet Propulsion Laboratory, California Institute of Technology 4800 Oak Grove Dr., Pasadena, California 91109, USA

WG4. (2:21)

THE EXCITATION MECHANISM OF THE HCN FIR LASER

DAVID D. SKATRUD AND FRANK C. DE LUCIA

The post-discharge decay rates of vibrational state populations in a gated cw HCN FIR discharge laser have been measured by millimeter wave rotational absorption techniques. The data, in conjunction with the results of our earlier work on a cw HCN laser[1], provide a detailed map of the important energy flow pathways in the laser. This makes possible, for the first time, the construction and verification of a simple model for the cw HCN laser excitation and inversion mechanisms. In addition, these data provide the requisite information for the quantification of this model. The resulting predictions, which were obtained with essentially no free parameters, are in excellent agreement with our extensive data set and a substantial body of work reported in the literature.

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[1] David D. Skatrud and Frank C. De Lucia, Appl. Phys. B35, 179-193 (1984).

Address of Skatrud and De Lucia: Department of Physics, Duke University, Durham, North Carolina 27706.

WG5. (2:38)

SMALL OPTICALLY PUMPED FAR INFRARED LASERS

HENRY EVERITT AND FRANK C. DE LUCIA

The operating parameters of small optically pumped FIR lasers at relatively high pressures have been investigated. In these studies typical dimensions for the Far Infrared Laser are 2mm in radius by 5cm in length. For the 1.2μ $^{13}CH_3F$ laser, pressures to a few Torr were used. It is shown that in these lasers the maximum pressure for oscillation is a strong function of CO_2 laser pump power. These results will be compared with the parameters derived from our earlier studies of rotational and vibrational collisional processes in $^{13}CH_3F$. $^{12}CH_3F$ and CH_3OH have also been studied.

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WG6. (3:10)

PULSED MICROWAVE FOURIER TRANSFORM SPECTROSCOPY OF SPHERICAL TOPS IN GROUND AND EXCITED VIBRATIONAL STATES

A. BAUDER, M. OLDANI, A. G. ROBIETTE, M. LOETE, J. P. CHAMPION, G. PIERRE, AND J. C. HILICO

Pulsed Fourier transform spectroscopy over the range of 8-18 GHz is shown to be an extremely useful method for the study of the rotational spectra of tetrahedral molecules. Rotational transitions were observed between all symmetry species allowed by centrifugal distortion in the ground vibrational state of SiH_4. The set of the tensorial centrifugal distortion constants was fitted up to the eighth order from 45 newly measured transition frequencies combined with data from other sources. In addition, rotational and rovibrational transitions of CD_4 and SiH_4 in the ν_2/ν_4 dyade were assigned and measured for the first time. They were analyzed together with the data from high resolution Fourier transform infrared spectra.

Address of Bauder and Oldani: Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, CH-8092 Zürich, Switzerland.
Address of Robiette: Oxford University Computing Service, 13 Banbury Road, Oxford OX2 6NN, England.
Address of Loëte, Champion, Pierre, and Hilico: Laboratoire de Spectronomie Moléculaire de l'Université de Dijon, 6 Boulevard Gabriel, F-21000 Dijon, France.

WG7. (3:25)

PURE ROTATIONAL SPECTRA OF ASYMMETRICALLY DEUTERATED BENZENES OBSERVED BY PULSED MICROWAVE FOURIER TRANSFORM SPECTROSCOPY

M. OLDANI, T.-K. HA, AND A. BAUDER

R- and Q-branch rotational transitions of ortho- and meta-benzene-d_2 have been assigned over the 8-18 GHz range. Rotational constants and centrifugal distortion constants were fitted to the measured transition frequencies. The coordinates of the hydrogen nucleus were calculated in different ways from moments of inertia and their differences with respect to parent and monodeuterated species. The individual results are affected differently by zero-point vibrational effects.

The deuterium quadrupole splitting of the $1_{01}-0_{00}$ transition at 8073 MHz has been resolved. The measured coupling constant is compared to results from NMR measurements in nematic solvents and to results from ab initio calculations.

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WG8. (3:40)

MICROWAVE SPECTRUM OF METHYL HYDRODISULFIDE

M. TYBLEWSKI, T.-K. HA, AND A. BAUDER

The rotational spectrum of methyl hydrodisulfide is typical of a rigid asymmetric top in contrast to the microwave spectrum of methyl hydroperoxide. Transitions for all three dipole selection rules were assigned and measured. The internal rotation barriers for the SH group are high as shown by the absence of splittings and shifts due to non-rigidity. This fact is further supported by ab initio calculations of selected conformations. The internal rotation of the methyl group give rise to small splittings of the rotational transitions with higher J. The analysis of the rotational spectrum of methyl deuterodisulfide provided a reliable value of 88° for the CSSH dihedral angle.

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WG9. (3:58)

ROTATIONAL ENERGY LEVELS AND PRESSURE BROADENING OF $^{12}CH_3F$ IN ITS GROUND AND $\nu3$ EXCITED VIBRATIONAL STATES

RICHARD L. CROWNOVER, DAVID D. SKATRUD AND FRANK C. DE LUCIA

The rotational spectrum of $^{12}CH_3F$ in its ground and $\nu3$ excited vibrational states has been investigated in the millimeter and submillimeter spectral region. In addition, pressure broadening has been studied for a number of transitions in both states. The J=12-11, K=2, $\nu3$ transition that is the basis of the well known FIR laser has been observed both in absorption and emission. The absorption measurement and the results of the spectroscopic analysis of the $\nu3$ state give the frequency of this laser transition to very high accuracy. This represents the frequency of this laser unbiased by either pump offset or cavity pulling effects.

Address of Crownover, Skatrud and De Lucia: Department of Physics, Duke University, Durham, North Carolina 27706.

WG10. (4:15)

TIME RESOLVED ROTATIONAL RELAXATION IN $^{13}CH_3F$

RODNEY I. McCORMICK, DAVID D. SKATRUD AND FRANK C. DE LUCIA

Rotational relaxation has been studied in the excited vibrational state of optically pumped $^{13}CH_3F$ by means of millimeterwave spectroscopy. The excitation is provided by a Q-switched CO_2 laser whose pulse width is less than 1 μsec. We have previously reported the results of a cw study[1] of this system in which a rate equation model was used to calculate collisional transition probabilities. The results of these studies will be compared.

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[1] W.H. Matteson and F.C. De Lucia, IEEE J. Quant. Electronics QE-19, 1284 (1983).

Address of McCormick, Skatrud and De Lucia: Department of Physics, Duke University, Durham, North Carolina 27706.

WG11. (4:32)

THE DISTORTION MOMENT ROTATIONAL SPECTRUM OF AsD_3 AND THE ROTATIONAL SPECTRA OF AsH_2D AND AsD_2H

G.A. McRAE, M. WONG, M.C.L. GERRY AND I. OZIER

This talk examines the rotational spectra of the deuterated arsines. In the first instance we shall look at forbidden centrifugal distortion transitions of AsD_3. Fourteen Q branch transitions, with peak absorption coefficients on the order of 10^{-11} cm^{-1}, in the frequency range 13.0 to 14.3 GHz and with J in the range 8 to 24 have been measured and assigned. The assignment was based on the experimentally observed quadrupole splitting and on the goodness of a global fit that included both the distortion spectrum reported here, and previously measured allowed transitions.

For the partially deuterated forms, an analysis of a large number of allowed hyperfine split lines is examined. The frequencies of all these transitions ranged from 9 to 300 GHz., for J's up to 16.

A harmonic force field, r_z structure and equilibrium structure for arsine will also be presented.

Address of McRae[1] and Gerry: Dept. of Chemistry, University of British Columbia, Vancouver, Canada

Address of Wong[2] and Ozier: Dept. of Physics, University of British Columbia, Vancouver, Canada

Present Addresses: 1) Jet Propulsion Laboratory, Pasadena, California 91109 USA
2) Canada Center for Remote Sensing, Ottawa, Ontario, Canada

WG12. (4:49)

Internal Rotation in Simple, Unsaturated Thiols and Alcohols

C. Plant and J.N. Macdonald

The results of a study of internal rotation in the compounds XCH = CHSH and XCH = CHOH, X = CN, H, CH_3 and F, using a combination of the methods of microwave spectroscopy and ab-initio molecular orbital calculations will be described. Quite extensive relaxation of the framework of these molecules during the internal rotation of the OH or SH fragments has been identified and the significant influence of the substituent, X, on the internal rotation potential functions established.

Address of Plant and Macdonald Department of Chemistry, University College of North Wales, Bangor, Gwynedd, North Wales, U.K.

WG13. (5:01)

PRESSURE BROADENING OF MM-WAVE OZONE LINES BY ATMOSPHERIC GASES

BRIAN J. CONNOR AND H.E. RADFORD

Pressure broadened linewidths of the 4_{13}-4_{04}, 6_{15}-6_{06}, $14_{3\,11}$-$15_{2\,14}$, and $28_{5\,23}$-$29_{4\,26}$ rotational transitions of ozone have been measured, for the foreign gases N_2 and O_2, over a pressure range of 200-1000 m Torr. The temperature dependence of the broadening has been measured, for the 4_{13}-4_{04} and 6_{15}-6_{06} transitions, over the range 195-320 K.

The air-broadened linewidth, of the 6_{15}-6_{06} transition, was measured at 294 K, and is readily calculated, for other temperatures and transitions, from the N_2 and O_2 results.

The results are compared with recent theoretical calculations and also with previous measurements, where these are available.

These measurements have direct application to the interpretation of observations of microwave emission of middle atmosphere ozone. Mixing ratios of ozone, inferred from such observations, are as much as 15% less using the present results than those inferred using previously available values. The results also serve as reference points for theoretical linewidth calculations applicable from the microwave to the infrared spectral regions.

Address of Connor and Radford: Center for Astrophysics, 60 Garden St., Cambridge, MA 02138

WH1. (1:30)

ELECTRONIC ENERGY LEVELS IN LONG POLYENES: $S_2 \leftarrow S_0$ EMISSION IN ALL-TRANS-1,3,5,7,9,11,13-TETRADECAHEPTAENE

R. CHRISTENSEN, L. MCLAUGHLIN, AND S. SMITH

Absorption, fluorescence, and fluorescence excitation spectra of all-trans-1,3,5,7,9,11,13-tetradecaheptaene have been obtained in room temperature solutions and 77K glasses. The heptaene, unlike shorter fluorescent polyenes, does not exhibit the characteristic gap between the origins of absorption ($1^1A_g^- \rightarrow 1^1B_u^+$) and emission. Excitation spectra and solvent shift studies lead to the assignment of two distinct emisisons, $S_2 \rightarrow S_0$ ($1^1B_u^+ \rightarrow 1^1A_g^-$) and $S_1 \rightarrow S_0$ ($2^1A_g^- \rightarrow 1^1A_g^-$), with the ratio of S_2 to S_1 emission increasing with the S_2-S_1 energy gap. Extrapolation of room temperature solution data gives a gas phase S_2-S_1 difference of 8400 cm^{-1}. Tetradecaheptaene's "anomalous" $S_2 \rightarrow S_0$ emission, the first observed for a linearly conjugated system, is compared to similar violations of Kasha's Rule by azulene and other molecules. Solvent and substituent effects on the S_2 and S_1 emissions also will be discussed.

Address: Department of Chemistry, Bowdoin College, Brunswick, Maine 04011

WH2. (1:42)

RYDBERG TRANSITIONS IN POLYENES: 1,3,5-HEXATRIENES

R. McDIARMID, AND A. SABLJIĆ

The lower Rydberg spectra of cis- and trans-hexatrienes were studied by optical and two and three photon resonant multiphoton ionization spectroscopies. The different selection rules appropriate to the different symmetry groups of the two geometric isomers were exploited to enable the two active 3p-Rydberg transitions to be assigned. The $\delta = 0.46$ Rydberg transition has been previously assigned as arising from a promotion to the out-of-plane 3p-Rydberg orbital.[1] The $\delta = 0.54$ transition is now assigned as arising from a promotion to the in-plane, perpendicular 3p-Rydberg orbital. Evidence is observed for Rydberg-valence mixing. The applicability of Fourier transformation techniques to the RMPI data will be presented.

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[1] D. H. Parker, S. J. Sheng, and M. A. El-Sayed, J. Chem. Phys. 65, 5534 (1976).

Address of McDiarmid: Bldg. 2, Rm. B1-07, National Institutes of Health, Bethesda, Md. 20205
Address of Sabljić: Institute Rudjer Bošković, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia.

WH3. (1:59)

APPLICABILITY OF RESONANT TWO PHOTON IONIZATION IN SUPERSONIC BEAMS TO HALOGENATED AROMATIC HYDROCARBONS

R. TEMBREULL AND D. M. LUBMAN

This work investigates problems encountered in the application of one color resonant two-photoionization as an ionization source in supersonic beam mass spectroscopy. Of particular interest is the fact that photons of one color may not provide sufficient energy to cause ionization even when the laser source is tuned to an excited vibronic molecular state. We have therefore correlated trends in ionization potential with molecular structure for simple systems, specifically, halogenated aniline, phenol and toluene derivatives and mono- and disubstituted benzenes. In the case of para-substituted compounds where there is little substituent group interaction ionization occurs efficiently at the $S_0 \rightarrow S_1$ origin, provided ultrafast processes are not active as in the case of iodo substituted benzenes. Many ortho compounds, however, are found not to ionize efficiently. This is probably due to a combination of coulombic and steric interactions which result in an increase in ionization potential. These types of effects have been qualitatively related to the electron releasing and withdrawing properties of the substituent groups thereby allowing reasonable predictions to be made regarding those types of substituted benzenes which can be probed with R2PI.

Address of Tembreull and Lubman: Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

WH4. (2:11)

THE LASER PHOTOELECTRON SPECTRUM OF GAS PHASE p-DIFLUOROBENZENE

E. SEKRETA, K. S. VISWANATHAN, AND J. P. REILLY

Gas phase p-difluorobenzene (PDFB) has been ionized from several vibronic levels of the excited $^1B_{2u}$ electronic state via two photon, two color laser ionization. Kinetic energy analysis of the ejected photoelectrons indicates that ions are generated in their ground electronic state. The vibrational state distribution is dependent on the vibronic level from which ionization occurs.

Analysis of vibrational structure in the photoelectron spectra identifies seven vibrational frequencies of the PDFB cation. In many cases band intensities reflect the presence of Fermi resonance which exists in the $^1B_{2u}$ state. Results also indicate that the ion is slightly nonplanar in its equilibrium geometry.

When PDFB is ionized from high vibronic levels of the $^1B_{2u}$ state ($E_{vib} > 1600$ cm^{-1}), congestion occurs in the photoelectron spectra. This is interpreted as being due to severe vibrational state mixing which exists in the $^1B_{2u}$ state. This effect is also observed in a similar experiment when ionizing from vibronic levels of the $^1B_{2u}$ electronic state of benzene.

Address of Sekreta, Viswanathan and Reilly: Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

WH5. (2:28)

HIGH RESOLUTION PULSED LASER OPTOGALVANIC SPECTROSCOPY OF RYDBERG STATES IN XENON IN RF DISCHARGE

D. KUMAR, L. KLASINC, P. L. CLANCY, R. V. NAUMAN, AND S. P. MCGLYNN

High resolution Laser Optogalvanic (LOG) spectra of xenon in an rf discharge (~30MHz) have been studied using a flash-lamp pumped tunable dye laser. Signals were normalized before averaging, on a pulse-by-pulse basis, and the effective duty-cycle was forced towards unity in order to obtain smooth spectra even at low pulse-repetition rates.

Excellent LOG signals were obtained when the pick-up coil was displaced relative to the rf electrodes and when a transverse optical excitation was imposed in the region between the pick-up coil and the rf electrode. In addition, this arrangement produces signals of the same polarity. The spectra observed with laser excitation between 13,900 - 17,000cm^{-1} display several rydberg series that originate from various excited states of the 5d configuration.

Spectroscopic analysis is presented and broadening of rydberg levels below the first ionization limit is discussed.

Address: Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803

WH6. (2:45)

PULSED LASER OPTOGALVANIC SPECTROSCOPY OF NITROGEN IN RF DISCHARGE

D. KUMAR, L. KLASINC, P. L. CLANCY, R. V. NAUMAN, AND S. P. MCGLYNN

The Laser Optogalvanic (LOG) spectra of nitrogen (N_2) have been studied using a flash-lamp pumped tunable dye laser. Signals were normalized before averaging on a pulse-by-pulse basis, and the effective duty cycle was forced towards unity in order to obtain smooth high resolution spectra even at low pulse repetition rates.

Excellent LOG signals were obtained when the pick-up coil was situated below the rf electrodes and when transverse optical excitation was imposed between the pick-up coil and the lower rf electrode. In contrast to LOG signals obtained with CW lasers using axial exectation, which produces both positive and negative signals, our technique produces signals which do not change polarity. The spectra were observed with laser excitation between 15,600-17,000cm^{-1} and with nitrogen flowing through the discharge cell. Spectral analysis will be presented.

Address: Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803

WH7. (3:15)

VERSATILE MULTIPLE MODULATION SCHEME FOR TWO-BEAM LASER SPECTROSCOPY

P. ANFINRUD AND W. S. STRUVE

Multiple modulation techniques afford shot noise-limited detection sensitivity for two-beam laser spectroscopy. Single side-band (SSB) detection of the sum or difference frequency offers the advantage of response linearity over amplitude modulation (AM) detection, but requires frequency synthesis techniques to ensure phase-locking of the signal carrier frequency to the detector reference frequency.

We report here an inexpensive SSB detection scheme which provides continuous tunability of both modulation frequencies (limited only by frequency roll-off in the optical modulators). This enables the use of multiple modulation with lasers (e.g. cavity-dumped systems) whose repetition rates are too low for use with previously reported modulation frequencies.

Address: Department of Chemistry and Ames Laboratory - USDOE, Iowa State University, Ames, Iowa 50011.

WH8. (3:27)

FOUR-PHOTON LINE-STRENGTH AND SELECTION RULES OVER SYMMETRIC-TOP MOLECULES AND TIME-REVERSAL INVARIANCE, Y.-N. CHIU

Angular momentum and irreducible tensor methods[1] are used to elucidate the selection rules for a four-photon transition in symmetric-top molecules. The form of the eighty-one (3^4) radiative transition operators between electronic states of different irreducible representations in the molecular point groups will be derived. The concomitant line strength over N and K states as well as special selection rules such as those for $K = 0$, $\Delta K = 0$, etc. will also be obtained, using the symmetry and angular momenta of the transition operators. For four-photon scattering between degenerate states, the special spin-selection rule for the permutational symmetry of the degenerate-state self products will be explained from the view point of time-reversal invariance.

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[1] Y.-N. Chiu, J. Chem. Phys. 45, 2969 (1966); 52, 3641, 4950 (1970).

Address of Chiu: Department of Chemistry, The Catholic University of America, Washington, D. C. 20064

WH9. (3:44)

SOME NEW BANDS OF THE $\tilde{A}\ {}^2A' - \tilde{X}\ {}^2A''$ SYSTEM OF HNCN AND DNCN

BARBARA SWEETING, D. A. RAMSAY, AND C. WELDON MATHEWS

Initial data is now available for two new bands of the $\tilde{A} - \tilde{X}$ transition of HNCN and DNCN initially identified by Herzberg and Warsop[1]. The location of the bands, along with their similarity to the known 0-0 band, lead to the establishment of an upper state bending frequency (497 cm^{-1}) and an upper state stretching frequency (1130 cm^{-1}) for the DNCN molecule. Present data also permit a measurement of the $(A-\bar{E})$ values of DNCN based on resolved K-structure, and experiments are currently underway to provide more extensive data at higher resolution.

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[1] G. Herzberg and P. A. Warsop, Can. J. Phys. 41, 286-298 (1963).

Address of Sweeting and Mathews: Department of Chemistry, The Ohio State University, 140 West 18th Avenue, Columbus, Ohio 43210
Address of Ramsay: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

WH10. (3:56)

"A STUDY OF FLAME SPECIES USING THE COHERENT ANTI-STOKES RAMAN SCATTERING TECHNIQUE"

T. HAW, W.Y. CHEUNG, G.C. BAUMANN, D. CHIU, AND L.E. HARRIS

The technique of Coherent Anti-Stokes Raman Scattering (CARS) has been applied to a study of molecular species present in CH_4/N_2O, H_2/O_2 and nitramine propellant flames. The coherent nature of this technique facilitates the detection of the CARS signal with minimal interference from the pump beams. It offers orders of magnitude higher sensitivity over that of spontaneous Raman, and often allows spectra to be obtained within seconds.

While the present work concentrates on the diagnostic aspect of this method, its application to high resolution spectroscopy cannot be over-looked. The laboratory flame environment leads to the observation of hot bands of many species, such as N_2, N_2O and CH_4. Spectral regions of 1260-2400 cm^{-1} and 3650-4200 cm^{-1} have been investigated. Of particular interest is the observation of rotational S-transitions and vibrational Q-lines of the H_2 molecule. At a flame temperature of 2800K, Q-lines have been observed for $J \leq 11$ in the (1,0) band and for $J \leq 9$ in the (2,1) band. Line positions compare favorably with those calculated from constants derived from the $B' \Sigma u^+ - X'\Sigma g^+$ and $C' \pi u - X' \Sigma g^+$ bands of H_2.(1)

---

[1] I. Dabrowski, Can. J. Phys. 62, 1639 (1984).

Address of Haw and Cheung: Geo-Centers Inc., Newton, Mass.
(Contract Nos. - DAAK10-810266, DAAK10-810265).
Address of Baumann: NRC Research Associate, c/o ARDC, Dover, New Jersey.
Address of Chiu and Harris: ARDC, Dover, New Jersey.

WH11. (4:13)

LASER SPECTROSCOPY OF SiF_2 AND CHEMILUMINESCENCE IN REACTIONS WITH FLUORINE ATOMS AND MOLECULES

A.C. STANTON, A. FREEDMAN, J. WORMHOUDT, AND P.P. GASPAR

The SiF_2 radical is an important intermediate in the plasma etching of silicon in fluorocarbon plasmas, a widely used semiconductor device fabrication process. We report tunable dye laser fluorescence and tunable diode laser infrared absorption spectra of SiF_2, taken as part of a program of development of laser diagnostics for such processes.

We also used these diagnostics in a fast flow reactor to measure the kinetics of SiF_2[2] reactions with F and F_2. The chemiluminescence observed during plasma etching has been attributed to these reactions,[1] although some doubt remains.[2] The similarity in activation engergies for the emission and etching has been used as deciding evidence in a detailed model of the etching process. We will present results on the chemiluminescent spectrum from the reaction of F and F_2 with SiF_2 formed from two different sources, SiF_4 passed over hot Si, and thermal decomposition of Si_2F_6.

---

[1] J.A. Mucha, D.L. Flamm, and V.M. Donnelly, J. Appl. Phys. 53, 4553 (1982).

[2] H.F. Winters and F.A. Houle, J. Appl. Phys. 54, 1218 (1983)

[3] J.A. Mucha, V.M. Donnelly, and D.L. Flamm, J. Phys. Chem. 85, 3529 (1981)

Address of Stanton, Freedman, and Wormhoudt: Aerodyne Research, Inc., 45 Manning Road
Billerica, MA 01821
Address of Gaspar: Department of Chemistry, Washington University, St. Louis, MO 83130

WH12. (4:20)

MOLECULAR GEOMETRY AND PREDISSOCIATION TIMES IN THE $\tilde{A}^1A''$ ELECTRONIC STATE OF HCN AND DCN

A. MEENAKSHI AND K. K. INNES

Merging of the vibrational structures of the $\tilde{A}$ and $\tilde{B}$ electronic states of HCN and DCN into a single $\tilde{A}^1A''$ state[1], and new measurements of rotational fine structure between 1600 and 1950 Å, have made it possible to attempt refinement of the molecular geometry in the $\tilde{A}$ state; an attempt based on rotational constants of HCN, DCN, $D^{13}CN$ and $DC^{15}N$ will be described. The fine structure is mostly predissociated so that the rotational constants were determined by computer simulation of K_0^1 sub-band contours; in the simulation process it was convenient to measure and analyze also the line-widths of unblended lines in each simulated K_0^1 sub-band. It was then straight forward to estimate $\tilde{A}$-state lifetimes of the DCN's and their variations with vibrational quantum numbers. These lifetimes range from 120 to 0.4 ps; they will be compared with recently published[2], directly measured lifetimes for lower vibrational levels of the $\tilde{A}$-states of HCN and DCN.

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[1] G. A. Bickel and K. K. Innes, Can. J. Phys. 62, 1763-1774 (1984).

[2] Y. C. Hsu, M. A. Smith, and S. C. Wallace, Chem. Phys. Letters 111, 219-225 (1984).

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13901

WH13. (4:37)

DOPPLER-LIMITED DYE LASER EXCITATION SPECTROSCOPY OF HCCl:
THE $\tilde{A}\ ^1A''(010)-\tilde{X}\ ^1A'(000)$ VIBRONIC BAND

J. C. PETERSEN

The chloromethylene radical, HCCl, was first observed in the gas phase by Merer and Travis[1]. They found that the molecule in the excited state is "straightened" by vibration and that the (010) level is below the barrier to linearity. The (010)-(000) band around 13150 cm^{-1} has been observed with Doppler - limited resolution of 0.03 cm^{-1} using a CW dye laser. The HCCl molecule was generated by a reaction of discharged CF_4 with CH_3Cl. A rotational analysis will be presented.

[1] A. J. Merer and D. N. Travis, Can. J. Phys. 44 525 (1966)

Address: Herzberg Institute of Astrophysics, National
Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

WH14. (4:49)

ASSIGNMENT OF THE SCHUSTER BAND OF AMMONIA

JAMES K. G. WATSON

The Schuster band observed in emission from discharges through ammonia[1-3] is a broad diffuse feature with maxima at 5672 and 5639 Å. The corresponding band from ND_3 discharges shows resolved rotational structure [3,4] with a Q head at 5803 Å. It is shown here from its wavenumber, structure and isotope shift that this band can be assigned to the 2^1_1 band of the electronic transition $\tilde{C}'\,^1A_1' \rightarrow \tilde{A}\,^1A_2''$ of the ammonia molecule NH_3. The assignment of this band[3,4] as a transition of the ammonium radical NH_4 was mainly based on the occurrence of three intermediate bands[2-4] for isotopic mixtures of NH_3 and ND_3. It appears that one of these bands is an extraneous band of a mixed H-D species that unfortunately produces a very misleading spectrum in isotopic mixtures.

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[1] A. Schuster, Rep. Brit. Assoc. 38 (1872).

[2] H. Schüler, A. Michel, and A.E. Grün, Z. Naturforsch. A 10, 1-3 (1955).

[3] G. Herzberg, Faraday Discuss. Roy. Soc. Chem. 71, 165-173 (1981).

[4] G. Herzberg and J.T. Hougen, J. Mol. Spectrosc. 97, 430-440 (1983).

Address of Watson: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

WH15. (4:56)

ROTATIONAL STRUCTURE OF VIBRATIONAL BANDS IN THE SCHÜLER SYSTEM $3p^2F_2 - 3s^2A_1$ OF ND_4

JAMES K. G. WATSON

The main Schüler band[1,2] of the ammonium radical NH_4 has been assigned[3,4] as the 0-0 band of the transition $3p^2F_2 - 3s^2A_1$. In the vibrational structure of this system, bands near the positions expected for the 1-0 and 0-1 transitions of the bending vibrations $\nu_2(e)$ and $\nu_4(f_2)$ have been observed with partially resolved rotational structure[5]. The theory of the rotational structure of these bands, allowing for the doublet splitting and the Jahn-Teller effect in the upper state, will be discussed and compared with observed spectra for the ND_4 isotope.

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[1] H. Schüler, A. Michel, and A.E. Grün, Z. Naturforsch. A 10, 1-3 (1955).
[2] G. Herzberg, Faraday Discuss. Roy. Soc. Chem. 71, 165-173 (1981).
[3] J.K.G. Watson, J. Mol. Spectrosc. 107, 124-132 (1984).
[4] F. Alberti, K.P. Huber, and J.K.G. Watson, J. Mol. Spectrosc. 107, 133-143 (1984).
[5] G. Herzberg, J. Astrophys. Astron. 5, 131-138 (1984).

Address of Watson: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

RA1. (8:40)

TIME RESOLVED STUDIES OR REACTION DYNAMICS IN SOLUTION

G. R. FLEMING, AND S. H. COURTNEY

Photochemical isomerization provides an accessible model system with which to test theories of activated barrier crossing in solution. These theories lie at the heart of descriptions of chemical reaction dynamics in solution. Picosecond time resolved studies of stilbene in alkane solution, in the dense gas and in the isolated jet-cooled molecule reveal many of the qualitative features predicted by theory. Quantitative description of the isomerization dynamics will require an understanding of the influence of the vibrational modes (other than the reaction coordinate) on the frictional forces felt by the isomering molecule, and on the vibrational energy flows within the molecule. The comparison of isolated and solvated molecules reveals the importance of intramolecular vibrational redistribution on the isomerization dynamics.

Address: Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637.

RA2. (9:15)

SPECTROSCOPIC STUDIES OF CHAIN EXTENSION IN LONG CHAIN MOLECULES AND POLYMERS

JOHN F. RABOLT

Fourier Transform IR and Raman spectroscopy are non-destructive techniques which can provide specific structural information about conformational disorder in molecules. Changes in bandshapes and shifts in frequency provide a unique insight into the nature of molecular motion occurring prior to structural phase transitions. These techniques have recently been used to characterize the melting process in Langmuir-Blodgett monolayers of fatty acid molecules and submicron thin films of poly (di n-alkylsilanes). In addition, studies of short chain semifluorinated n-alkane oligomers indicate that only partial molecular disorder is introduced upon melting, suggesting that rigid rod-like segments continue to exist in the liquid state.

Address: IBM San Jose Research Laboratory, San Jose, CA 95193

RA'3. (10:34)

OBSERVATION OF THE v=20-17 BAND OF HD^+, EXPERIMENTAL EVIDENCE FOR AN ASYMMETRIC ELECTRON DISTRIBUTION

ALAN CARRINGTON AND RICHARD A. KENNEDY

The v=20-17 band of the HD^+ molecular ion has been observed using a sequential two-photon photodissociation technique. The experiments were performed by Doppler - tuning a fast beam of HD^+ into resonance with the fixed frequency of a collinear carbon dioxide laser beam. Doppler limited linewidths of about 5 MHz were achieved, permitting the partial resolution of the hyperfine structure.

The two lowest dissociation limits of HD^+, $H^+ + D(1s)$ and $H(1s) + D^+$, are separated by about 30 cm^{-1}, the former being the lower limit. For very high vibrational levels, such as v=20 which lies about 100 cm^{-1} below the $H^+ + D(1s)$ limit, the electron density about the deuteron is expected to be higher than about the proton. This suggestion is confirmed by simulations of the hyperfine structure for transitions of the 20-17 band.

Address of Carrington: Physical Chemistry Laboratory, South Parks Road, Oxford University, Oxford, U.K.
Address of Kennedy: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

RA'4. (10:49)

FLUORESCENCE EXCITATION SPECTROSCOPY OF MOLECULAR IONS IN A FREE JET EXPANSION

RICHARD A KENNEDY, YEN-CHU HSU, L. DI MAURO, AND TERRY A. MILLER

Two-photon photoionization is used to generate radical cations from molecules seeded into a free jet expansion of an inert carrier gas. Subsequent absorption by the cations of the output of a tunable dye laser is detected by monitoring the total fluorescence from the beam. The ions are found to be extensively cooled through collisions with the carrier gas. Clusters between the ions and carrier gas atoms have also been observed. The development of an instrument to identify these clusters by mass spectroscopy, and characterize them by laser spectroscopy will be described. The investigation of such clusters provides a means of probing ion-molecule interactions.

Address of Hsu, Kennedy, and Miller: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210
Address of Di Mauro: Department of Physics, Louisiana State University, Baton Rouge, Louisiana 70803

RA'5. (11:06)

DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF $HCNH^+$:OBSERVATION OF SEVERAL ISOTOPIC SPECIES AND HOT BANDS

T. AMANO and KEIICHI TANAKA

The ν_1 and ν_2 fundamental bands of $HCNH^+$ and the ν_1 fundamental band of $DCNH^+$ were recently observed in the laboratory by difference frequency laser spectroscopy. In the present work, measurements of the hot bands($\nu_1+\nu_4 \leftarrow \nu_4$, $\nu_1+\nu_5 \leftarrow \nu_5$) have been made possible with a hollow-cathode discharge cell. Also the measurement has been extended to the isotopic species, $HCND^+$ and $H^{13}CNH^+$. By combining these data with the already existing data on the normal species and $DCNH^+$, the r_s structure of this ion has been obtained with the aid of the first moment condition. The bond lengths are in very good agreement with the calculated values(r_e) by Botschwina.

Address of Amano: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

Address of Tanaka: Department of Chemistry, Kyushu University, Fukuoka

RA'6. (11:18)

DIFFERENCE FREQUENCY LASER SPECTROSCOPY OF THE ν_1 FUNDAMENTAL BAND OF $HOCO^+$

T. AMANO and KEIICHI TANAKA

We have demonstrated an enhancement of ion signals by about an order of magnitude in the 3 μm region obtained with a hollow-cathode discharge cell. This enabled us to detect the ν_1 fundamental band of $HOCO^+$, and we have already reported a preliminary result. Since then more lines have been observed, and now we report a more detailed analysis of the ν_1 band of this ion.

The $HOCO^+$ ions were generated in a modulated discharge through a flowing gas mixture of CO_2(20 mTorr) and H_2(250 mTorr). More than 500 lines of both the a-type and b-type transitions were observed in the range of 3300-3400 cm^{-1}. The molecular constants were determined for the ground and excited states. The molecular structure of this ion is similar to that of HNCO. The large centrifugal distortion constants (Δ_K, Φ_K,---) may be an indication of the quasi-linearity of this ion.

Address of Amano: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

Address of Tanaka: Department of Chemistry, Kyushu University, Fukuoka 812, Japan.

RA'7. (11:30)

DETECTION OF PROTONATED N_2O BY DIFFERENCE FREQUENCY LASER SPECTROSCOPY

T. AMANO

There seems to have been no spectroscopic work made on protonated N_2O, although it is well-known in mass spectrometry. Protonated N_2O is generated in a hollow-cathode discharge through a mixture of N_2O(15 mTorr) and H_2(300 mTorr) in a fast flow system. An infrared absorption band around 3330 cm^{-1} has been observed, and at the present stage about 150 a-type R- and P-branch lines and a number of b-type Q-branch lines(K_a=0←1 and K_a=1←0) have been assigned. Two questions arise about the molecular structure. Which isomer, the O-protonated form or the N-protonated form, is more stable? Is it a well-bent molecule or a quasi-linear molecule? A tentative analysis suggests that the species detected here is an O-protonated form($HONN^+$), and that it is a well-bent molecule similar to HN_3.

Address: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

RA'8. (11:45)

"TRANSIT" BROADENING OF ION SPECTRAL LINES

Takeshi Oka

In the usual spectroscopy we study molecules which are moving with uniform velocities between collisions. In ion spectroscopy, however, the molecular ions are constantly accelerated and thus velocity changes linearly with time. Because of the Doppler shift, a molecule is in resonance with the applied radiation for only a limited time which, under certain conditions, is shorter than the collision interval. This brings about a new source of uncertainty broadening which has not been considered before. As in the case of Dicke narrowing,[1] this effect depends on the wavelength of radiation. In the infrared region such "transit" broadening is calculated to be significant and comparable to pressure broadening.

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[1] R.H. Dicke, Phys. Rev. 89, 472 (1953).

Address: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago.

RB1. (10:00)

THE EFFECT OF AN AVOIDED CROSSING ON THE O_2 SCHUMANN-RUNGE PHOTODISSOCIATION CONTINUUM

Bruce C. Garrett, Lynn T. Redmon, and Michael J. Redmon

Photodissociative excitation of O_2 from the ground $X^3\Sigma_g^-$ state to the $B^3\Sigma_g^-$ state (the Schumann-Runge transition) yields an absorption spectrum which is asymmetric and exhibits fine structure. Ab initio potential energy curves for the B state and the X-to-B dipole transition moment have been calculated as a function of internuclear distance. An avoided crossing between the B and E states occurs near the X-state equilibrium geometry. This causes the B-state to have a shoulder in its repulsive wall and the X-to-B dipole transition moment to change rapidly in this region. We find that this shoulder in the B-state potential curve is responsible for both the asymmetry of df/dE and the fine structure at high transition energies. The rapid variation in the X-to-B dipole transition moment does not affect the absorption spectrum, as evidenced by the validity of the Franck-Condon approximation for this transition.

This research was supported by the Air Force Wright Aeronautical Laboratories, Aero Propulsion Laboratory, Air Force Systems Command, United States Air Force, under contract no. F33615-82-C-2241.

Address: Chemical Dynamics Corporation, 1550 West Henderson Road, Columbus, Ohio 43220

RB2. (10:12)

ELECTRONIC AND GEOMETRIC STRUCTURE OF ScH^+ AND ScH_2^+

AILEEN E. ALVARADO-SWAISGOOD AND JAMES F. HARRISON

The electronic and geometric structures of ScH^+ and ScH_2^+ have been studied using ab-initio MCSCF and CI tychniques. The calculated bond length, D_e and ω_e for the first three states of ScH^+ are:

State	$R_e(A^o)$	D_e(kcal/mol)	$\omega_e(cm^{-1})$
$X^2\Delta$	1.83	50.7	1559
$^2\pi$	1.83	45.6	1492
$^2\Sigma^+$	1.79	44.6	1479

We calculate the bond length in $(^1A_1)$ ScH_2^+ to be 1.75A^o with an H-Sc-H angle of 105.6^o. While ScH_2^+ is strongly bound relative to $ScH^+ + H$, preliminary results suggest the reaction $ScH_2^+ \rightarrow Sc^+ + H_2$ is isoergic. In addition to comparing these results to experiment we will present an analysis of the bonding.

Address: Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322

RB3. (10:24)

ELECTRONIC AND GEOMETRIC STRUCTURES OF THE CHROMIUM CATIONS CrH^+, $CrCH_3^+$, $CrCH_2^+$ AND $CrCH^+$

AILEEN E. ALVARADO-SWAISGOOD, JOHN ALLISON AND JAMES F. HARRISON

The electronic and geometric structures of the chromium cations CrH^+, $CrCH_3^+$, $CrCH_2^+$ and $CrCH^+$ have been studied using ab-initio MCSCF and CI techniques. The calculated Cr-C bond lengths and bond energies (in kcal/mol) are

Molecule	(State	Cr-C(A°)	bond energy
CrH^+	$(^5\Sigma^+)$	1.63	25.1
$CrCH_3^+$	$(^5A_1)$	2.14	18.0
$CrCH_2^+$	$(^6B_1)$	2.06	21.0
$CrCH_2^+$	$(^4B_1)$	1.92	38.7
$CrCH^+$	$(^3\Sigma^-)$	1.77	53.7 *

* relative to $CH(^2\pi)$ and $Cr^+(^6S)$.

These data suggest that CH_3, CH_2 and CH form single, double (in the $^4B_1$ state) and triple bonds respectively with Cr^+. In addition to comparing these data with the available experimental values we will present a detailed analysis of the role played in the bonding by the Cr^+ 4s and 3dσ electrons.

Address: Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322.

RB4. (10:41)

STRUCTURES AND SPECTROSCOPIC CONSTANTS OF SOME PROTONATED GROUP VIA MOLECULES

P. G. JASIEN AND W. J. STEVENS

We report the results of theoretical calculations of the proton affinities and structures of several series of molecules containing Group VIA atoms. The series studied included CX, OCX, XCX, and H_2CX where X=O, S, Se, Te. In those cases where multiple protonation sites are available, a definitive assignment of the most stable site was determined. Excellent agreement with the experimentally measured proton affinities is found in most cases. These results indicate that the intuitive chemical trend which one would expect as one moves down a column of the periodic table is upheld, with a large change on going from the first to the second row. In addition, we report calculated vibrational frequencies for both neutral and protonated systems.

Calculations were performed at both the SCF and CIDS levels with full geometry optimizations at the SCF level. Basis sets were of at least DZ+P quality. The effect of the chemically unimportant core electrons in these systems was represented by compact effective potentials.

Address of Jasien and Stevens: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.

RB5. (10:58)

AB INITIO CALCULATIONS ON SMALL BE CLUSTERS

M.M. MARINO AND W.C. ERMLER

Restricted Hartree-Fock, unrestricted Hartree-Fock and Moller-Plesset perturbation theory calculations are reported for clusters of three through seven Be atoms. Ground and low-lying excited states for all symmetrical nuclear configurations of each cluster are discussed. The ground state electronic configuration and geometry for the clusters of three, four and five atoms reported by Whiteside et al.[1] are reproduced in most cases. Be-Be internuclear separations for the lowest electronic state of each cluster range from 1.9Å to 2.2Å.

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[1] R.A. Whiteside, R. Krishnan, J.A. Pople, M. Krogh-Jespersen, and P. von Rague Schleyer, J. Comput. Chem. 1, 307 (1980).

Address of Marino and Ermler: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030.

RB6. (11:15)

AB INITIO CALCULATIONS ON LARGE BE CLUSTERS

W.C. ERMLER, C.W. KERN, R.M. PITZER, AND N.W. WINTER

Closed and open shell self-consistent field calculations are reported for clusters of 13, 19, 21, 33, and 39 Be atoms. Geometrical arrangements correspond to the second through sixth coordination spheres of a central Be atom with internuclear separations all derived from the lattice constants of the bulk metal (a=2.2866Å, c=3.5833Å). Each cluster possesses D_{3h} point group symmetry. Nineteen electronic states of Be_{13} and six states of Be_{13}^+ are discussed. Electric field gradients, nuclear electron potentials, second moments, and orbital energy diagrams are given for each cluster. The convergence of properties having origin at the central Be atom as a function of cluster size is slow and is not yet achieved with the inclusion of the sixth coordination sphere.

Address of Ermler: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030.
Address of Kern: Chemistry Division, National Science Foundation, Washington, D.C. 20550.
Address of Pitzer: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.
Address of Winter: Chemistry Division, Lawrence Livermore National Laboratory, Livermore, California 94550

RB7. (11:32)

ELECTRONIC STRUCTURE OF POLYHEDRAL ALKANES

Carol A. Scamehorn, Susan M. Hermiller, and Russell M. Pitzer

The electronic structure and bond distances for the three polyhedral alkanes, tetrahedrane (C_4H_4), cubane (C_8H_8), and dodecahedrane ($C_{20}H_{20}$) have been studied with Hartree-Fock-Roothaan molecular orbital wavefunctions. Contracted Gaussian (9s5p/4s), [4s3p/2s] basis sets of atomic orbitals were used. These are somewhat superior to double-zeta or split-valence basis sets, but lack polarization functions. Full use was made of the symmetry of the molecules.

Both the CC and CH bond distances were optimized. As expected, C_4H_4 has the shortest CC bond distances, and C_8H_8 has the longest. The CH bond distances varied also, but to a somewhat smaller extent.

All (vertical) valence ionization potentials were computed, both from the neutral molecule orbital energies (Koopmans' Theorem) and from calculations of all of the positive-ion energies (ΔSCF method). Relaxation energies of 0.1 eV were typical. The majority of the ion states are spatially degenerate, and the resulting Jahn-Teller splittings should have a large effect on the photoelectron spectra.

Address of Scamehorn, Hermiller, and Pitzer: The Ohio State University, Department of Chemistry, 140 West 18th Avenue, Columbus, Ohio 43210.

RB8. (11:49)

MOLECULAR PHOTOIONIZATION CROSS SECTIONS BY THE COMPLEX BASIS FUNCTION METHOD

C. W. McCurdy, C-H Yu, and R. M. Pitzer

The photoionization cross section can be expressed as a particular matrix element of the resolvent of the molecular electronic Hamiltonian,

$$\sigma(\omega) = -\frac{4\pi\omega}{c}\lim_{\varepsilon\to 0}\mathrm{Im}\langle\Psi_0|\mu(E_0+\omega-H+i\varepsilon)^{-1}\,\mu|\Psi_0\rangle$$

where Ψ_0 is the ground state electronic wave function, μ is the dipole operator, ω is the frequency, c is the speed of light, and atomic units are employed. We have shown recently that by using a mixture of real and complex Gaussian basis functions to form a matrix representation of the Hamiltonian it is possible to use this expression to compute molecular photoionization cross sections from the results of a matrix diagonalization.[1] The working expression of this approach has the form

$$\lim\,(f,(E-H+i\varepsilon)^{-1}f) = \sum_{i=1}^{N}\frac{(f,\Phi_i)(\Phi_i,f)}{E-E_i}$$

where $f = \mu\Psi_0$, and the functions Φ_i, and associated eigenvalues, E_i, are from a finite-basis diagonalization of the Hamiltonian. This procedure is based on a variational principle for the matrix element from which the photoionization cross section is calculated, and can be applied in the presence of coupling between ionization channels. The interference between resonance features and the electron-ion scattering background is naturally incorporated by this method, and the method is easily implemented for polyatomic systems. Results are reported for K-shell and valence shell ionization of N_2 at the static-exchange level. Excellent agreement with most other calculations is obtained, especially those which explicitly compute the photoionization cross section from the electron-ion scattering wavefunction. The complex basis function technique is particularly successful in reproducing resonance features in these cross sections.

A discussion of the variational behavior of the amplitude is given, and it is shown that the variational nature of these calculations provides a useful computational diagnostic.

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[1] T. N. Rescigno and C. W. McCurdy, Phys. Rev. A **31**, 624 (1985).

Address of McCurdy, Yu, and Pitzer: Department of Chemistry, Ohio State University, Columbus, Ohio 43210.

RB9. (Last Minute Addition) (12:06)

THEORETICAL STUDY OF THE N_3 MOLECULE

S.R. LANGHOFF

The electronic structure of the N_3 molecule is studied at the complete-active space self-consistent field and multi-reference singles plus doubles configuration-interaction levels. The vertical excitation spectrum is delineated for both the doublet and quartet manifolds.

Preliminary results will be presented for the N_2+N exchange reaction occuring on the lowest quartet surface. The importance of this study to the phenomenon of non-equilibrium air chemistry occuring in the hot shock layers of the proposed aero-assisted transfer vehicle (AOTV) will be discussed.

Address of Langhoff: Mail Stop 230-3, NASA/Ames Research Center,
Moffett Field, CA. 94035.

RC1. (10:00)

VIBRATIONS OF A BORON ICOSAHEDRON*

C.L. BECKEL AND J.P. VAUGHAN

The B_{12} icosahedron is a unit of α- and β- boron crystals and of a number of boron molecules. Group properties of a regular icosahedron are well-known, but the normal modes have not been pictured heretofore. There are eight distinct frequencies for the thirty modes with 1-fold, 3-fold, 4-fold. and 5-fold degeneracies. Oscillations are here pictured in terms of three equilibrium icosahedral descriptions: one involves two parallel regular pentagons and two polar atoms, a second has two polar triangles and an equatorial puckered hexagon, while the third consists of six pairs of atoms on opposite faces of a cube. The visualizations should prove useful in application to heat conduction, substituent atom localization, and polaron electrical conduction in boron-rich borides.

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*Supported by the Center for High Technology Materials, University of New Mexico and the Jet Propulsion Laboratory sponsored by NASA.

Address: Department of Physics and Astronomy, The University of New Mexico, Albuquerque, NM 87131

RC2. (10:17)

EFFECT OF COLLISIONS ON LINE PROFILES IN THE QUADRUPOLE AND RAMAN SPECTRA OF MOLECULAR HYDROGEN*

J. D. KELLEY AND S. L. BRAGG

An extensive set of data now exists for line shifts and collision broadening coefficients in molecular hydrogen. Collision broadening has been studied in the pure rotational Raman spectrum,[1] the fundamental (1-0) Raman[2] and quadrupole[3] vibrational bands, and in the 2-0 to 4-0 quadrupole overtone bands.[3] Line-shift measurements in the fundamental and first overtone bands are also available.[2-4] This data set allows decomposition of the total broadening coefficient into separate contributions from collisional effects on the rotational and vibrational degrees of freedom. Moreover, comparison of line shift and broadening coefficients permits subdivision of the vibrational effects into collisional phase-shift and near-resonant vibrational energy exchange processes. The various collisional contributions to the broadening and line-shift coefficients will be discussed, with emphasis on the relationship of these quantities to the H_2-H_2 intermolecular potential.

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*This work is sponsored by the McDonnell Douglas Independent Research and Development Program.

[1] For example, R. A. J. Keiser, J. R. Lombardi, K. D. Van Den Hout, B. C. Sanctuary, and H. F. P. Knaap, Physica 76, 585 (1974).

[2] For example, J. R. Murray and A. Javan, J. Mol. Spectrosc. 29, 502 (1969).

[3] S. L. Bragg, Thesis (Washington University, 1981).

[4] C. Chackerian, Jr. and L. P. Giver, J. Mol. Spectrosc. 58, 339 (1975).

Address of Kelley and Bragg: McDonnell Douglas Research Laboratories, P.O. Box 516, St. Louis, Missouri, 63166.

RC3. (10:39)

THE INFRARED SPECTRUM OF LIQUID HD

M.J. CLOUTER AND A.R.W. McKELLAR

We have measured the spectrum of liquid hydrogen deuteride in the region of the fundamental band (3500-4000 cm^{-1}) and of the pure rotational R(0) transition (80-90 cm^{-1}). The experiments were performed using a Bomem DA3.002 spectrometer and a 1 cm path; the liquid was followed along the gas-liquid coexistence line from 18 to 35 °K. Of special interest are the effects of interference between the permanent dipole moment of HD and the transient dipoles induced during molecular collisions. These effects have been studied in the gas phase,[1] and were also observed in solid HD.[2] We observe a pronounced anomalous dispersion (Fano) lineshape for the $R_1(0)$ transition around 3715 cm^{-1}, whereas the $R_0(0)$ transition around 88 cm^{-1} is only slightly asymmetric. A weak, sharp absorption feature was observed in the liquid at 18 °K on the high frequency side of the broader Fano $R_1(0)$ profile; this feature resembles the beginning of the stronger sharp feature observed in the solid.[2]

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[1] N.H. Rich et al., Can. J. Phys. 61, 1648 (1983); 62, 1665, 1673 (1984).

[2] A. Crane and H.P. Gush, Can. J. Phys. 44, 373 (1966).

Address of Clouter and McKellar: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

Permanent Address of Clouter: Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada.

RC4. (10:56)

RESONANCE ROTATIONAL RAMAN SCATTERING AS A PROBE OF SUBPICOSECOND PHOTODISSOCIATION DYNAMICS

L.D. ZIEGLER

The pattern of resonance enhanced rotational ($\Delta J \neq 0$) Raman transitions may be analyzed to reveal subpicosecond excited rovibronic lifetimes.[1] This novel scattering technique is applied to determine quantum specific photodissociation rates in small molecules. UV Raman excitation at 212.8 nm, 208 nm, 217 nm, 204 nm, 200 nm, and 192 nm is produced by mixing and anti-stokes Raman shifting Nd:YAG frequencies. Excited state lifetimes of 0.15, .096, and .056 picoseconds ($\pm$10%) are found for the V_2' = 1, 2, 3 levels of the $A \leftarrow X$ transition in NH_3 using this resonance rotational Raman scattering technique. The quantum yield for photodissociation is unity at these excitation wavelengths. Results for ND_3 and NO_2 will also be presented.

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[1] L.D. Ziegler, P.B. Kelly and B. Hudson, J. Chem. Phys. 81, 6399 (1984).

Address of Ziegler: Department of Chemistry, Northeastern University, Boston, MA 02115.

RC5. (11:13)

NEAR-CRITICAL RAMAN SPECTRA OF N_2, CO_2, H_2

M. J. CLOUTER, H. KIEFTE, AND C. G. DEACON

High resolution vibrational Raman spectra have been obtained for nitrogen, carbon dioxide (ν_1), and parahydrogen, under near-critical conditions. Inhomogeneous broadening of the Q branch profiles is observed in all three cases as the critical point is approached along the critical isochore. Analysis of the spectra reveals new information pertaining to critical fluctuations.

Address of Clouter, Kiefte, and Deacon: Department of Physics, Memorial University, St. John's, Newfoundland, Canada A1B 3X7.

Current address of Clouter: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Canada K1A 0R6.

RC6. (11:30)

CARS SPECTRA OF CO_2 AT DIFFERENT TEMPERATURES
EXPERIMENTAL RESULTS AT 300, 800, 1200, 1500 K AND THEORETICAL SIMULATION

N. PAPINEAU, M. LEFEBVRE AND M. PEALAT

The CARS spectra of natural CO_2 have been recorded over the entire ν_1 and $2\nu_2$ spectral region with a resolution of 0.07 cm^{-1} for different temperatures: 300, 800, 1200 and 1500 K. As a first step, we have studied carefully the spectra at 300 and 800 K. Eleven different bands have been identified in the room temperature spectra whereas 46 vibrational bands appear in the spectrum at 800 K. We have not only assigned the Q branches but also many O and S rotational lines mainly for the first hot bands. A theoretical calculation of the CARS intensities has been performed. For this purpose, the CO_2 wave functions have been calculated taking into account the Fermi resonance as well as the ℓ-type doubling and the Coriolis interaction. In addition, for the simulation of the Q branches, a simple theoretical model describing the motional narrowing phenomenon has been used. Under these conditions, it has been possible to compute theoretical spectra which are in excellent agreement with the experimental ones. Moreover, new experimental values have been determined for the centers of five bands originating from highly excited states of CO_2. Finally, in the spectra at 1200 and 1500 K, we have identified several hot bands which had never been observed before.

Address of Papineau, Lefebvre and Péalat: Office National d'Etudes et de Recherches Aérospatiales, BP 72, 92322 Châtillon Cedex, France.

RC7. (Last Minute Addition) (11:47)

OVERTONE STIMULATED RAMAN PUMPING OF H_2 FROM V = 0 TO V = 2 AND SUBSEQUENT TIME DOMAIN PHOTOACOUSTIC DETECTION OF VIBRATIONAL RELAXATION

J. GELFAND, R.B. MILES, AND T.G. KREUTZ

We report preliminary data showing the first stimulated Raman overtone pumping of a molecule. Using this method we have excited H_2 into the V = 2 vibrational state, followed by time domain photoacoustic detection of the vibrational relaxation. The stimulated Raman pumping is generated with the 1.06μ output of a Nd:YAG laser in combination with 572 nm radiation from a tunable dye laser. The difference in energy of these two is equal to the V = 0 to V = 2 transition in H_2. The laser beams are combined and focused through a 10 cm photoacoustic cell. Subsequent analysis of this data will allow a direct determination of vibration-vibration (V-V) and vibration-translation (V-T) relaxation rates from V = 2 to V = 1 in hydrogen.

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Address of Kreutz: Department of Chemistry, Princeton University, Princeton, New Jersey 08544.

RC8. (Last Minute Addition) (12:04)

HIGH-RESOLUTION COHERENT ANTI-STOKES RAMAN SPECTROSCOPY OF H_2

Anthony M. Toich, David W. Melton, and Won B. Roh

High-resolution Coherent Anti-Stokes Raman Spectroscopy (CARS) has been performed in hydrogen gas using a CW system employing single-mode Ar-ion and ring dye lasers. Accurate measurements of the Raman frequencies and linewidths of the Q(o) through Q(3) transitions of molecular hydrogen have been made at pressures ranging from 0.75 to 40 atm. All four lines exhibit the usual "Dicke narrowing" and pressure broadening. The pressure-broadening and pressure-shift coefficients determined from the data are presented and their implications on diagnostic applications are discussed.

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RE1. (1:30)

THE USE OF EXTENDED PERMUTATION-INVERSION GROUPS FOR CONSTRUCTING HYPERFINE HAMILTONIANS FOR SYMMETRIC TOP INTERNAL ROTOR MOLECULES LIKE $H_3C\text{-}SiH_3$

JON T. HOUGEN

The m-fold extended group $G_{18}^{(m)}$, corresponding to the permutation-inversion group G_{18} derived by Bunker for molecules like $H_3C\text{-}SiH_3$, has been obtained. In this treatment, 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 the extended group it is possible to assign definite symmetry species in an internal-axis-method treatment to top-fixed projections, frame-fixed projections, molecule-fixed projections, and laboratory-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 of known symmetry species and selection rules in the internal-axis-method basis set. Such operators may be useful in treating the selection rule anomalies uncovered in the ingenious molecular beam avoided crossing studies of Meerts and Ozier on molecules like $H_3C\text{-}SiH_3$.

Address of Hougen: Molecular Spectroscopy Division, National Bureau of Standards,
Gaithersburg, MD 20899.

RE2. (1:47)

NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF $NO^-(N_2O)_1$ AND $NO^-(N_2O)_2$

K. H. BOWEN, J. V. COE, J. S. SNODGRASS, C. B. FREIDHOFF, AND K. M. MCHUGH

Negative ion photoelectron spectroscopy (NIPES) involves the kinetic energy analysis of electrons which are photodetached when a mass-selected beam of negative ions is crossed with a fixed-frequency laser beam. This technique has been applied for the first time to negative cluster ions. The species, $NO^-(N_2O)_n$, were generated by placing a biased hot filament very near a supersonic nozzle expansion of N_2O. The NIPES spectra of $NO^-(N_2O)_1$ and $NO^-(N_2O)_2$ are highly structured and resemble that of NO^- except for being successively shifted to lower electron kinetic energies and broadened. The transition corresponding to $NO(X^2\Pi, v'=0) \leftarrow NO^-(X^3\Sigma^-, v''=0)$ is stabilized by 0.221eV and 0.476eV in $NO^-(N_2O)_1$ and $NO^-(N_2O)_2$, respectively. Implications with respect to bonding in negative cluster ions will be discussed.

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RE3. (2:02)

NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF $H^-(NH_3)_1$ AND $H^-(NH_3)_2$

J. T. SNODGRASS, J. V. COE, C. B. FRIEDHOFF, K. M. MCHUGH, AND K. H. BOWEN

The negative ion photoelectron spectra of the cluster ions, $H^-(NH_3)_1$ and $H^-(NH_3)_2$, have been obtained. The negative cluster ions were produced by placing a biased hot filament on the high vacuum side of a nozzle expansion of NH_3. The transition corresponding to the photodetachment of H^- is stabilized by 0.353 eV and 0.702eV in the spectra of $H^-(NH_3)_1$ and H^- $(NH_3)_2$, respectively. In addition to the main peak, both cluster ion spectra exhibit a second smaller peak to the low electron kinetic energy side of the dominant peak, and this is related to the asymetric stretch in ammonia. The present results will be compared to theortical calculations[1] which have recently been performed on $H^-(NH_3)_1$.

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[1] P. Rosmus, et. al., Can. J. Phys. 62, 1323 (1984).

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Baltimore, Maryland 21218

RE4. (2:19)

NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF $NH_2^-(NH_3)_1$ AND $NH_2^-(NH_3)_2$

J. V. COE, J. T. SNODGRASS, K. M. McHUGH, C. B. FREIDHOFF, AND K. H. BOWEN

The negative ion photoelectron spectra of the cluster ions, $NH_2^-(NH_3)_1$ and $NH_2^-(NH_3)_2$, have been obtained. The negative cluster ions were produced by placing a biased filament on the high vacuum side of a nozzle expansion of NH_3. The transitions corresponding to that appearing in the photodetachment spectrum of NH_2^- are stabilized by 0.518 eV and 0.996 eV in the spectra of $NH_2^-(NH_3)_1$ and $NH_2^-(NH_3)_2$, respectively. Just as in $H^-(NH_3)_1$, a second peak at lower electron kinetic energy is observed in the spectrum of $NH_2^-(NH_3)_1$, and this is related to the asymetric stretch of ammonia. Implications of the fact that $NH_2(NH_3)_1$ has a greater electron affinity than $H(NH_3)_1$, even though NH_2 and H have almost the same electron affinities, will be explored.

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RE5. (2:36)

NEGATIVE ION PHOTOELECTRON SPECTROSCOPY OF SeO^-

J. V. COE, J. T. SNODGRASS, C. B. FREIDHOFF, K. M. McHUGH, AND K. H. BOWEN

Negative ion photoelectron spectroscopy (NIPES) involves a kinetic energy analysis of electrons which are photodetached when a mass selected beam of negative ions is crossed with a fixed frequency laser beam. The photodetachment spectra of SeO^- displays transitions from the $X\ ^2\Pi$ state of SeO^- to both the $X^3\Sigma^-$ and $a^1\Delta$ states of SeO. The singlet-triplet splitting of SeO is readily observable since selection rules regarding spin do not apply in the bound to free state process of photodetachment. The electron affinity of SeO and the negative ion potential parameters of SeO^- have been determined.

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RE6. (3:15)

SPECTROSCOPY OF TRYPTOPHAN IN A SUPERSONIC MOLECULAR BEAM

THOMAS R. RIZZO, YOUNG D. PARK, LINDA PETEANU, AND DONALD H. LEVY

We have produced a supersonic molecular beam of tryptophan by using a combination of thermospray and seeded molecular beam techniques. The neutral molecules in the molecular beam were photoionized and the resulting mass spectrum was observed. The mass spectrum indicates that the molecular beam contains single, neutral tryptophan molecules as well as small clusters of tryptophan with one or several solvent molecules. The wavelength dependence of the resonantly enhanced two-photon ion signal of the tryptophan parent reveals sharp spectral features containing progressions in one or more low frequency vibrations.

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RE7.

(3:32)

THE ROTATION-INVERSION SPECTRUM OF $(SO_2)_2$

D.D. Nelson, Jr., G.T. Fraser, and W. Klemperer

The radiofrequency and microwave spectrum of $(SO_2)_2$ has been measured using the molecular beam electric resonance technique. The spectrum is characteristic of an asymmetric top in which the two nonequivalent SO_2 subunits interchange roles through a low frequency (70 kHz) tunnelling motion. The spectroscopic constants obtained for SO_2 dimer are:

$\frac{B+C}{2}$ (MHz)	926.160(2)	Δ_J (MHz)	0.00217(2)
$\frac{B-C}{2}$ (MHz)	22.3207(1)	Δ_{JK} (MHz)	0.0995(1)
$A-\frac{B+C}{2}$ (MHz)	6032.3(6)	δ_{inv} (MHz)	0.070(1)
μ_a (D)	1.4052(13)		

The average distance between the center of masses of the two subunits, R_{CM}, is 3.825(10) Å. The magnitude of the weak bond stretching force constant, k_s, is 0.0264(4) mdynes/Å. The relative orientation of the subunits is not well determined, but is demonstrated to be unlike the orientation of the nearest neighbors in the sulfur dioxide crystal. Furthermore, R_{CM} differs greatly from the nearest neighbor R_{CM} observed in the crystal (4.28 Å).

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RE8.

(3:44)

INFRARED STUDIES OF SEVERAL WEAKLY BOUND COMPLEXES OF NH_3

D.D. Nelson, Jr., G.T. Fraser, A. Charo, G.J. Gerfen, and W. Klemperer

We present the results of infrared spectroscopic studies of several van der Waals complexes of NH_3. These results were obtained with a molecular beam electric resonance spectrometer. Infrared studies of the complexes NH_3-HCCH, NH_3-CO_2, NH_3-N_2O, and NH_3-HCN have been carried out with a line tuneable CO_2 laser. Only for NH_3-HCN were no infrared resonances discovered. Photodissociative transitions are observed in all of the other systems. Band origins for the photodissociative infrared transitions involving the ν_2 umbrella motion of NH_3 were determined for NH_3-HCCH (984.4(9) cm^{-1}), NH_3-CO_2 (987.1(2) cm^{-1}), and NH_3-N_2O (980(2) cm^{-1}). NH_3-HCCH, NH_3-CO_2 and NH_3-N_2O were studied in microwave-infrared double resonance experiments in order to eliminate much of the inhomogeneous broadening present in their infrared spectra and to aid in the rotational assignment of the infrared spectra. Linewidths were determined for NH_3-HCCH (0.15 GHz) and for NH_3-CO_2 (14(6) GHz). An important result of this study is that the dissociation energies of all the complexes studied, except for NH_3-HCN, are established to be less than 990 cm^{-1}, i.e. 2.8 Kcal/mole.

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RE9. (4:06)

Rotational Spectroscopic Studies of Weakly Bound Complexes of NH_3

G.T. Fraser, D.D. Nelson, Jr., G.J. Gerfen and W. Klemperer

Radiofrequency and microwave spectra of NH_3-CO and NH_3-N_2O have been measured using the molecular beam electric resonance technique. For NH_3-N_2O an asymmetrical top spectrum is observed and is complicated by internal rotation of the NH_3 subunit. The rotational constants for the ground internal rotor state are: A=12722.6(8) MHz, B=4083.4(3) MHz, and C=3070.8(3) MHz. NH_3-N_2O is a T-shaped complex with a N---N weak bond length of 3.2 Å. The electric dipole moment component along the a-inertial axis is 1.514(9) D. Attempts are presently underway to determine the height of the threefold barrier to internal rotation. It should be noted that the structurally similar complex, NH_3-CO_2, has no threefold barrier.

The K=0, J=0-1, 1-2 transitions have been observed for NH_3-CO, NH_2D-CO, NHD_2-CO, ND_3-CO, NH_3-^{13}CO. The spectroscopic constants are:

	$\frac{B+C}{2}$ (MHz)	μ_a (D)	eQq^N_{aa} (MHz)
NH_3-CO	3485.757(2)	1.2477(9)	-1.890(7)
NH_3-^{13}CO	3451.684(5)	1.2452(12)	-1.870(15)
NDH_2-CO	3338.235(4)	1.2546(12)	-1.916(12)
ND_2H-CO	3202.303(4)	1.2686(13)	-1.972(11)
ND_3-CO	3078.440(7)	1.2845(15)	-2.028(15)

The observed isotopic dependence of the rotational constants is consistent with a structure which has the nitrogen directed toward the carbon. The spectrum is complicated by non-rigidity and is not completely understood. The structure determined from the K=0 transitions is consistent with the orientation of amine-carbonyl groups observed in organic crystals.

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RE10. (4:23)

ROTATIONAL SPECTRA OF WATER-N_2O AND WATER-CO VAN DER WAALS COMPLEXES

K. I. PETERSON, D. J. YARON, T. A. FISHER AND W. KLEMPERER

In an effort to describe the internal motions of a water molecule in a van der Waals cluster, rotational spectra were obtained for water-N_2O and water-CO using the molecular beam electric resonance technique. The structure of water-N_2O has the oxygen of water bound approximately to the center of N_2O. The following constants were obtained for HDO-N_2O (units of MHz except where noted).

(B+C)/2	3716.869 (20)	Δ_J	0.0271 (30)
(B-C)/2	550.518 (20)	Δ_{JK}	0.155 (16)
A-(B+C)/2	8795.575 (87)	δ_J	0.0150 (35)
μ (Debye)	1.496 (1)	δ_K	0.111 (21)
R_{cm} (A)	2.960 (1)	Δ_K	-0.101 (27)

In the water-CO complex, water is hydrogen bonded to the carbon producing a structure which is very close to linear. As expected for a molecule with an A rotational constant above 300 GHz, only K=0 transitions were observed despite extensive searches for K=1 transitions. The following constants were obtained.

	H_2O-CO	D_2O-CO	HDO-CO
(B+C)/2 (MHz)	2750.487	2617.244	2727.381
D_J (MHz)	------	0.01854	0.01813
μ (Debye)	3.985 (3)	3.952 (1)	3.934 (3)
eqQ_{aa} (kHz)	------	------	230

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RE11. (4:40)

HCl BF_3, A LEWIS ACID - LEWIS ACID VAN DER WAALS COMPLEX

JAMES M. LOBUE, JANE K. RICE, AND STEWART E. NOVICK

The structure of the van der Waals complex HCl BF_3 has been determined by molecular beam electric resonance spectroscopy. The molecule is a near symmetric top with the chlorine atom 3.185 Å from the boron atom and located on the BF_3 three-fold axis. The spectroscopic constants are $(B+C)/2 = 1774.378$ MHz, $D_J = 61.6$ kHz, $eqQ(^{35}Cl) = -19.893$ MHz, $\mu = 0.60$ D. A structural determination will be presented.

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RF1. (1:30)

SUB-DOPPLER LASER-STARK MEASUREMENTS OF HYPERFINE STRUCTURE IN EXCITED VIBRATIONAL STATES OF NH_3

W.H. WEBER

Laser-Stark spectra showing well resolved hyperfine structure on 13 transitions in the ν_4 and $2\nu_2$ bands of $^{14}NH_3$ are obtained and analyzed. Direct least-squares fits of the spectra yield determinations of the nuclear quadrupole coupling constant eqQ in the various states, accurate to about ±1% (40 kHz) in favorable cases. To this accuracy, eqQ is the same in the ground and ν_4 states, but it shows sizable changes in the $2\nu_2$ state, in agreement with the predictions of Spirko.

The data are obtained using a CO laser and two precision Stark cells. One cell, placed inside the laser cavity, is used to Lamb-dip stabilize the laser on an NH_3 transition Stark-tuned into resonance with it. The other cell, placed in an external cavity, is used to record the data. Spectra of isolated lines, fit to a Lorentzian lineshape, show widths of 600 kHz (FWHM), a factor of 250 below the Doppler width. The key parameters needed to obtain such linewidths are the laser frequency stability, which is found to be ±10 kHz for periods of an hour or more, and the homogeneity of the Stark field, which is demonstrated through an analysis of broadening mechanisms to be $\pm1.7 \times 10^{-4}$.

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RF2. (1:47)

ROTATIONAL ASSIGNMENT OF OVERTONE BANDS OF NH_3

K. K. LEHMANN, AND S. COY

Last year at this conference, we reported the development of microwave-detected microwave-optical double resonance. This new technique had given us sufficient sensitivity to make rotational assignments of the NH_3 overtone bands with 3,4,5, and 6 quanta of NH stretch. The spectra are analyzed by combining the MODR signals and their polarization dependence with high quality line positions and intensities from absorption spectra. For $\nu=5$ and $\nu=6$ the spectra were obtained by photoacoustic spectroscopy, and for $\nu=3$ and $\nu=4$ were supplied by Bill Neal and Don Ramsey of the Herzberg Institute. The results of the analyses will be presented.

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Address of Coy: Department of Chemistry, Harvard University, Cambridge, MA 02138.

RF3. (2:04)

The $v_2=2,a \leftarrow v_2=1,s$ SPECTRA OF $^{14}NH_3$ AND $^{15}NH_3$[*]

H. SASADA, R. H. SCHWENDEMAN, G. MAGERL, R. L. POYNTER AND J. S. MARGOLIS

More than 40 vibration-rotation transitions in the $v_2=2,a \leftarrow v_2=1,s$ hot bands of $^{14}NH_3$ and $^{15}NH_3$ have been recorded by using the sidebands on CO_2 laser lines generated in a CdTe crystal by application of an X-band or P-band microwave electric field. The spectra were observed at Doppler-limited resolution and individual lineshapes were fit to a Voigt profile. The experimental accuracy of the center frequencies is better than 0.00003 cm^{-1} in favorable cases.

Hot band transitions have also been recorded for $^{14}NH_3$ at 0.005 cm^{-1} resolution by the Kitt Peak McMath Solar Telescope 1 m interferometer. Similar transitions in $^{15}NH_3$ have been obtained at Michigan State University at 0.01 cm^{-1} resolution by means of a BOMEM Fourier transform spectrometer. Nearly all of the measured frequencies from the Kitt Peak spectra agree with the sideband laser values to better then 0.00007 cm^{-1}. Molecular constants for the $v_2=2,a$ states for both isotopic species will be reported.

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[*] This research was supported by the U.S. National Science Foundation.

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Address of Poynter and Margolis: Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109

RF4. (2:21)

INFRARED-RADIO-FREQUENCY DOUBLE-RESONANCE SPECTROSCOPY OF CF_3I[*]

WAFAA FAWZY AND R. H. SCHWENDEMAN

Approximately 120 pure quadrupole transitions in more than 6 vibrational states in CF_3I have been observed by means of an infrared-radio-frequency double resonance spectrometer operating near 1075 cm^{-1}. Double-resonance spectra were observed for five $^{12}C^{16}O_2$ and three $^{12}C^{18}O_2$ laser lines. The radio frequency source was a 1-500 MHz computer-controlled frequency synthesizer. Although preliminary spectra were recorded with an intra-cavity coaxial cell, the best spectra were obtained with an extra-cavity cell of stripline design. The quadrupole hyperfine structure was calculated by direct diagonalization of the energy matrices. Quadrupole coupling constants obtained for the ground and several excited vibrational states will be compared with previous results obtained by other spectroscopic techniques.

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[*] This research was supported by the U.S. National Science Foundation.

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RF5. (2:38)

INFRARED-MICROWAVE SIDEBAND LASER SPECTROSCOPY OF THE ν_3 AND $2\nu_3 \leftarrow \nu_3$ BANDS OF $^{13}CH_3F$[1]

SANG LEE, R. H. SCHWENDEMAN, AND GOTTFRIED MAGERL

Approximately 350 transitions in the ν_3 band and 80 transitions in the $2\nu_3 \leftarrow \nu_3$ band of $^{13}CH_3F$ have been recorded by means of an infrared-microwave sideband laser spectrometer.[2] The infrared source for the CdTe sideband generator is a Lamb-dip stabilized CO_2 laser. The microwave source is a computer-controlled frequency-stabilized backward wave oscillator operating in the 8-18 GHz region and amplified by a traveling wave tube amplifier. The effect of radiation at the infrared carrier frequency was suppressed by using a polarizer and by chopping the microwave field at 33 kHz. Only the 33 kHz component of the output of the infrared detector was recorded. The sideband generator was operated in the traveling wave mode and the Doppler-limited spectra were recorded in a single pass of a 1-meter cell at pressures ranging from 100 mTorr for the fundamental transitions to 2 Torr for the hot band. The recorded lineshapes were fit to a Gaussian function and the accuracy of the center frequencies is estimated to be better than ±0.00003 cm^{-1} in favorable cases. Nearly all of the transitions have been assigned and the frequencies of non-overlapping lines have been fit to power series in $J(J+1)$ and K^2. Transitions included in the fitting involve J and K values up to $J=47$ and $K=18$ for the fundamental and $J=25$ and $K=10$ for the hot band. The resulting vibration-rotation parameters will be reported.

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[1] This research was supported by the U.S. National Science Foundation.

[2] G. Magerl, W. Schupita, and E. Bonek, IEEE J. Quantum Electron. **QE-18**, 1214 (1982).

Address of Lee and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824
Address of Magerl: Institut für Nachrichtentechnik, Technische Universität Wien, Gusshausstrasse 25, A-1040 Vienna, Austria.

RF6. (2:55)

FOURIER TRANSFORM SPECTRA OF ν_1 BANDS OF HCN AND $3\nu_2$, $2\nu_2 + \nu_6$ and $\nu_3 + \nu_5$ bands of H_2CO

J. I. Choe, T. Tipton, R. Hubbard and S. G. Kukolich

Fourier transform spectra of HCN and H_2CO were obtained using the FTS spectrometer at the National Solar Observatory, at Kitt Peak, Arizona. Samples were contained in a 6 m multipass White Cell and the resolution was 0.01 to 0.02 cm^{-1}. 910 lines of three isotopic species of HCN were obtained in the 3300 cm^{-1} region with an accuracy of approximately 0.0001 cm^{-1}. Spectra were analysed to obtain band origins, rotational constants and ℓ-doubling constants. For H_2CO, asymmetric rotor parameters and band origins were obtained for $3\nu_2$, $2\nu_2 + \nu_6$ and $\nu_3 + \nu_5$ bands. Lines could be fit to a precision of 0.01 cm^{-1} with partial treatment of perturbations. A 432 m optical path length was used for H_2CO measurements.

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Address of Kukolich: Department of Chemistry, University of Arizona, Tucson, AZ 85721.

RF7. (3:20)

ROTATIONAL ANALYSIS OF VINYLSILANE

J. K. McDONALD, J. A. S. SMITH, AND V. F. KALASINSKY

The infrared spectra of gaseous vinylsilane has been recorded at a resolution of .04 cm^{-1}. Several of the vibration bands are sufficiently resolved for partial rotational analysis. The results of the analysis of a coriolis interaction which was observed between the SiH_3 rocks, ν_{12} and ν_{19} will be discussed.

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Address of Smith and Kalasinsky: Department of Physics, Mississippi State University, Mississippi State, Mississippi 39762, USA.

RF8. (3:32)

HIGH RESOLUTION INFRARED SPECTRUM OF NITROSYL CHLORIDE

J. K. McDONALD, J. A. MERRITT, V. F. KALASINSKY*, AND J. R. DURIG*

High resolution FT-IR spectra of nitrosyl chloride, ClNO, has been recorded with a Bomem interferometer. Rotational analysis of the ν_1 and ν_2 bands at 1800 and 596 cm^{-1} has been performed. The higher resolution allowed a better set of rotational constants for the ν_2 band to be obtained than the previously reported values[1].

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*Work partially funded under Battelle Columbus Laboratories Contract DAAG29-81-D-0100.

[1] J. K. McDonald, J. A. Merritt, and J. R. Durig, "Infrared and Raman Spectra of Gaseous and Solid Nitrosyl Chloride", Abstracts, Thirty-Ninth Symposium on Molecular Spectroscopy, Columbus, OH, June 11-15, 1984.

Address of McDonald and Merritt: Research Directorate, US Army Missile Laboratory, US Army Missile Command, ATTN: AMSMI-RRD, Redstone Arsenal, Alabama 35898-5248, USA.
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Address of Durig: College of Science and Mathematics, University of South Carolina, Columbia, South Carolina 29208, USA.

RF9. (3:44)

LOW-FREQUENCY VIBRATIONAL SPECTRA OF THE RING-BENDING AND RING-TWISTING VIBRATIONS OF CYCLOHEXENE.

V. GAINES AND J. LAANE

The vapor-phase far-infrared and low-frequency Raman spectra of cyclohexene have been recorded and analyzed. The observed spectra occur primarily in three regions. The far-infrared spectrum in the 155-170 cm^{-1} region shows a series of bands arising from the ring bending motion, whereas the Raman bands resulting from the ring twisting occur near 275 cm^{-1}. In addition, a number of difference bands between 90 and 120 cm^{-1} were also observed. Both kinetic energy expansion calculations and two-dimensional potential energy surface calculations have been carried out. The results will be compared to those previously reported of similar molecules.

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RF10. (3:56)

FAR-INFRARED SPECTRUM AND RING-PUCKERING VIBRATION OF BICYCLO[3.2.0]HEPT-1-ENE

M. TECKLENBURG, J. R. VILLARREAL, AND J. LAANE

A series of ring-puckering transitions have been observed in the far infrared spectrum of bicyclo[3.2.0]hept-1-ene in the region 30-120 cm^{-1}. A reduced mass calculation has been carried out in order to obtain the kinetic energy expansion, which was in turn used for the one-dimensional potential energy calculation. The results show the molecule to be non-planar with a double-minimum potential energy function similar to that of cyclopentene.

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RF11. (4:08)

τ-DEPENDENCE OF THE VIBRATIONAL ZEROPOINT ENERGY IN THE PARTIALLY DEUTERATED METHYL ALCOHOLS, REVISITED

T. L. CHANG AND C. R. QUADE

The contribution of the zeropoint energy from the 3N - 7 other vibrations to the effective potential energy for internal rotation have been calculated for eight isotopic species of methyl alcohol. The basis of the calculation is the set of force constants determined by Serrallach, Meyer, and Gunthard[1] from infrared analyses. The calculated results for CH_2DOH are $V_1 = 11.93 cm^{-1}$ and $V_2 = 0.17 cm^{-1}$ with $\Delta V_3 < 0.05 cm^{-1}$. These values agree favorably with the experimental results as previously determined by Quade and Suenram[2] from analysis of the microwave torsional-rotational spectra of CH_2DOH.

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1. A Serrallach, R. Meyer, and Hs. H. Gunthard, J. Mol. Spec. 52, 94(1974).
2. C. R. Quade and R. D. Suenram, J. Chem. Phys. 73, 1127(1980); 81, 1054(1984).

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RF12. (4:20)

REDUCTION OF THE VIBRATION-ROTATION-LAM HAMILTONIAN

YUHUA GUAN AND RICHARD QUADE

The vibration-rotation-LAM Hamiltonian requires two independent separation conditions to reduce the Coriolis interaction and the vibration-LAM kinetic energy interaction. In the limit of the LAM approaching a SAM, the effective vibration-rotation Hamiltonian and/or energy must reduce to the usual vibration-rotation Hamiltonian when no internal motion is a LAM. We show how to perform this reduction, especially as it relates to the T- and R-transformations and the normal coordinate transformation.

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RF13. (4:37)

ISOMORPHIC HAMILTONIAN OF ACETYLENE WITH EXCITATION IN LOCAL MODES

G. A. NATANSON

The Hougen-Watson isomorphic Hamiltonian of a linear molecule (1,2) is related to skewed coordinates of a special kind allowing one to treat the linear molecule as a "quasi-diatom". Orientation of the quasi-diatom in space is determined by the vector (3)

$$\underset{\sim}{F} = \sum m_D r^0_{zD} \underset{\sim}{r}_D ,$$

where r^0_{zD} are constants parametrizing a linear equilibrium configuration (2), m_D and $\underset{\sim}{r}_D$ are respectively mass and the radius-vector of the D-th nucleus. Transverse projections of "quasi-electrons perform vibrations with frequencies of bending modes.

The local-mode picture is analogous to the separated-atom model of the hydrogen molecule (4) and the appropriate vibrational coordinates coicide with those introduced by Suzuki and Overend (5). The isomorphic Hamiltonian is derived by means of an imaginary particle in a state with zero angular momentum. The relationship of the derived Hamiltonian to the formalism developed by Pack and Hirschfelder (4) and to the variational procedure recently suggested by Carter and Handy (6) for the nonrotating acetylene molecule is analyzed.

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[1] J.T.Hougen, J.Chem.Phys. 36, 519 (1962).
[2] J.K.G.Watson, Mol.Phys. 19, 465 (1970).
[3] M.N.Adamov and G.A.Natanson, Vestn.Leningr.Univ., No.22, 30 (1970).
[4] R.T.Pack and J.O.Hirschfelder, J.Chem.Phys. 49, 4009 (1968).
[5] I.Suzuki and J.Overend, Spectrochim.Acta 25A, 977 (1969).
[6] S.Carter and N.C.Handy, Mol.Phys. 53, 1033 (1984).

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RF14. (4:49)

VARIATIONAL CALCULATIONS OF ROTATIONAL-VIBRATIONAL ENERGY LEVELS OF WATER FOR DIFFERENT FORCE FIELDS AND GEOMETRIES

B. MAESSEN AND M. WOLFSBERG

Variational calculations of rotational-vibrational energy levels are carried out on H_2O, D_2O, and DHO for $J \leq 10$ within the framework of the Watson Hamiltonian. The basis functions are products of vibrational functions and symmetric top rotor functions, where the vibrational functions diagonalize the rotationless (J=0) Hamiltonian. Calculations for the vibrational rotational states using different force fields and different equilibrium geometries are compared with experimental observations. The importance of vibrational rotational interactions on the energy levels and wavefunctions is demonstrated.

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RF15. (4:59)

ON THE EQUIVALENCE OF INTRAMOLECULAR POTENTIAL EXPANSIONS IN NORMAL AND VALENCE DISPLACEMENT COORDINATES

B. MAESSEN, M. WOLFSBERG, AND L.B. HARDING

The present study presents a numerical test on the equivalence of potential expansions in normal and valence displacement coordinate space by calculating the lower vibrational states in a variational procedure. The calculations are performed for H_2O and they indicate that a fourth order Taylor series expansion in valence coordinates is not well represented by an expansion in normal coordinates which is truncated at fourth order.

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RG1. (1:30)

HYPERFINE SPLITTING OF $2^3\Pi_g$, $3^3\Pi_g$, AND $2^3\Pi_g$-$2^1\Pi_g$ MIXED LEVELS OF Na_2

LI LI AND R. W. FIELD

The hfs of some Na_2 $2^3\Pi_g$, $3^3\Pi_g$, and $2^3\Pi_g$-$2^1\Pi_g$ mixed levels have been observed by OODR fluorescence excitation spectroscopy. Both $2^3\Pi_{1g}$ and $3^3\Pi_{1g}$ levels have no resolved hfs within our OODR excitation resolution. $2^3\Pi_{0g}$ and $3^3\Pi_{0g}$ levels have hfs and their magnetic dipole hf constants are positive. The $2^3\Pi_g$ V= V*-11, J=13,14 levels are perturbed by the $2^1\Pi_g$ V=27 levels of the same J. The OODR excitation lines to these perturbed levels from $A^1\Sigma_u(V'=22)$-$b^3\Pi_{0u}(V'=25)$ J'=13,14 levels have totally resolved hfs. From the intermediate level's hfs, the magnetic dipole hf constants of these $2^3\Pi_g$-$2^1\Pi_g$ mixed levels have been determined and are negtive.

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RG2. (1:47)

STIMULATED EMISSION BASED ON TWO-STEP HYBRID RESONANCE [illegible] $A^1\Sigma_u^+$ OR $B^1\Pi_u$ STATE OF Na_2^*

[illegible] Qin, Z.-G. Wang, K.-C. Zhang and I.-S. Cheng

The first step of the hybrid excitation in the experiment was achieved by using a pulse broadband (~200 Å) dye laser beam through a heat pipe oven. For the total covered pumping wavelength region from 4600 Å to 6800 Å the populated upper electronic state in Na_2 should be either $A^1\Sigma_u$ or $B^1\Pi_u$ state. The excited sodium dimers Na_2^* transfered their energy to sodium atoms Na by near resonance collisions and the Na then would populate up the 3P level from ground state 3S. The Na were consequentely pumped up to 4D, 5D, 5S or 6S level from 3P by using a narrowband dye laser pumped by the same N_2 laser. The infrared stimulated radiation corresponding to the transitions of 4D-4P(2.34 μm), 5D-4P(5.02 μm), 5S-4P(3.42 μm) and 6S-5P(7.52 μm) with cascade stimulated emission from 4P to 4S (2.20 μm) and from 5P to 5S (5.43 μm) were then obtained. Furthermore the dependence of the output energy on the pumping wavelengthes was measured and discussed.

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* Projects Supported by the Science Fund of the Chinese Academy of Sciences.

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RG3. (2:04)

TWO- AND THREE-PHOTON ABSORPTION STUDIES OF THE O_2 MOLECULE

Abha Sur, C.V. Ramana and Steven D. Colson
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Resonance enhanced multiphoton ionization studies in the 275-330 nm region reveal a large number of 2- and 3-photon transitions to previously unknown states. We have analyzed, in detail, four vibrational components of a rotationally resolved electronic transition at 8.2 eV. The vibrational frequency of 1870 cm^{-1} and a rotational constant of 1.68 cm^{-1} suggest that the upper state is the lowest Rydberg state ($3s\sigma$) of O_2. The rotational structure is consistent with an electronic designation of ${}^3\Pi_{0_g^-}$ for this state.

RG4. (2:21)

HIGH RESOLUTION ONE-PHOTON IONIZATION CROSS SECTION OF NO USING THIRD-HARMONIC GENERATION

Paul J. Miller, Peter Chen, and William A. Chupka
Dept. of Chemistry, Yale University, New Haven, CT 06511

The high resolution ($\lesssim 1.5$ cm^{-1}) one-photon ionization cross section of NO is obtained in a section of the vacuum ultraviolet (VUV) region (77200 cm^{-1} to 78600 cm^{-1}). VUV radiation is produced by frequency tripling the output of a pulsed UV dye laser (third-harmonic generation). This provides a tunable VUV source of much narrower bandwidth than can usually be obtained when using conventional continuum lamp or synchrotron radiation sources. Further simplification of rotational congestion is achieved by rotationally cooling the seeded gas sample in a pulsed supersonic jet expansion. The rotationally resolved one-photon ionization spectrum of NO can be compared with a recent theoretical treatment on the competition between photoionization and photodissociation processes in the $np\pi$ Rydberg states above the first ionization potential.[1] Several new features in the spectrum are also observed, and the $ns\sigma(v=2)$ series is extended by two new members.

[1] A. Giusti-Suzor and Ch. Jungen, J. Chem. Phys., 80, 986 (1984).

RG5. (2:38)

MEASUREMENT OF AUTOIONIZATION RATES IN THE NON-PENETRATING 4F STATE OF NO

D.T. Biernacki, E.E. Eyler, Steven D. Colson and William A. Chupka
Yale University

Using a combination of pulsed and cw dye lasers to excite a beam of NO molecules, we have measured autoionization rates for a number of levels in the 4f complex, in the $v=3$ vibrational level. These states lie a few hundred cm^{-1} above the ionization potential for $v=0$, and can ionize only via $\Delta v = -3$. Since previous spectroscopic analyses indicate that the 4f Rydberg electron exhibits essentially no core penetration, one would expect little of the configuration interaction in the core region that normally gives rise to autoionization. Nonetheless, autoionization rates ranging from about 20 psec to 200 psec are observed, with a strong and complicated dependence on core rotation and the projection of L on the rotational axis. The autoionization is probably mediated by the long range interaction of the Rydberg electron with the multipole moments of the NO^+ core, a mechanism recently postulated by Herzberg and Jungen.[1] Analysis of this process is in progress, and it is likely that similar effects occur in the Rydberg states of many molecules, leading to much shorter lifetimes than were previously predicted.

[*] Supported in part by the Research Corporation and the National Science Foundation, grant number PHY-8403324.

[1] G. Herzberg and Ch. Jungen, J. Chem. Phys, 77, 5876 (1982).

RG6. (3:15)

RESONANCE ENHANCED MULTIPHOTON IONIZATION OF FREE RADICALS IN A SUPERSONIC EXPANSION. NEW BANDS AND ROTATIONAL ANALYSIS FOR CH AND CH_2

Peter Chen, Steven D. Colson, William A. Chupka, and Jerome A. Berson
Department of Chemistry, Yale University, New Haven CT

Methine and methylene, produced by UV photolysis of organic precursors in a supersonic expansion, are detected by REMPI. Rotational analysis of the $E \leftarrow X$ system of CH allows positive identification of the previously unassigned upper state as v=2 of the D ${}^2(\Pi_i)$ state. *A complex, rotationally resolved band is tentatively assigned to a previously* unobserved Rydberg transition originating in the ${}^1A_1$ state of methylene. Mechanisms for formation of these radicals are discussed.

RG7. (3:32)

MS-PES MULTIPHOTON IONIZATION STUDIES OF AMMONIA

C.V. Ramana and Steven D. Colson
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We have used resonance-enhanced multiphoton ionization, in conjunction with photoelectron spectroscopy to probe the dynamics of ionization from electronically excited states of NH_3. Energy analysis of the emitted electrons enables us, for the first time, to deconvolute the optically overlapped $\tilde{B}({}^1E'')$ and $\tilde{C}'$ $({}^1A_1')$ states by recording excitation spectra of the respective photoelectron peaks. We have unambiguously assigned the vibrational numbering in the $\tilde{C}$ and $\tilde{C}'$ states, and established an ionization potential of 10.07 eV for NH_3.

RG8. (3:44)

PICOSECOND PHOTOELECTRON STUDIES OF THE EXCITED ELECTRONIC STATES OF AZAAROMATICS

J.B. Pallix and Steven D. Colson
Department of Chemistry, Yale University, New Haven, CT 06511

Multiphoton ionization has been used to obtain photoelectron spectra from different excited electronic states in s-triazine, pyrazine, pyridine and benzene. Photoelectron spectra of s-triazine obtained as a function of wavelength and excitation laser pulsewidth reveal two distinct sets of peaks separated by 0.5 eV. In this 1+2 ionization of s-triazine, the prepared electronic state is the lowest singlet $S_1({}^1E'')$. The higher energy set of peaks in the photelectron spectrum is assigned to the ionization of the S_1 state and the lower to the vibrationally hot T_1 state. Intramolecular vibrational relaxation (IVR) is studied by obtaining the singlet state PES spectra as a function of excess vibrational energy, using both 2 ns and 5 ps pulsed lasers. The competition between relaxation and ionization of the pumped level is studied as a function of excess vibrational energy, laser power and pulsewidth.

RG9. (4:01)

CONFIGURATION INTERACTION AND SPIN-ORBIT COUPLING IN THE FOX-HERZBERG SYSTEM OF C_2

J.L. Hardwick and D.H. Winicur

Spin-orbit coupling constants have been obtained for the $e\,^3\Pi_g$ state of C_2 from a re-measurement of several bands of the $e\,^3\Pi_g - a\,^3\Pi_u$ band system and a re-analysis of some of the published measurements. The spin-orbit constants A_v of the upper state are small, and the change of A_v with v is anomalously large. This behavior is entirely consistent with the assumption of a large change in orbital configuration for the e state, as predicted by ab initio calculations.

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RG10. (4:18)

ERGODIC BEHAVIOR AND THE ANOMALOUS CONTINUUM FLUORESCENCE OF SMALL MOLECULES

John L. Hardwick

The anomalous continuum fluorescence and absorption spectra of NO_2 is interpreted as resulting from the coupling between the excited electronic states and high-lying levels of the ground electronic state which are ergodic in nature. This behavior is intimately related to the anomalous lifetime lengthening (the Douglas effect), and is proposed to account for similar anomalous continua in CS_2 and SO_2.

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RG11. (Last Minute Addition) (4:35)

MICELLAR EFFECTS ON DUAL FLUORESCING COMPOUNDS

Atu A. Ayuk , and F. S. Sadek

Dual fluorescing compounds emit from two states. The local (short wavelength) fluorescence band is less polar than the long wavelength band resulting from charge transfer of a strong donor substituent.

Three micellar types have been used to study the effect of the π- and n- electron systems of dual fluorescing compounds in the excited state. Enhancement and spectral changes are evaluated.

Determined suitable micellar concentration will provide information for the separation of charges necessary to study the association energy of the miceller aggregates.

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F. S. Sadek : Department of Natural Science, Winston-Salem State University, Winston-Salem, NC 27110.

RG12. (Last Minute Addition) (4:47)

QUENCHING STUDIES OF DUAL FLUORESCING 1-N,N-DIMETHYLAMINO-4-METHOXY-CARBOXYLIC ACID BENZENE (DMABMCA) BY KI IN 2-PROPANOL/WATER MIXED SOLVENTS

ATU A. AYUK

DMABMCA fluoresces from a double potential minimum in the excited state in polar solvents. The high energy band decays from S_1 (π-π^*) state whereas the low energy fluorescence band originates from a closely-lying S_1 (1-α_π) state. Stern-Volmer kinetics is applied to study the dynamic quenching process of both states by iodide ion.

The results of this investigation will serve as a preliminary study towards the interpretation of the nature of fluorescence quenching mechanism, the nature and efficiency of the electronic energy transfer and the dependence of both excited state potential minima with one another.

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RH1. (1:30)

TIME RESOLVED RESONANCE RAMAN SCATTERING STUDIES OF INTERFACIAL CHEMICAL KINETICS IN MICELLAR AND COLLOIDAL SOLUTIONS, LOUIS BRUS

Vibrational Raman spectra often provide positive structural identification of transient species and, additionally, may indicate differing states of solvation through subtle changes in line shapes and intensities. Time resolved Raman spectra can unravel complex reaction schemes in condensed heterogeneous phase systems. We describe nanosecond and picosecond experiments probing A) molecular photoionization at the hydrocarbon-aqueous interface of ionic micellar solutions, and B) redox reactions of molecules adsorbed on semiconductor crystallites in liquid colloids.

Address: AT&T Bell Laboratories, Murray Hill, New Jersey, 07974, USA

RH2. (2:05)

NEW TECHNIQUES FOR THE VIBRATIONAL SPECTROSCOPY OF GASES WITH ULTRASHORT LASER PULSES

A. LAUBEREAU, H. GRAENER, AND H.-J. HARTMANN

A high resolution Fourier transform Raman spectroscopy of supersonic expansions is demonstrated. The technique applies stimulated Raman excitation of molecular transitions in a small frequency interval ($\sim 1\ \text{cm}^{-1}$) by the help of two synchronized pump pulses and subsequent coherent Raman scattering of delayed probing pulses. Measuring over a long delay time interval (10^{-8} s) numerical Fourier *transformation* of the scattering signal transient yields precise spectroscopic information with a resolution of < 50 MHz. Experimental data will be presented for the Q-band of the ν_1-vibration of CH_4, resolving for the first time the tensor splitting of the $J=2$ transitions.

As a first demonstration of a picosecond infrared spectroscopy coherent pulse propagation of ultrashort infrared pulses is discussed. The drastic reshaping of the investigated resonant pulses provides direct information on various interesting parameters, e.g. dephasing time T_2 and molecular frequency differences. The technique is particularly interesting because of the different selection rules of the IR transitions as compared with Raman scattering. Experimental data will be presented for the R-branch of the system HCl:Ar and compared with corresponding time-resolved Raman measurements.

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RH3. (3:00)

RESONANCE CARS OF α,ω-DIPHENYLPOLYENES IN THE LOWEST EXCITED SINGLET AND TRIPLET STATES

A. KASAMA, T. KAMISUKI, Y. ADACHI, AND S. MAEDA

Transient CARS and/or CSRS spectra of α,ω-diphenylbutadiene(DPB), -diphenylhexatriene(DPH) and -diphenyloctatetraene(DPO) in the lowest excited singlet[S_1] and triplet[T_1] states have been recorded with the resonance enhancement by the transient S_n—S_1 or T_n—T_1 absorption. The measurement was made on room temperature solutions($\sim 10^{-4}$M) in various solvents, by using temporally coincident exciting(UV) and probe(visible dye) laser pulses of several nsec duration and by scanning a dye laser frequency. The S_1 and T_1 signals were distinguished from each other by the different resonant behaviors and by using delayed measurement if necessary. The obtained vibrational frequencies were in fair agreement with those from the two-photon excitation or transient resonance Raman spectra reported for some of the states, but generally more abundant and much better resolved. The assignment and the interpretation of frequency shift from the ground state are discussed by referring to the theoretical calculations.

An unusual $\nu_{C=C}$ frequency of S_1 DPO, as already known in the two-photon spectrum, was observed at 1755 cm^{-1}(in n-heptane) with striking resonance enhancement. The anomalous value has been suggested to arise from the vibronic interaction with the ground state, but does not seem to have been interpreted conclusively. No such anomalous frequencies were detected in the present observation except above. The above frequency was found to be shifted appreciably($\sim$ 25cm^{-1}) depending upon the solvent in distinction from the other modes, possibly indicating the cause of anomaly. On the other hand, the S_1 spectrum of DPH showed some different features depending on the solvent polarity. This observation and the marked abundance of S_1 DPH lines might suggest the conformational variety.

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RH4. (3:35)

TRIPLET STATE RESONANCE RAMAN SPECTRA OF SMALL POLYENES

R. WILBRANDT, F.W. LANGKILDE AND N.-H. JENSEN

In the present paper vibrational spectra of various methyl-substituted trienes and of other polyenes in their ground state and lowest excited triplet state in solution shall be compared. The spectroscopy of the ground state includes Raman and FTIR spectra, the triplet states were studied by time-resolved absorption and resonance Raman spectroscopy. These latter spectra were obtained from pump-probe experiments using two independent pulsed lasers as excitation sources. Triplet states were produced using acetone or biphenyl as sensitizers, and spectra were recorded by means of an optical multichannel analyzer.

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DK-4000 Roskilde

RH5. (4:10)

TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF TRANSIENT SPECIES FORMED DURING THE OXIDATION OF CYTOCHROME OXIDASE BY DIOXYGEN**

GERALD T. BABCOCK,*[b] JOHN M. JEAN,[a] LEAH N. JOHNSTON,[a] GRAHAM PALMER*[c], AND WILLIAM H. WOODRUFF*[a]

Cytochrome oxidase is responsible for perhaps 90% of the aerobic metabolism on earth. Time resolved resonance Raman spectroscopy has been used to study the reoxidation of the reduced and mixed valence forms of this enzyme by dioxygen. Laser flash photodissociation of CO from the carbonmonoxy complex of the enzyme, after this species had been rapidly mixed with oxygenated buffer, was used to initiate the reaction. The immediate product of the flow-flash reaction of the CO-blocked, fully reduced enzyme has a Raman spectrum which is undistinguishable from that of the reduced enzyme. This intermediate is replaced in the first few microseconds by a photolabile species which has Raman frequencies characteristic of oxygenated heme. This indicates the formation of an oxyhemoglobin-like O_2 complex of cytochrome $\underline{a}_3$ as the precursor of dioxygen reduction. The O_2 complex is the major species during the 10-50 μs of the reaction but converts subsequently to a series of nonphotolabile intermediates as the oxidation reaction proceeds. The CO photolysis product of the mixed valence enzyme contains cytochrome $\underline{a}^{3+}$ and cytochrome $\underline{a}_3^{2+}$ in its unligated form. This species reacts with O_2 to form an oxyhemoglobin-like complex of oxygen with $\underline{a}_3^{2+}$ similar to the one formed in the fully reduced enzyme reaction. In the mixed valence oxidase system, the oxy intermediate is replaced by a nonphotolabile species in which $\underline{a}_3$ is oxidized with $t_{\frac{1}{2}}$ 200 μs. These results demonstrate the feasibility of applying time-resolved vibrational techniques to physiologically important, irreversible electron transfer reactions and, in particular, elucidate some of the transient species in the cytochrome oxidase/O_2 system.

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** This work performed in part under the auspices of the U.S. Department of Energy.

FA1. (8:30)

VIBRATIONAL SPECTRA, FORCE CONSTANTS AND Si-O BOND CHARACTERS IN CALCIUM SILICATE CRYSTAL STRUCTURES

M. HANDKE

The vibrational spectroscopic methods were used to study the Si-O bond character in silicates with different complex anions and crystal structures. The following calcium silicates were examined: $Ca_3(SiO_5)$, γ-$Ca_2(SiO_4)$, β-$Ca_2(SiO_4)$, $Ca_3(Si_2O_7)$, $Ca(SiO_3)^1_\infty$ and $Ca_3(Si_3O_9)$. The bond assignments in IR and Raman spectra of these compounds have been deduced mainly from ^{28}Si- ^{30}Si and ^{40}Ca- ^{44}Ca isotopic shifts.

GF matrix methods and molecular approximation for force constant calculations in silicate anions have been used.

The Si-O bond parameters such as: bond order, charge distribution and bond ionicity were obtained from calculated force constants. The nature of Si-O bonds with respect to complex anion and crystal structure will be discussed.

M. Handke: Harrick Scientific Corporation, 88 Broadway, Ossining, NY 10562 - on sabbatical from Institute of Material Science AGH Cracow, Poland

FA2. (8:42)

INFRARED OPTICAL AND DIELECTRIC CONSTANTS OF LIQUID ALIPHATIC ALCOHOLS AND THE MAGNITUDE OF THE CHANGE IN MOLECULAR DIPOLE MOMENT DURING THE OH STRETCHING VIBRATION

J.E. BERTIE, V. BEHNAM, AND H.H. EYSEL

The CIRCLE attenuated total reflection FTIR accessory is used to measure infrared optical and dielectric constants and the infrared conductivity, with a Bruker IFS 113V FTIR spectrometer. The method, calculations, and programs (written for the Bruker Aspect 2000 computer in Pascal with some assembly language routines) will be described.

For condensed phases it is the infrared conductivity, not the Beer-Lambert coefficient, that provides the simple measure of absorption, i.e. of $(\partial\mu/\partial Q)^2$, that the Beer-Lambert coefficient provides for a gas. The infrared optical and dielectric constants and the infrared conductivity of liquid aliphatic alcohols will be presented, including the evidence that the magnitude of the dipole moment change during an O-H stretching vibration is independent of the alcohol within ±2% for liquid CH_3OH, C_2H_5OH, n-C_3H_7OH, n-C_4H_9OH, and n-$C_7H_{15}OH$.

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FA3. (8:59)

VIBRATIONAL SPECTRA AND CONFORMATIONAL BEHAVIOR OF 1,1-DIETHYLCYCLOPROPANE

C.J. WURREY, P.M. GREEN AND V.F. KALASINSKY

Infrared spectra (from 4000-400 cm^{-1}) of solid, liquid and gaseous 1,1-diethylcyclopropane and Raman spectra of the condensed phases of this compound have been recorded. Evidence for two conformational isomers, one of which vanishes in the polycrystalline solid phase, is found in two conformer doublets observed in the liquid phase spectra. It has been concluded that these rotational isomers are the gauche/gauche conformers which arise when the two methyl groups of the title compound are displaced in a conrotatory sense (C_2 symmetry) and a disrotatory sense (C_s symmetry) from a hypothetical cis/cis (C_{2v}) structure. These conclusions are consistent with the conformational results obtained previously for ethylcyclopropane and ethyloxirane.[1] In addition, from the variable temperature liquid phase Raman intensity measurements, the C_2 rotamer of 1,1-diethylcyclopropane has been calculated to be 1.1 ± 0.2 kcal/mole more stable than the Cs form, and is the sole conformer remaining in the solid phase. Tentative vibrational assignments, in agreement with those for related molecules, are proposed for the major spectral bands of 1,1-diethylcyclopropane.

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[1] A.B. Nease and C.J. Wurrey, J. Raman Spectrosc., 9, 107 (1980).

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Address of Kalasinsky: Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762.

FA4. (9:11)

VIBRATIONAL SPECTRA OF CYCLOPROPYL CYANIDE AND CYCLOPROPYL CYANIDE-α-d_1

C.J. WURREY, P.M. GREEN, R. KRISHNAMOORTHI AND Y.Y. YEH

Two recent publications have corrected earlier work on cyclopropyl cyanide (CPCN), providing more complete spectra and new assignments for this molecule.[1,2] As yet, however, no deuterium labelling has been reported for CPCN (or any other monosubstituted cyclopropane) to lend support to these assignments. We have synthesized CPCN-α-d_1 and recorded its infrared spectra in all phases and Raman spectra for the condensed phases. In addition, we have obtained the solid phase Raman spectrum, and a higher resolution (0.5 cm^{-1}) gas phase infrared spectrum of the light compound, CPCN. On the basis of Raman depolarization ratios, gas-phase infrared band contours, and isotopic shifts, we have proposed assignments for the vibrational fundamentals of these two molecules. Since the CH in-plane bending mode in CPCN falls 50-60 cm^{-1} higher than typical for substituted cyclopropanes, and since the CD out-of-plane bend in CPCN-α-d_1 occurs at an anomalously low frequency, it would appear that the CN group perturbs the electronic structure of the three membered ring, especially in the vicinity of the C_1 carbon atom. In addition, some large gas-phase to liquid-phase frequency shifts may indicate that self-association occurs in the liquid phase of CPCN.

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[1] J. Maillols, V. Tabacik, and S. Sportouch, J. Raman Spectrosc., 11, 312 (1981).

[2] G. Schrumpf, Spectrochim. Acta, 39A, 511 (1983).

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FA5. (9:28)

VIBRATIONAL SPECTRA OF FLUOROMETHYLCYCLOPROPANE AND BISOXIRANE

J. A. Smith, K. G. Whitehead, C. Saiwan, and V. F. Kalasinsky

The infrared and Raman spectra of fluoromethylcyclopropane and bisoxirane (butadiene bisepoxide) have been recorded. At least two conformers of the d,ℓ isomer of bisoxirane exist in the fluid state, but only one conformer, tentatively identified as the trans, exists in the crystalline solid. The second conformer appears to be the gauche form and, from variable temperature data, has been determined to be approximately .2 kcal/mole less stable. Fluoromethylcyclopropane, unlike other halomethylcyclopropanes, is only stable for relatively short periods at ambient temperature. The most stable conformation has the gauche orientation, and, contrary to expectations, there is very little of the second conformer (trans) in the fluid states. Based on all the available spectroscopic data, complete vibrational assignments for both molecules will be proposed and their conformational preferences will be discussed.

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FA6. (9:45)

FORCE CONSTANTS FOR THE CYCLOPROPENYL CATION

NORMAN C. CRAIG, JULIANTO PRANATA, SARA JAMIE REINGANUM, AND PHILIP S. STEVENS

Key force constants among the seven that were fitted to the vibrational assignments for the in-plane modes of $C_3H_3^+$, $C_3D_3^+$, and $C_3H_2D^+$ were larger than the corresponding ones for benzene.[1] To offset the considerable strain in the sigma bonds in the C_3 ring system, the π-bonding in $C_3H_3^+$ must be exceptionally strong, indeed "superaromatic." Infrared and Raman spectra of the new species, $C_3D_2H^+$ give as assignments (in cm^{-1}) (a_1), 3154, 2423, 1535, 1268, 675; (a_2) ___; (b_1) 2353, 1256, 973, 767; (b_2) ___, 603. Using these new frequencies along with the ones previously assigned for the other three isotopomers, we have fitted a full set of ten general valence force constants to the in-plane modes of the cyclopropenyl cation. The force constants are (in mdyn $Å^{-1}$ for stretch-stretch, mdyn Å rad^{-2} for bend-bend, and mdyn rad^{-1} for stretch-bend) CC str, 7.890(056); CH str, 5.280(009); CH bd, 0.598(008); CC str/CC str, -0.424(029); CH str/CH str, 0.031(006); CH bd/CH bd, -0.043(004); CC str/CH str (same C), -0.236(016); CC str/CH str (different C), 0.378(034); CC str/CH bd, 0.212(023); CH str/CH bd, 0.225(041). For benzene some comparative force constants are 6.578 for CC stretching, 5.176 for CH stretching, and 0.514 for CH in-plane bending.[2]

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[1] N. C. Craig, J. Pranata, J. R. Sprague, and P. S. Stevens, J. Am. Chem. Soc., 106, 7637 (1984)

[2] P. Pulay, G. Fogarasi, and J. E. Boggs, J. Chem. Phys., 74, 3399 (1981)

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FA7. (9:57)

VIBRATIONAL SPECTRA OF TRANS-1,2-DIFLUOROETHYLENE OXIDE

J. W. AGOPOVICH, N. C. CRAIG. C. W. GILLIES, AND D. J. MCGARVEY

Infrared and Raman spectra have been recorded for *trans*-$\overline{\text{CFHCFHO}}^{18}$ and *trans*-$\overline{\text{CFDCFDO}}$. From good band shapes in the gas-phase infrared spectra, Raman depolarization ratios, and close parallels with the spectra of *trans*-$\overline{\text{CFHCFHCH}_2}$ and $\overline{\text{CFDCFDCH}_2}$ other than for the CH_2-rich modes,[1] we have secured a virtually complete assignment of the vibrational fundamentals of the ethylene oxides.

This work marks the first observation of the effect on vibrational spectra of heavy atom substitution on a three-atom ring system. Only a limited-range survey of the infrared spectrum of the normal isotopic species of *trans*-difluoroethylene oxide is available. However, frequency shifts (or non-shifts) due to O-18 substituion imply that ν_2(a) at 1480 cm^{-1} is largely CC (and CF) stretching, whereas ν_6(a) at 950 cm^{-1} contains appreciable COC stretching and ν_7(a) at about 520 cm^{-1} contains appreciable COC bending.

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[1] N. C. Craig, T.-N. Hu Chao, E. Cuellar, D. E. Hendriksen, and J. W. Koepke, *J. Phys. Chem.*, 79, 2270 (1975).

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FA8. (10:20)

INFRARED AND RAMAN SPECTRA AND CONFORMATIONAL STABILITY OF ETHYLDIMETHYLPHOSPHINE

T. J. HIZER AND J. R. DURIG

The infrared and Raman spectra have been recorded for gaseous and solid ethyldimethylphosphine, $CH_3CH_2P(CH_3)_2$. Additionally, the Raman spectra of the liquid has been recorded and qualitative depolarization values have been obtained. From the fact that several distinct Raman lines disappear on going from the fluid phases to the solid state, it is concluded that the molecule exists as a mixture of the *gauche* and *trans* conformers in the fluid phases with the *gauche* conformer being more stable and the only one present in the spectrum of the solid. A complete vibrational assignment is proposed for the *gauche* conformer, and is supported by a normal coordinate calculation which was carried out utilizing a modified valence force field to obtain the frequencies of the normal modes and the potential energy distribution. The asymmetric torsional mode has been observed for the *gauche* conformer in both the infrared and Raman spectra of the gas at 91 cm^{-1} with evidence of "hot bands" at lower frequencies.

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FA9. (10:37)

INFRARED AND RAMAN SPECTRA OF 4-(DIMETHYLAMINO)BENZALDEHYDE AND ITS ZINC COMPLEX

J. G. Rosencrance and P. W. Jagodzinski

The resonance enhanced Raman spectrum of 4-(dimethylamino)benzaldehyde (DABA) bound to Zn^{+2} in nonaqueous solution is essentially identical to that obtained from DABA bound to the catalytic zinc in equine liver alcohol dehydrogenase. The vibrational spectra of DABA and the DABA-Zn complex will be presented and discussed.

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FA10. (10:54)

VIBRATIONAL SPECTRA OF SUPERSOLVENTS: TETRAMETHYLUREA AND HEXAMETHYLPHOSPHORAMIDE

D. L. McCarty, R. L. Hunt-Kramer and P. W. Jagodzinski

The infrared and Raman spectra of tetramethylurea (TMU, $((CH_3)_2N)_2CO$) and hexamethylphosphoramide (HMPA, $((CH_3)_2N)_3PO$) have been obtained. The pyrimidal configuration about the nitrogens and the deviation from C_{2v} point group symmetry as reflected in the spectra of TMU will be discussed. Preliminary vibrational assignments for HMPA will be presented.

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FA11. (11:06)

AN *AB INITIO* MOLECULAR ORBITAL STUDY OF THE VIBRATIONAL FREQUENCIES OF ONF AND NOF

L. A. Curtiss and V. A. Maroni

The optimized geometries and vibrational frequencies of ONF and NOF are determined using second order Møller Plesset perturbation theory with the 6-31G* basis set. The geometry and frequencies of ONF are in good agreement with experiment,[1] whereas the vibrational frequencies of NOF are in poor agreement with the observed frequencies.[2,3] The theoretical predictions support the contention of Jacox[3] that the band observed by Smardzewski and Fox[2] at 1886 cm^{-1} is not the NO-stretching fundamental of NOF. Also, the predicted shifts in frequencies of the ν_2 and ν_3 bands upon isotopic substitution are in sharp disagreement with experimental shifts,[2] raising the question of whether NOF has actually been observed in low temperature matrices. The NOF isomer is calculated to be 40 kcal/mol less stable than ONF with a barrier of 13 kcal/mole for conversion of NOF to ONF. The possibility that the ground state of NOF is a triplet was also investigated.

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[1] L. H. Jones, L. B. Asprey, and R. R. Ryan, J. Chem. Phys. 47, 3371(1967).
[2] R. R. Smardzewski and W. B. Fox, J. Chem. Phys. 60, 2104(1974).
[3] M. E. Jacox, J. Phys. Chem. 87, 4940(1983).

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FA12. (11:23)

A COMPARISON OF QUANTUM MECHANICAL AND SEMI-CLASSICAL SCF THEORIES FOR H_3^+, H_2O, AND O_3

G. D. CARNEY. D. LESSESKI, W REED, AND L. PAVLOVICH

This study uses quantum mechanical and semi-classical SCF theory to determine molecular vibration energies, and compares the results to values obtained by more accurate quantum mechanical and semi-classical methods. The SC Hamiltonian retains Coriolis and anharmonic potential energy terms while the QM Hamiltonian retains these and the Watson term $-\frac{h^2}{8}\sum_\alpha \mu_{\alpha\alpha}$.

These numerical experiments provide a meaningful test of semi-classcial SCF and quantum mechanical SCF methods, and are being done by senior students (D.L., W.R., and L.P.) as undergraduate research projects in physical chemistry at Allegheny College.

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FA13. (11:38)

AB-INITIO QUARTIC FORCE FIELDS IN DIMENSIONLESS NORMAL COORDINATES FOR H_3^+

G. D. CARNEY AND D. LESSESKI

This study determines molecular potential functions as quartic polynominals in dimensionless rectilinear normal coordinates q_i for molecules H_3^+, D_3^+, T_3^+, H_2D^+, D_2H^+, H_2T^+, T_2H^+, D_2T^+, and T_2D^+. The force constants are obtained by numerical differentiation of an accurate least squares curve fit of Dykstra and Swope's H_3^+ ab-initio potential surface.[1] The curve fit function is a 6th degree symmetry adapted polynominal function expressed in the variables $\rho_i = (R_i - R_{eq} / R_i$ with R_{eq} = equilibrium bond length and R_i = instantaneous bond length.

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[1] C. E. Dykstra and W. C. Swope, J. Chem. Phys. 70, 1 (1979)

Address: Department of Chemistry, Allegheny College, Meadville, PA 16335

FA14. (11:55)

THE ^1L_b STATE OF 1,6:8,13-ETHANO[14]ANNULENE. VIBRATIONAL STRUCTURE AND THE "A BAND"

K.A. Klingensmith, H.J. Dewey, J. Michl

Measurements of the single-site selected flourescence excitation spectra of matrix isolated 1,6:8,13-ethano[14]annulene and its deuterated analog in solid nitrogen are presented. Utilizing molecular mechanics extended to delocalized systems by combining it with the PPP formalism, a ground state force field is constructed. INDO/S calculations of the excitation energy are used to build the harmonic force fields for vibrations in the first excited singlet state assuming the normal modes remain the same. Calculated Franck-Condon intensities for the transition from the ground to the first excited singlet state account for the majority of observed spectra features. The observed long progression in a vibration involving the transannular distance. The previously unassigned "A band" is proposed to be a part of the fine structure of the L_b band. It provides evidence for a pseudo Jahn-Teller coupling of the ground and first excited singlet state through a non-totally symmetric vibration. It can also be interpreted in terms of the two Kekulé structures of the perimeter and its origin related to the onset of bond length alternation expected for annulenes.

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FA15. (Last Minute Addition) (12:12)

FAR INFRARED AND RAMAN VAPOR PHASE SPECTROSCOPY OF HETEROCYCLIC COMPOUNDS

W. B. COLLIER AND M. M. STRUBE

The vapor phase vibrational spectra of quinoline, isoquinoline, benzofuran, N-methylpyrrole, and 2,5-dimethylpyrrole were examined by Fourier transform infrared and Raman spectroscopy.

Quinoline, isoquinoline, and benzofuran vapor Raman spectra of the lowest vibrational modes revealed distinct O, Q, and S branch contours. In addition, these compounds displayed an unusual cluster of bands in the 450-300 cm^{-1} region which were resolved and assigned to various combinations and overtones of the lower fundamentals.

Several spectral differences were observed between the liquid and vapor phases of these heterocyclics. Both the intensities and frequencies of several low frequency modes changed dramatically. These vapor phase out-of-plane modes are sometimes red-shifted from their liquid frequency values by as much as 20 cm^{-1}.

The ideal gas thermodynamic entropies were calculated and compared with calorimetrically determined entropies. The effect of the vapor-liquid spectral shifts on thermodynamic calculations can be significant and will be discussed.

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FA16. (Last Minute Addition) (12:29)

OVERTONE SPECTRA AND LOCAL MODE ANALYSIS OF CHLOROTRIFLUOROMETHANE

A. M. DeSouza and D. S. Perry

Using Photoacoustic Spectroscopy and Fourier Transform Infra-Red Spectroscopy, the fundamental and overtone spectra of chlorotrifluoromethane up to the v=5 manifold was obtained. Rotational contour analysis of the C-F overtone bands and combination bands with C-Cl stretch yields new values for the harmonic frequencies and anharmonicity constants.

Chlorotrifluoromethane has a greater normal mode character than local mode character due to the fact that the substitutent atoms are heavier than the central atom. The local mode analysis was carried out to extend the analysis to such extreme molecules. The local mode predictions are compared to the observed distribution of intensities among the 31 bands in the overtone region

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FB1. (8:30)

ANALYSIS OF THE ν_3 BAND OF $^{32}SF_6$ FROM SATURATED ABSORPTION SPECTROSCOPY

B. BOBIN, Ch. BRÉANT, J. BORDÉ and Ch.J. BORDÉ

We analyse the vibration-rotation structure of the ν_3 band of $^{32}SF_6$ from the measurements of the frequencies for 136 transitions in near coincidence with CO_2 or N_2O laser lines (saturated absorption spectroscopy near 28 THz). After deconvolution of hyperfine structures, the centers of vibration-rotation transitions are accurate to 5 to 10 kHz. They are analysed using the tensorial Hamiltonian of Moret-Bailly, developed to 5th order of approximation. An iterative procedure, using full diagonalization of hamiltonian matrices, allows the determination of 18 molecular constants related to the ν_3 excited state, together with 6 constants of the ground-state (scalar and tensorial), with a very high accuracy.
For instance : $\beta^o = B^o = 0.0910842001(10)$ cm^{-1} ; $\Delta\beta = B_3 - B^o = -1.3105551(70)\times10^{-4}$ cm^{-1} ; $\epsilon^o = -(\sqrt{3}/2\sqrt{7})D_t^o = 1.86383(63)$ Hz ; $\nu_3 = 948.10252340(40)$ cm^{-1} (band center) ; and $\zeta_3 = 0.69344341(20)$, the Coriolis coupling coefficient.

The experimental transitions (ranging from P84 to R94) are then reproduced with a standard deviation of 30 kHz only, which is a considerable improvement with regard to previous analyses. Only 8 transitions remain out of the fit (deviation larger than 100 kHz), but this may reasonably be explained by a resonance with the $\nu_4 + \nu_6$ level, which is located only 13.8 cm^{-1} higher than ν_3.

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FB2. (8:42)

THE ν_3 BANDS OF NATURAL OsO_4 FROM FT-IR SPECTRUM

B. BOBIN, L. HENRY and A. VALENTIN

The infrared spectrum of natural OsO_4 has been recorded from 930 to 985 cm^{-1} *on* the FT-IR spectrometer of the Laboratoire de Spectronomie of Paris. The resolution is 1.2×10^{-3} cm^{-1}, and the absolute calibration of single lines, around 0.2×10^{-3} cm^{-1}.

Using the tensorial Hamiltonian of Moret-Bailly, developed to 5th order, we analysed the ν_3 band of the 4 main isotopic species. In each case, 18 molecular constants are derived for the excited state. The scalar constants of the ground-state are also refined : $\beta^o = B^o = 0.13490(15)$ cm^{-1} ; $\gamma^o = -D_s^o = -2.79(36)\times10^{-8}$ cm^{-1} and $\pi^o = 1.057(95)\times10^{-12}$ cm^{-1}. Some results are summarized below.

Os Isotopic species (%)	Max. J	Assigned lines total	Assigned lines in fit	Std. dev. (cm^{-1}) total	Std. dev. (cm^{-1}) on fit	Band centers (cm^{-1})
192 (41.0%)	55	784	724	.00083	.00053	960.739916(72)
190 (26.4%)	45	529	495	.00076	.00052	961.266549(88)
189 (16.1%)	45	529	495	.00094	.00057	961.53412(10)
188 (13.3%)	45	529	468	.00095	.00066	961.80479(13)

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FB3. (8:54)

MEASUREMENT OF THE INFRARED-ACTIVE STRETCHING FUNDAMENTAL (ν_3) OF UF_6

R. S. McDOWELL, J. P. ALDRIDGE, H. FILIP, H. FLICKER, R. F. HOLLAND, K. C. KIM, D. W. MAGNUSON, W. B. MAIER II, W. B. PERSON, D. F. SMITH, AND G. K. WERNER

High-resolution (Doppler-limited) spectra of the infrared-active stretching fundamental ν_3 of $^{238}UF_6$ have been obtained between 620.6 and 633.5 cm^{-1} using tunable semiconductor diode lasers. Interference from hot bands was suppressed by cooling the UF_6 in a supersonic expansion, and useful monomer concentrations were produced with effective temperatures of <100 K. Portions of the band from P(77) to R(66) will be shown. All transitions from the vibrational ground state have been assigned; the ν_3 Q branches of both $^{238}UF_6$ and $^{235}UF_6$ have been analyzed, and the isotope shift accurately measured. The isotope shift and the Coriolis constant ζ_3 have been used to refine the general quadratic force field of UF_6. The Cartesian displacement coordinates of both infrared-active fundamentals will be illustrated and compared with those of SF_6.

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FB4. (9:11)

ANALYSIS OF THE INFRARED-ACTIVE STRETCHING FUNDAMENTAL OF UF_6

B. J. KROHN, E. G. BROCK, K. FOX, H. W. GALBRAITH, R. S. McDOWELL, AND C. W. PATTERSON

Assignments of the UF_6 spectra described in the preceeding paper will be discussed. A total of 43 line frequencies and 110 frequency differences extending in J to P(77), Q(91), and R(67) has been used to fit seven spectroscopic constants. High-J data allowed the independent fitting of $(B\zeta)_3$ and hence of the rotational constants B' and B_0. The derived U-F bond length in the ground vibrational state is $r_0 = 1.9962 \pm 0.0007$ Å. The use of frequency differences as a supplement to absolutely-calibrated transition frequencies in fitting spectroscopic and molecular constants will be discussed.

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FB5. (9:28)

LINE WIDTHS AND THEIR TEMPERATURE DEPENDENCE IN THE ν_9-FUNDAMENTAL BAND OF ETHANE

S. CHUDAMANI*, P. VARANASI*, L. P. GIVER, AND F. P. J. VALERO

Using the spectral transmittance data on N_2-broadened and H_2-broadened lines in the ν_9-fundamental of C_2H_6 at 150, 200 and 296 K, and the spectral catalog generated recently by Atakan et al[1], we have been able to derive simple and useful results for the half-widths of lines of planetary atmospheric relevance. In H_2-broadening, a single value of 0.104 cm^{-1} atm^{-1} seems to fit most of the lines well. In N_2-broadening, $0.14\ (150/T)^{0.75}$ when K=0, and $0.168\ (150/T)^{0.75}$ when $K \neq 0$, have yielded excellent comparison between theoretical and experimental transmittance data.

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* Supported by NASA Grant-in-Aid NGR 33-015-139 through the Planetary Atmospheres Program to Varanasi.

[1] A. K. Atakan, W. E. Blass, J. W. Brault, S. J. Daunt, G. W. Halsey, D. E. Jennings, D. C. Reuter, and J. Susskind, NASA Tech. Memo. 85108.

Address of Chudamani and Varanasi: Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York 11794-2300
Address of Giver and Valero: Astrophysical Experiments Branch, NASA Ames Research Center, Moffett Field, California 94035

FB6. (9:45)

SIMULTANEOUS ANALYSIS OF VIBRATIONAL POLYADS IN SYMMETRIC AND SPHERICAL TOPS. THEORETICAL AND NUMERICAL ASPECTS ILLUSTRATED ON CH_4, CD_4 AND CH_3F

J.P. CHAMPION

Two types of spectroscopic data are currently available :

1) High resolution data covering wide spectral regions (for instance infrared Fourier transform data with a typical precision of 0.0001 cm^{-1}).

2) Very high resolution data on a restricted number of transitions (such as laser experiments or microwave data with a typical precision of 50 kHz).

From the theoretical point of view, considerable progress has been achieved

1) by developing effective Hamiltonians adapted to the study of vibrational polyads (including all important interactions).

2) by reducing such effective Hamiltonians (i.e. by removing any theoretical ambiguity affecting spectroscopic parameters).

The present work is a comprehensive approach of the question : How to get reliable spectroscopic constants from fitting spectroscopic data ? The consequences of the experimental and theoretical conditions mentionned above on the computer treatment of the problem are analysed and illustrated by the following applications :

- $^{12}CD_4$	Dyad ν_2/ν_4 (IR+MW)	J_{max} = 20	σ = 0.0002 cm^{-1}.
- $^{12}CH_4$, $^{13}CH_4$	Ground state (MW) + Dyad ν_2/ν_4 (IR) preliminary results (Feb.85)	J_{max} = 13	σ = 0.0001 cm^{-1}.
- $^{12}CH_3F$	Dyad (MW+IR) + Pentad (IR)	J_{max} = 20	σ = 0.001 - 0.013 cm^{-1}.

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FB7. (10:15)

FURTHER ANALYSIS OF EFFECTIVE HAMILTONIANS FOR TRIPLY DEGENERATE FUNDAMENTALS OF TETRAHEDRAL MOLECULES. UNAMBIGUOUS FIT OF q^2J^5 AND q^2J^6 TERMS FOR ν_4 OF $^{12}CH_4$

VL.G.TYUTEREV, G.PIERRE, J.P.CHAMPION, V.I.PEREVALOV and B.I.ZHILINSKII

The further study of ambiguities among q^2J^5 and q^2J^6 terms in effective Hamiltonians for triply degenerate fundamentals of tetrahedral molecules is presented. It is shown that, in agreement with theory, q^2J^5 and q^2J^6 diagonal coupling parameters cannot be considered as constants having definite values for a given F_2 vibrational state, just like q^2J^4 terms previously studied (Vl.G.TYUTEREV, J.P.CHAMPION, G.PIERRE and V.L.PEREVALOV, J.Mol.Spectrosc. 105, 113-138 (1984)). The use of reduced Hamiltonians containing fewer (but unambiguous) parameters is suggested and applied to the ν_4 band of $^{12}CH_4$.

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FB8. (10:27)

MEASUREMENTS OF CH_4 ν_4 HALFWIDTHS USING TWO HIGH-RESOLUTION TECHNIQUES

V. MALATHY DEVI, M. A. H. SMITH, C. P. RINSLAND, AND D. C. BENNER

Air-broadened and N_2-broadened halfwidths at room temperature for 25 lines in the ν_4 band of $^{12}CH_4$ have been determined from infrared absorption spectra recorded with a tunable diode laser (TDL) system in selected spectral regions between 1250 and 1360 cm^{-1}. Air-broadened halfwidths for 20 of these lines were also determined from additional spectra at 0.01 cm^{-1} resolution recorded with the Fourier transform spectrometer (FTS) system in the McMath solar telescope complex on Kitt Peak. The air-broadened halfwidth values obtained from these two techniques are very consistent with agreement to better than 3% for most lines. Several additional lines of $^{13}CH_4$ and $^{12}CH_3D$ were also measured in the same spectral region with the diode laser system. The measured N_2-broadened and air-broadened halfwidths will be reported.

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FB9. (10:39)

LINE STRENGTHS OF METHANE IN THE 2.2 MICRON REGION

J. C. HILICO, M. LOETE, and L. R. BROWN

Absolute strengths and wavenumbers of 1500 vibration-rotation lines of natural methane have been measured at 297 K in the spectral region 4433-4719 cm^{-1} from high resolution spectra recorded on the F. T. spectrometer at Kitt Peak. Accuracy of the strengths can be estimated to 3 % for clean lines. Most of these lines belong to the $\nu_2 + \nu_3$ combination band. The upper state levels being largely perturbed, the analysis of strengths on the basis of an isolated band model -the only one presently available- requires a second order development of the dipole moment including 8 parameters. The strengths of a severe selection of 229 single lines are reproduced with a relative standard deviation of 5.4 % whereas reduced developments with only 3 parameters (first order) or 1 parameter (zero order) lead to 16 % and 133 % respectively.

The obtained parameters are used to predict the associated $\nu_3 - \nu_2$ difference band.

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FB10. (10:51)

DIPOLE MOMENT PARAMETERS OF METHANE

M. LOETE and J. C. HILICO

The line strengths of five bands (ν_2, ν_4, $\nu_1 + \nu_4$, $\nu_2 + \nu_3$, $\nu_3 - \nu_4$) of methane $^{12}CH_4$ have been analysed on the basis of the general tensorial expansion of the dipole moment operator in XY_4 molecules(1). The parameters determined from these analyses have been used to calculate the line strengths of several other bands.

Using an extrapolation method, the line strengths of the $2\nu_4 - \nu_4$, $\nu_2 + \nu_4 - \nu_2$, $2\nu_2 - \nu_2$ and $\nu_2 + \nu_4 - \nu_4$ hot bands have been calculated from the parameters obtained in the ν_4 and ν_2 analyses.

The parameters of the $\nu_1 + \nu_4$, $\nu_2 + \nu_3$ and $\nu_3 - \nu_4$ bands are connected to those of the $\nu_1 - \nu_4$, $\nu_2 - \nu_3$ and $\nu_3 + \nu_4$ bands respectively. The line strengths of the last three bands can be predicted from the relations between these parameters.

More generally, the relations between the dominant parameters of the transformed dipole moment of XY_4 molecules will be described and discussed, both for isolated bands or polyads, and the main numerical results for methane will be presented.

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(1) M. LOETE, Can. J. Phys. 61, 1242-1259 (1983)

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FB11. (11:08)

HIGH RESOLUTION INFRARED SPECTRUM OF SiH_3D

R. W. LOVEJOY, R. D. SCHAEFFER AND W. B. OLSON

The infrared ν_2, ν_3, ν_5 and ν_6 bands of $^{28}SiH_3D$ have been recorded at a spectral resolution of 0.004 cm^{-1}. Approximately 2400 lines have been assigned. The results will be discussed with emphasis being given to values for the ground state constants of this molecule. Several perturbation allowed transitions have been identified, covering a wide range in K, permitting a precise determination of the parameters $A_o - B_o$ and D_o^K.

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FC1. (8:30)

LASER-INDUCED FLUORESCENCE STUDY OF VIBRATIONAL RELAXATION IN XeF(B)

G. BLACK, L. E. JUSINSKI, D. C. LORENTS, AND D. L. HUESTIS

We have used a doubled dye laser to excite individual vibrational transitions of the $XeF(B \leftarrow X)$ system (v'=0-4), and have observed the spectrally resolved $B \rightarrow X$ fluorescence as a function of time and buffer gas pressure (using He, Ne, Ar, Kr, N_2, and SF_6). The initial ground state XeF(X) is produced by KrF laser photodissociation of XeF_2.

We observe surprisingly effective vibrational redistribution at low buffer gas pressures (the half-relaxation pressure in Ne is about 150 torr). Even more surprising, the rate of decay of $XeF(B)_{v'=0}$ is unaffected by the Ne buffer up to 600 torr, and the decay of $XeF(B)_{v'=1}$ is much slower than would be anticipated based on the extent of vibrational redistribution. We feel that these observations reflect the intimate participation of the nearby XeF(C) vibrational levels in the relaxation of XeF(B).

Supported by DARPA/ONR Contract N00014-84-C-0256

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FC2. (8:47)

ABSORPTION LINES IN THE KrCl LASER SPECTRUM AND THE SPONTANEOUS EMISSION OF KrCl

M. SHIMAUCHI, K. OIKAWA

The KrCl laser spectrum recorded on the third order of a 6.65m concave grating spectrograph shows more than thirty absorption lines in the region 2216 - 2224A. The laser was made by ourselves with particular caution against impurity contamination. As was expected from our previous work[1,2], many absorption lines were assigned to rotational lines of the several O_2 Schumann-Runge bands appeared as absorption. Some stronger lines were assigned to rotational lines of the 0-14 and 0-13 bands of HCl V-X system based on the wavenumbers observed by Jaques and Barrow[3]. Spontaneous emission spectra obtained with quartz prism spectrographs show eleven peaks of the B-X system, two continua probably arising from the C-X and B-A transitions in the region 2220-2085A, around 1987A and 2320-2490A, respectively. A continuum observed around 2570A was identified as the V-A system of HCl, since it appeared even when the discharging gas consists of He and HCl only. For the laser or spontaneous emission of KrCl the gas consists of HCl/Kr/He = 0.4/20/79.6, where impurities of HCl, Kr and He are stated to be 99.9, 99.995 and 99.9999%, respectively. The maximum total pressure investigated was 1500 Torr. At this pressure the laser power about 10 mJ/pulse was obtained when the carrier gas He(79.6%) was replaced by a mixture, He(39.6%) and Ne(40%), though this replacement made no change in the laser spectrum. Experimental results when HCl was replaced by Cl_2 will be presented.

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[1] M. Shimauchi: Jpn. J. Appl. Phys. 20, L473 (1981).
[2] M. Shimauchi and K. Oikawa: Can. J. Phys. 62, Dec. (1984).
[3] J. K. Jacques and R. F. Barrow: Proc. Phys. Soc. London 73, 538 (1958).

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FC3. (9:04)

CHARGE-TRANSFER SPECTRA OF $(ArKr)^+$ AND $(ArXe)^+$

R.H. Lipson and K.P. Huber

The charge-transfer spectra of the heteronuclear rare gas ions have been studied previously.[1] Furthermore,rotational analyses have been accomplished for $(HeNe)^+$ [2] and $(HeAr)^+$.[3] Nevertheless,the spectra due to the heavier ions are not well understood.

New resolved spectra of the charge-transfer transitions of the rare gas ions $(ArKr)^+$ and $(ArXe)^+$ are presented.The spectra were obtained from a D.C. discharge in a supersonic jet.

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1) Y. Tanaka,K. Yoshino and D.E. Freeman,J.Chem.Phys.62,4484 (1975)
2) I. Dabrowski and G. Herzberg,J.Mol.Spect.73,183 (1978)
3) I. Dabrowski,G. Herzberg and K. Yoshino,J.Mol.Spect. 89,491 (1981)

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FC4. (9:21)

BREAKDOWN OF THE BORN-OPPENHEIMER APPROXIMATION IN THE LEAST SQUARES FITTING OF SPECTROSCOPIC LINE POSITIONS: THE $X^1\Sigma^+$ STATE OF HYDROGEN CHLORIDE

J.A. COXON

Although it is well known that breakdown of the Born-Oppenheimer approximation has significant effects on the vibration-rotational eigenvalues of light molecules, rarely has full consideration of these effects been made in experimental determinations of the vibration-rotation Hamiltonians. A well known exception is the work of Bunker *et al.*[1] on H_2 and D_2, in which effective, but constant, vibrational and rotational reduced masses, μ_v and μ_r, were employed. Following the more recent formalism of Watson[2], the effective vibration-rotation Hamiltonian for a $^1\Sigma$ state can be written as

$$\hat{H}_{eff} = -(\hbar^2/2\mu_a)d^2/dR^2 + [V_{eff}(R) + (\hbar^2/2\mu_a R^2)\{1 + g(R)\}J(J+1)], \qquad [1]$$

where $V_{eff}(R)$ is the effective internuclear potential taking account of adiabatic and J-independent non-adiabatic corrections, and g(R), from the remaining non-adiabatic terms, introduces non-mechanical J-dependent corrections to the eigenvalues of the rotating molecule. μ_a is the atomic reduced mass. A direct least-squares fitting procedure has been developed for the determination of $V_{eff}(R)$ and g(R) from measured line positions. This procedure, which is based on the "Inverse Perturbation Analysis" method of Kosman and Hinze[3], has been applied to the extensive data that are available for the ground state of HCl. The pure rotation and vibration-rotation data on levels $v \leq 7$, which include precise line positions from microwave and Fourier transform near-ir spectroscopy, have been combined with the new and rotationally extensive data on levels $7 \leq v \leq 17$ from the V → X system[4]. The effective Hamiltonians, in the form of Eq. [1], are found to reproduce ~2000 line positions to within the associated estimated absolute errors.

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[1] P.R. Bunker, C.J. McLarnon and R.E. Moss, Mol. Phys. 33, 425 (1977).
[2] J.K.G. Watson, J. Mol. Spectrosc. 80, 411 (1980).
[3] W.E. Kosman and J. Hinze, J. Mol. Spectrosc. 56, 93 (1975).
[4] J.A. Coxon, U.K. Roychowdhury and A.E. Douglas, to be published.

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FC5. (9:38)

VIBRATIONAL POTENTIAL REPRESENTATION FOR THE X AND A ELECTRONIC STATES OF N_2*

C.L. BECKEL, E.R. NELSON, AND D.L. LOVERRO

Rational fractions in nuclear separation R have been used to represent the RKR potential $V(R) - V(\infty)$ for the ground state of N_2. Variable parameters are adjusted to the best available C_6 in the long-range C_6/R^6 form, to the Coulomb interaction $7 \times 7e^2/R$ near R=0, and to the RKR V for the 22 lowest-lying vibrational energy levels. The simplest suitable form, a [1/7] fraction, appears to represent V(R) as accurately as the RKR procedure warrants. Without fitting, $V(\infty)$ is 2.6% higher than the experimental dissociation limit. With $V(\infty)$ set equal to 79,850 cm^{-1},all bound vibrational energies are determined in the first-order WBK approximation. In this approximation there are 63 bound levels.

A [1/7] fraction adjusted to the same C_6 and to a Coulomb pole with nuclear charge Z=7 at R=0, fits the A-state RKR potential as accurately as data warrant. With $V(\infty)$ fixed at 29,640 cm^{-1},38 bound vibrational energies are extracted by WBK intergration. The v=37 level is within 2 cm^{-1} of the dissociation limit.

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*Supported in part by the Air Force Weapons Laboratory, Kirtland Air Force Base under Contract No. F29601-84-K-0038.

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FC6. (10:15)

ANALYSIS OF THE OPTICAL-OPTICAL DOUBLE RESONANCE SPECTRUM OF THE $3^1\Sigma_g^+$ STATE OF Li_2

R. A. BERNHEIM, L. P. GOLD, AND C. A. TOMCZYK

We have used the method of pulsed optical-optical double resonance spectroscopy to extend our earlier observations of the $3^1\Sigma_g^+$ state of Li_2 to levels through v = 29. *Ab initio* calculations predict a shallow outer minimum[2] or a shelf[3] for this state in the region of v = 13-15. Our observations are consistent with these calculations and show better agreement with the more recent calculation.[3] We will present detailed comparisons of theory and experiment.

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1. R. A. Bernheim, L. P. Gold, P. B. Kelly, T. Tipton, and D. K. Veirs, J. Chem. Phys. 76, 57 (1982).
2. D. D. Konowalow and J. L. Fish, J. Chem. Phys. 76, 1571 (1982).
3. I. Schmidt-Mink, W. Müller, and W. Meyer, Chem. Phys., in press.

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FC7. (10:32)

ROTATIONAL ANALYSIS OF THE $A^3\Pi_0 \rightarrow X^1\Sigma_0^+$ AND $B^3\Pi_1 \rightarrow X^1\Sigma_0^+$ SYSTEMS OF InBr

W.E. JONES AND V.N. SARMA

Two band systems attributed to InBr, $A^3\Pi_0 \rightarrow X^1\Sigma_0^+$ and $B^3\Pi_1 \rightarrow X^1\Sigma_0^+$ have been known since 1933[1]. However, no rotational analysis of these bands has yet been reported. We will report results from an analysis of high resolution plates (~0.15 Å/mm reciprocal dispersion) taken at the Herzberg Institute of Astrophysics NRCC Ottawa. The bands are reasonably well resolved, but are complicated by the presence of two isotopes of Br and severe overlapping by sequence bands.

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[1] Miescher, Wehrli, Helvetica Physica Acta, 6, 457 (1933): 7, 298 (1934).

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B3H 4J3.

FC8. (Last Minute Addition) (10:44)

HIGH RESOLUTION STUDY OF THE B $\leftrightarrow$ X SYSTEM OF ISOTOPIC SPECIES OF CO

M. EIDELSBERG, J.-Y. RONCIN, A. LE FLOCH, F. LAUNAY, C. LETZELTER AND J. ROSTAS

The Vacuum Ultra-Violet Band Spectrum System $B^1\Sigma^+ - X^1\Sigma^+$ of 12C16O, 13C16O, 12C18O and 13C18O have been extensively studied at High Resolution in both Absorption and Emission.

In Absorption a band, observed in all isotopes, is shown to be B $\leftarrow$ X (v'=2,v"=0) with however anomalous vibrational spacing and rotational constants and a local perturbation.

Some of the observed emission bands have not been reported before even at low resolution and none at high resolution. All of them exhibit sharp breaking off typical of predissociation of CO, giving directly an improved upper limit for the Dissociation Energy of the ground state of CO into C(3P)+O(3P).

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FC9. (10:56)

ROTATIONALLY RESOLVED PHOTOELECTRON SPECTRA OF GAS PHASE NO

K. S. Viswanathan, Ellen Sekreta, W. G. Wilson and J. P. Reilly

Rotationally resolved photoelectron spectra of gas phase NO obtained by ionizing from specific rovibronic levels of the three Rydberg states, $A(^2\Sigma^+)$, $C(^2\Pi)$ and $D(^2\Sigma^+)$, will be presented. For the first time, rotational resolution in a photoelectron experiment has been achieved on a molecule other than H_2. These experiments were performed to understand the rotational propensity rules in photoionization. The results are in agreement with the theoretical predictions of Bonham [1,2] and can also be explained on the basis of the model used by Pratt et al. [3] in their work on H_2. Results on the angular distribution of photoelectrons will also be presented.

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[1] R. A. Bonham and M. L. Lively, Rev. A.29, 1224 (1984).
[2] R. A. Bonham, Private Communication, 1984.
[3] S. T. Pratt, P. M. Dehmer and J. L. Dehmer, J. Chem. Phys., 78, 4315 (1983).

TE13.

10 min.(5:09)
(Last Minute Addition)

INFRARED SPECTRUM OF PROTONATED ACETYLENE

MARK W. CROFTON AND TAKESHI OKA

We have observed some 300 lines which are most likely due to protonated acetylene H_2CCH^+. The band origin is at 3141.4 cm^{-1}. The rotational structure of the band fits approximately to a parallel ($\Delta K_a = 0$) band of the H_2CO-type classical structure but does not fit well to the usual asymmetric rotor pattern for high J levels. This is probably due to the theoretically predicted existence of the other (non-classical) structure and the very low barrier separating them[1,2,3]. Based on the ab-initio prediction by Raine and Schaeffer[3], we assign the band tentatively to the CH stretching mode of the classical structure.

The possibility of tunneling protons between the two equivalent classical forms through the non-classical form causes the "splitting" of levels. When the whole problem is treated by using D_{6h} symmetry, the "internal rotation" around the c-axis is also feasible.

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[1] J.A. Pople, Proceedings of the Robert A. Welch Foundation, XVI. Theoretical Chemistry, Houston, Texas (1973).

[2] J. Weber, M. Yoshimine and A.D. McLean, J. Chem. Phys. 64, 4159 (1976).

[3] G.P. Raine and H.F. Schaefer III, J. Chem. Phys. 81, 4034 (1984).

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