Forty-Third
symposium on
MOLECULAR
SPECTROSCOPY

THE OHIO STATE UNIVERSITY
June 13-17, 1988

UNDER THE SPONSORSHIP OF
THE DEPARTMENT OF PHYSICS
THE DEPARTMENT OF CHEMISTRY
THE GRADUATE SCHOOL
OF THE UNIVERSITY
AND
THE U.S. ARMY RESEARCH OFFICE
THE U.S. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
INFORMATION

INFORMATION. The location for dormitory accommodations is
Taylor Tower, Columbus, Ohio.

PROGRAM: This will take place at the Center for Tomorrow
(May 1st, 1970), preceded by a reception
and a program. The keynote speaker will be Kenneth Wilson from
the Ohio State University.

Please call for delivery during the Symposium to:
THE OHIO STATE UNIVERSITY. Department of Physics. The
Center for Tomorrow, 155 West 12th Avenue, Columbus, Ohio,
U.S.A.

REGISTRATION: Please purchase your parking permits when you check
in at the dorm or at the Registration Desk. These permits allow
you to park in the Northwood parking lot only. The permits must be displayed on the front windshield of your car.
In addition, you must follow all traffic rules to avoid the issuance of ticket.

REGISTRATION: The Registration Desk will be located in Front
123 Physics Laboratory. It will be kept open between
8:00 a.m. and 4:00 p.m. Monday through Friday. The
registration fee is $25.00 per participant and $50.00 if paid
by June 1. The special rate of $20.00 per Graduate Student will be
reduced to $10.00 if paid by June 1. Please send the complete
registration form along with your check by June 1.

SESSIONS: They will be held in: Independence Hall (2), Physics
Laboratory (4), and Evans Chemical Lab (5). Digits in parentheses
will 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
### 11. TITLE (Include Security Classification)

41st, 42nd, and 43rd International Symposium on Molecular Spectroscopy

### 12. PERSONAL AUTHOR(S)

K. Narahari Rao

### 14. DATE OF REPORT (Year, Month, Day)

15. PAGE COUNT

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### 16. SUPPLEMENTARY NOTATION

The 43rd Symposium on Molecular Spectroscopy was convened at Ohio State University during the period 13-17 June 1988. Over 300 scientists attended, representing research organizations from the US and fourteen foreign countries. Topical areas included electronic characteristics of molecules, energy transfer, infrared and microwave spectra, liquid and solid state phenomena, laser spectra, Raman spectra, molecular beams, vibrational analysis, and experimental techniques.
Professor E. BRIGHT WILSON
MONDAY, JUNE 13, 1988 -- 8:45 A.M.

Auditorium, Independence Hall

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

GREGORY P. LAFYATIS, Department of Physics,
The Ohio State University, Columbus, Ohio.

Plenary Session

OPENING REMARKS: J. C. GARLAND, Chairman, Department of
Physics, The Ohio State University.

MA1. TUNABLE DIODE LASER SPECTROSCOPY: PAST, PRESENT
AND FUTURE.................................35 min.

A. W. MANTZ, Laser Analytics, Inc.
25 Wiggins Avenue, Bedford,
Massachusetts, 01730.

MA2. THE VERSATILITY OF FOURIER TRANSFORM SPECTROSCOPY...35 min.

HENRY BUIJS, Bomem, Inc., 635 rue Marais,
Vanier, Quebec, Canada. G1M 2Y2.

MA3. THE TORSION-ROTATION SPECTRA OF ACCIDENTALLY SYMMETRIC
TOP MOLECULES: CARBODI-IMIDE, HNCNH, AND DISULFANE,
HSSH.................................35 min.

MANFRED WINNEWISSER, Physikalisch-Chemisches
Institut, Justus-Liebig-Universitat Giessen,
Heinrich-Buff-Ring 58, D-6300 Giessen,
West Germany.

Intermission

COBLENTZ PRIZE AND AWARD LECTURE (11:15 A.M. - 12 NOON)

MA4. PHASE-COHERENT MOLECULAR DYNAMICS AND PHASE-COHERENT
CHEMISTRY..........................30 min.

KEITH A. NELSON, Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts, 02139.

PLEASE NOTE:

BOTH THE PLENARY SESSIONS ON MONDAY AND
WEDNESDAY MORNINGS (JUNE 13 AND 15) WILL
START AT 8:45 A.M.
ME1. OPTICAL DESIGN OF EFFICIENT ABSORPTION SAMPLING SYSTEMS FOR FTIR SPECTROMETERS...10 min.(1:30)

W. B. Olson, Molecular Spectroscopy Division, National Bureau of
Standards, Gaithersburg, Maryland, 20899.

ME2. ULTRA-HIGH RESOLUTION WITH A BOMEM SPECTROMETER..................10 min.(1:41)

J.W.C. Johns, Herzberg Institute of Astrophysics, National Research
Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

ME3. SELECTIVE FOURIER TRANSFORM SPECTROSCOPY OF RADICALS..............10 min.(1:52)

M. Elhanine, R. Farrenq, and G. Guelachvili, Laboratoire d'Infrarouge,
Universite de Paris-Sud, 91405 Orsay, France.

ME3'. HIGH PRECISION IR SPECTROSCOPY: THE STATE OF THE ART AND ITS
EXPECTED LIMITATIONS..............................................................10 min.(2:03)

L. Henry and A. Valentin, Laboratoire de Physique Moleculaire et
Atmospherique, C.N.R.S. et Universite Pierre and Marie Curie,
4 place Jussieu, Paris 75005, France.

ME4. COMPUTATIONAL PROCEDURES IN INTERPRETING HIGH RESOLUTION SPECTRA
Invited Paper.................................................................30 min.(2:14)

O. L. Polyansky, Applied Physics Institute, USSR Academy of
Sciences, Gorky, USSR 603600.

ME5. ANALYSIS OF Fermi RESONANCES AND LOCAL MODES IN CHCl3 AND C2HCl2 USING AN
INTERNAL COORDINATE HAMILTONIAN.......................................15 min.(2:46)

L. Halonen, Department of Physical Chemistry, University of Helsinki,
Meritullinkatu 1 C, SF-00170 Helsinki, Finland.

Intermission

ME6. ROTATIONAL PARTITION FUNCTIONS FOR SYMMETRIC-TOP MOLECULES........15 min.(3:13)

Robin S. McDowell, University of California, Los Alamos National
Laboratory, Los Alamos, New Mexico, 87545.

ME7. CALCULATION OF THE VIBRATIONAL ENERGY LEVELS OF TRIATOMIC MOLECULES........15 min.(3:31)

Viktor Szalay, Herzberg Institute of Astrophysics, National Research
Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

ME8. VARIATIONAL CALCULATIONS OF ROTATION-VIBRATION ENERGIES FOR TRIATOMIC
MOLECULES.................................................................15 min.

Per Jensen, Physikalisch-Chemisches Institut, Justus-Liebig-Universitat
Giessen, Heinrich-Buff-Ring 58, D-6600 Giessen, West Germany.

ME9. DEGENERATE AND STRONGLY INTERACTING VIBRATIONAL STATES OF POLYATOMIC MOLECULES:
THE PROBLEMS IN ROTATIONAL ANALYSIS AND DETERMINATION OF SPECTROSCOPIC
CONSTANTS............................................................Invited Paper...........................30 min(3:47)

V. I. Tyuterev, Institute of Atmospheric Optics SB USSR Academy of
Sciences, I, Akademicheskii Avenue, Tomsk, 634055, USSR.

ME10. PERTURBATIONS OF THE DOMINANT APPROXIMATION IN SPHERICAL-TOP MOLECULES........15 min(4:19)

B. J. Krohn, University of California, Los Alamos National Laboratory,
Theoretical Division, Mail Stop 3569, Los Alamos, New Mexico, 87545;
and J.K.G. Watson, Herzberg Institute of Astrophysics. National Research
Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

ME11. ROVIBRONIC ENERGY LEVELS AND INTENSITIES OF ROVIBRONIC TRANSITIONS OF
NONLINEAR TRIATOMIC OPEN-SHELL RARE GAS COMPLEXES....................15 min.(4:35)

Wafa Fawzy, Department of Chemistry, Emory University, Atlanta,
Georgia, 30322; and Jon T. Hugen, Molecular Spectroscopy Division,
National Bureau of Standards, Gaithersburg, Maryland, 20899.
It is gratifying to note that we have received an excellent response for this Bright Wilson Symposium on Molecular Spectroscopy. We need your help in the smooth conduct of the various contributed paper sessions. We have normally indicated a two-minute discussion period for each of the contributed papers. This year it became necessary to show only a one minute discussion time in some of the sessions to avoid having to schedule papers on Friday afternoon. We hope it would be possible for the speakers of 15 minute papers in these sessions to plan to talk for a minute or two less. That should surely help remove the pressures on everyone. The chairmen of these sessions will surely not want to prolong them beyond the scheduled periods. Thank you for your cooperation.
MONDAY, JUNE 15, 1988 -- 1:30 P.M.
Room 1009, Physics Laboratory

Chairman Before Intermission: COLIN FURION, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada.

Chairman After Intermission: T. K. BALASUBRAMANIAN, Spectroscopy Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay, India.

MF1. SPECTROSCOPY AND PHOTOPHYSICS OF REFRACTORY MOLECULES AT LOW TEMPERATURE.
THE GREEN SYSTEMS OF ZRS. ........................................... 10 min. (1:30)

MF2. NEW INFRARED ELECTRONIC SPECTRA OF C2 AND SiC. ........................................... 15 min. (1:41)
M. DOUY, ISEM, Universite des Sciences et Techniques de Lille, 59655 Villeneuve d’Ascq, France; R. A. NIELMANN, C. R. BRAZIER, I. C. O’REILLEN, P. F. BERNAULT, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721, S. A. ROGERS, Department of Chemistry, University of Colorado, Boulder, Colorado, 80309; and A. D. MCLEAN, IBM Research Laboratory, San Jose, California, 95120.

MF3. HIGH RESOLUTION LASER SPECTROSCOPY OF OH. ........................................... 15 min. (1:56)
D. J. RUBENS and P. J. SARRE, Department of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom.

MF4. ELECTRONIC SPECTROSCOPIC STUDIES AT BHABHA ATOMIC RESEARCH CENTRE
.................................................................Specially Requested........................................... 15 min. (2:12)
T. K. BALASUBRAMANIAN and S. L. N. G. KRISHNAMCHIARI, Spectroscopy Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay-400 085, India.

MF5. MAGNETIC DIPOLE TRANSITIONS IN DIATOMIC MOLECULES: SOME NEGLECTED ASPECTS. ....... 10 min. (2:24)
T. K. BALASUBRAMANIAN and V. P. BELLARY, Spectroscopy Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay-400 085, India.

MF6. ON THE WIGNER - WITMER CORRELATION RULES IN DIATOMIC MOLECULES. ................. 10 min. (2:39)
T. K. BALASUBRAMANIAN and V. P. BELLARY, Spectroscopy Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay-400 085, India.

Intermission

MF7. THE ELECTRONIC SPECTRUM OF MANGANESE MONOHYDRIDE. ........................................... 15 min. (3:00)
W. J. BALFOUR, Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada, V8W 2Y2; B. LINDGREN, Institute of Physics, University of Stockholm, Vandelisvägen 9, S-113 46 Stockholm, Sweden; and S. O’DONNOR, Department of Physics, University College Du’lin, Stillorgan Road, Belfield, Dublin, Eire.

MF8. VUV ABSORPTION SPECTROSCOPY OF SUPERSONIC JET-COOLED MOLECULES: THE SCHUMANN-RUNGE BANDS OF OXYGEN. ........................................... 10 min. (3:16)
K. YOSHINO, W. H. PARKINSON, D. E. FREEMAN, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, Massachusetts, 02138; and A. S. C. CHEUNG, Department of Chemistry, University of Hong Kong, Hong Kong.

MF9. LEVEL SHIFTS IN THE 3s + STATE OF MOLECULAR OXYGEN. ........................................... 15 min. (3:27)
R. S. FRIEDMAN and A. BACARD, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, Massachusetts, 02138. Also for FRIEDMAN: Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

MF10. BAND OSCILLATOR STRENGTHS OF THE SCHUMANN-RUNGE ABSORPTION BANDS OF MOLECULAR OXYGEN. ........................................... 15 min. (3:43)
R. S. FRIEDMAN, Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, Massachusetts, 02138 and Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.
THE RECENT DEMISE OF DR. M. R. ALIEV A DISTINGUISHED THEORIST OF THE U.S.S.R. ACADEMY OF SCIENCES, DURING A BRIEF SOJOURN IN CANADA IS DEEPLY REGRETTED.
A.

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Z.
THE FOLLOWING THREE CONFERENCES MAY BE OF INTEREST TO THE MOLECULAR SYMPOSIUM PARTICIPANTS:

SEPTEMBER 5-9, 1988
Xth International Conference on High Resolution Infrared Spectroscopy
Liblice near Prague

FOR MORE INFORMATION CONTACT:
Dr. Dusan Papousek
Czechoslovak Academy of Sciences
Dolejsova ul 3
182 23 Praha 8
Czechoslovakia

NOVEMBER 2-7, 1988
International Conference on Raman Spectroscopy and Raman Centenary Celebration
Calcutta, India

Prof. S. B. Banerjee
Indian Association for the Cultivation of Science
Calcutta 700 032, India

JUNE 19-23, 1989
7th International Conference on Fourier Transform Spectroscopy
George Mason University
Fairfax, Virginia

Dr. Robert F. Cozzens
George Mason Institute
George Mason University
Fairfax, VA. 22030-4444
SO FAR, THE FOLLOWING INVITED SPEAKERS HAVE ACCEPTED TO PRESENT PAPERS:

PETER BERNATH, UNIVERSITY OF ARIZONA
WOLFGANG E. ERNST, FREIE UNIVERSITAT BERLIN
ROBERT W. FIELD, MASSACHUSETTS INSTITUTE OF TECHNOLOGY
PER JENSEN, UNIVERSITAT GIESSEN
ROGER E. MILLER, UNIVERSITY OF NORTH CAROLINA
TUESDAY, JUNE 14, 1983 -- 8:30 A.M.
Room 1153, Physics Laboratory

Chairman Before Intermission: C. AMAT, Laboratoire de Physique Moleculaire et Atmospherique
Universite Pierre et Marie Curie et C.N.R.S.,
75252 Paris Cedex 05, France.

Chairman After Intermission: J. S. MUENTER, Department of Chemistry,
University of Rochester, Rochester, New York.

TA1. AN OVERVIEW OF CURRENT RESEARCH AT GORKY-RAD SPECTROMETER AND MOLECULAR
COMPLEXES............................. 30 min.(8:30)
A. F. KRUPNOV and E. N. KARYAKIN, Applied Physics Institute, USSR
Academy of Sciences, Gorky, USSR 603600.

TA2. UPTHERMAL-INFRARED AND PULSED-NOZZLE FOURIER-TRANSFORM MICROWAVE
SPECTROSCOPY OF RARE GAS-CO₂ COMPLEXES....................... 15 min.(9:05)
G. T. FRASER, A. S. PINE, and R. D. SUENRAM, Molecular Spectroscopy
Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

TA3. VIBRATIONAL PREDISSOCIATION IN THE CO₂ DIMER AND TRIMER AND RARE GAS-CO₂
COMPLEXES........................................ 15 min.(9:30)
A. S. PINE and G. T. FRASER, Molecular Spectroscopy Division,
National Bureau of Standards, Gaithersburg, Maryland, 20899.

TA4. VIBRATIONAL, ROTATIONAL, AND TUNNELING DEPENDENCE OF VIBRATIONAL
PREDISSOCIATION IN THE HF DIMER.................. 15 min.(9:45)
A. S. PINE and G. T. FRASER, Molecular Spectroscopy Division,
National Bureau of Standards, Gaithersburg, Maryland, 20899.

TA5. UPTHERMAL SPECTROSCOPY OF HF COMPLEXES WITH CO₂, OCS, AND NO........ 15 min.(4:51)
G. T. FRASER and A. S. PINE, Molecular Spectroscopy Division,
National Bureau of Standards, Gaithersburg, Maryland, 20899.

TA6. INFRARED AND MICROWAVE INVESTIGATIONS OF INTERCONVERSION TUNNELING
IN THE ACETYLENE DIMER.................... 20 min.(10:07)
G. T. FRASER, R. D. SUENRAM, F. J. LOVAS, A. S. PINE, J. T. HOUGEN,
W. J. LAFFERY, Molecular Spectroscopy Division, National Bureau
of Standards, Gaithersburg, Maryland, 20899; and J. S. MUENTER,
Department of Chemistry, University of Rochester, Rochester,
New York, 14627.

Intermission

TA7. LASER-INDUCED FLUORESCENCE MOLECULAR-BEAM OBSERVATIONS OF THE HYPERFINE
STRUCTURE IN THE NO₂ SPECTRUM AT 593.5 nm AND 585.1 nm........ 15 min.(10:40)
A. G. ADAM, M. C. L. GERRY, A. J. MERER, D. M. STEUNENBERG, Department of
Chemistry, University of British Columbia, Vancouver, British Columbia,
Canada, V6T 1Y6; and I. OZIER, Department of Physics, University of

TA8. MOLECULAR BEAM OBSERVATIONS OF HYPERFINE TRANSITIONS IN KOH........ 10 min.(10:56)
J. CEDERBERG, D. RIOUX, D. NITZ, and D. OLSON, Department of Physics,
St. Olaf College, Northfield, Minnesota, 55057.

TA9. OBSERVATION OF (H₂O)₂ K=1 TRANSITIONS OF E SYMMETRY AND DISCUSSION OF
NUCLEAR HYPERFINE SPLITTINGS.................. 15 min.(11:07)
A. HC and T. R. DYKE, Department of Chemistry, University of Oregon,
Eugene, Oregon, 97403.

TA10. ROTATIONAL SPECTRA OF CARBOXYLIC ACID DIMERS..................... 15 min.(11:23)
K. KRESA and A. BAUDER, Laboratorium für Physikalische Chemie,
Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.

TA11. E2 WILL BE PRESENTED HERE (D. DAYTON).......................... 10 min.(11:39)

TA12. E3 WILL BE PRESENTED HERE (Z. S. HUANG)......................... 10 min.(11:50)
TUESDAY, JUNE 14, 1988 -- 8:30 A.M.
Room 1009, Physics Laboratory

Chairman Before Intermission: W. A. KREINER, Abteilung Physikalische Chemie, University of Ulm, Ulm, West Germany.

Chairman After Intermission: D. F. EGGER, Department of Chemistry, University of Washington, Seattle, Washington.

TB1. ANALYSIS OF THE v_6 BAND IN CH_DF, AND ASSIGNMENT OF SOME SMMW LASER LINES .......................................................... 15 min.(8:30)
D. F. EGGER, Department of Chemistry BG-10, University of Washington, Seattle, Washington 98195; W. LEWIS-BEVA, M.C.L. GERRY, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, VT6 Y6; Y. S. TOBIN, and T. W. DALEY, U.S. Army Electronics Research and Development Command, Harry Diamond Laboratories, 2900 Powder Mill Road, Adelphi, Maryland, 20783.

TB2. THE INFRARED SPECTRUM OF AMINODEFLUOROBORINE, NHBF_3: PARTIAL ASSIGNMENT OF THE FUNDAMENTALS AND ANALYSIS OF THE 2_v_6 BAND-NEAR 1608 CH^-1 ....................... 15 min.(9:00)
W. LEWIS-BEVA, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois, 62901; H. M. JESM, Scitex Ltd New Zealand Limited, 60-66 France Street, South New, P.O. Box 68-232, Auckland, New Zealand; and M.C.L. GERRY, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada, VT6 Y6.

TB3. HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CH_2=O: THE v_8 BAND AT 1435 CM^-1 .................. 15 min.(9:02)
R. D'CUNHA, P. K. WAHL, Y. B. KARTHA, Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India; and A. WEBER, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

TB4. INFRARED-INFRARED FOUR-LEVEL DOUBLE RESONANCE IN NH_3 .................................................. 15 min.(9:18)
TUTAKI MATSUKO, R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824; and SANG K. LEE, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

TB5. LINEAR AND NONLINEAR SPECTROSCOPY BY USE OF MICROWAVE MODULATION SIDEBANDS IN THE CO LASER REGION .............................................. 15 min.(9:34)
SHIN-CHU HSU and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

Intermission

TB6. HIGH RESOLUTION INFRARED STUDY OF THE v_2 BAND OF CD_3I ................................................. 15 min.(10:00)
HAN-G. CHO and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

TB7. STARK EFFECT OBSERVATIONS WITH IR LASER SIDE BANDS .................................................. 15 min.(10:16)
W. A. KREINER, H. PRINZ, W. HÖHE, Abteilung Physikalische Chemie, University of Ulm, P.O.B. 4066, D-7900 Ulm, West Germany; and C. MÀGERL, Institut für Nachrichtentechnik, Technische Universität Wien, Gusshausstr. 25, A-1040 Wien, Austria.

TB8. COLOR CENTER LASER SPECTROSCOPY OF C_2H AND C_2H .................................................. 15 min.(10:32)
J. W. STEPHENS, M. L. RICHNOW, and R. F. CURL, Department of Chemistry, Rice University, Houston, Texas, 77251.

TB9. INFRARED-RADIOFREQUENCY DOUBLE RESONANCE SPECTROSCOPY OF CH_3F USING A COLOR CENTER LASER .................................................. 15 min.(10:48)
C. J. PURSELL, W. C. HO, T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637; and P. SCAPPINI, Istituto Di Spettrofobia Molecolare Del C.N.R., Via De' Castagnoli 1, 40126 Bologna, Italy.

TB10. THE INFRARED SPECTRUM OF THE FOUR LOWEST FUNDAMENTAL BANDS OF NITRIC ACID .................... 15 min.(11:04)
A. G. MÁKI, W. B. OLSON, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899; R. ESCRIBANO, Instituto de Electromagnetismo de la Materia, Serrano 119 - 28006 Madrid, Spain; A. GOLEMAN, Department of Physics, University of Denver, Denver, Colorado, 80208; J. BURKHOLDER, and C. H. HOWARD, NOAA Aeronomy Laboratory, 325 Broadway, Boulder, Colorado, 80303.
TH11. A FORBIDDEN BAND IN THE FAR INFRARED SPECTRUM OF $\text{H}^{13}\text{CN}$. ........................................ 14 min. (11:20)

M. WINNEKISSE, G. WAGNER, and B. P. WINNEKISSE, Physikalisch-Chemisches Institut, Justus Liebig Universität, D-6300 Giessen, West Germany.

TH12. THE LOWEST SKELETAL BENDING MODE OF $\text{N}_2\text{O}_3$ IN THE GAS PHASE. ......................... 10 min. (11:30)

F. DELIOT, Department of Physics, Duke University, Durham, North Carolina, 27706; M. WINNEKISSE, B. P. WINNEKISSE, Physikalisch-Chemisches Institut, Justus Liebig Universität, D-6300 Giessen, West Germany; and G. PAWELEK, FB 9, Anorganische Chemie, Gesamthochschule Kuppertal, D-5000 Kuppertal 1, West Germany.

TH13. HIGH RESOLUTION INVESTIGATION OF $\text{CH}_3\text{CO}$ IN THE INFRARED. ............................ 10 min. (11:47)

J. KLEINER, M. GODFROID, M. HERMAN, Laboratoire de Chimie Physique Moleculaire - CP 100, Université Libre de Bruxelles, Faculté des Sciences, 50, av. F.D. Roosevelt, B-1050 Bruxelles, Belgium; M. B. MARSHALL, Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002; J.W.C. JOHNS, and A.R.W. McKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

TH14. MOLECULAR BEAM SPECTRUM OF THE PERTURBED C-H STRETCHING REGION OF FLUOROFORM. 15 min. (11:58)

A. S. PINE, G. T. FRASER, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899; and J. PLIVA, Department of Physics, Pennsylvania State University, University Park, Pennsylvania, 16802.
TC1. PHOTO-CRACKING OF JET-COOLED DTTC WITH.................................15 min.(8:59)
   S. K. YEH and L. D. KOELSCH, Department of Chemistry, University of
   Cincinnati, Cincinnati, Ohio, 45221.

TC2. PHOTO-CRACKING OF DTTC AT THE SINGLE THRESHOLD..............................15 min.(8:47)
   L. CHEN, W. N. H. CHEN, J. L., and C. BRADLEY MOORE, Department
   of Chemistry, University of California-Berkeley, Berkeley, California, 94720.

TC3. PHOTOCHEMICAL INVESTIGATIONS OF THE VIBRATIONAL ENERGY DEPENDENCE
   OF INTER-LIGAND ELECTRON TRANSFER IN TRANSITION METAL COMPLEXES...............15 min.(9:04)
   I. K. OAKEN and J. R. HOPKINS, Department of Chemistry, Louisiana
   State University, Baton Rouge, Louisiana, 70803.

TC4. INVESTIGATION OF THE RESPONSE OF THE NO, N2, SYSTEM TO AN INTENSE
   OPTICAL PERTURBATION........................................10 min.(9:21)
   M. VAN ROOIJENMAEL, Y. DE WILDE, M. HERNAY, Laboratoire de Chimie
   Physique Moleculaire - CP 112, Universite Libre de Bruxelles,
   Bruxelles des Sciences, 50, ave F. D. Roosevelt, Bruxelles, Belgium; and
   F. MILLER, Department of Physics, Lowell University, Lowell, Massachusetts, 01854.

TC5. NON-LINEAR INVERSION ANALYSIS OF THE SINGLET MOLECULAR
   OXYGEN-INDUCED REACTION AND POPULATIONS OF THE 2,1 AND 1,0 STATES
   THROUGH NON LINEAR INVERSION OF EMISSION SPECTRA..................................................15 min.(9:33)
   D. CERNY, R. BACIS, Laboratoire de Spectrometrie Ionique et Moleculaire,
   43 Bd du 11 November 1918, 69622 Villeurbanne, France; and J. VERGES,
   Laboratoire AIM, CNRS 11, 91405 Orsay, France.

TC6. LASER EXCITED SPECTRA OF THE SINGLET MOLECULAR OXYGEN-INDUCED REACTION
   AND POPULATIONS OF INTERMEDIATE STATES..........................................................15 min.(9:50)
   P. CROZET, R. BACIS, A. BOUVIER, A. J. BOUVIER, and S. CHURASSY,
   Laboratoire de Spectrometrie Ionique et Moleculaire, 43 Bd du 11
   November 1918, 69622 Villeurbanne, France.

TC7. J-REORIENTATION IN THE H2CO \( 1 \Lambda_g^{(1)} \) \( \chi_{1} \) ROTATIONAL LEVEL......................15 min.(10:07)
   S. HALL, S. L. COY, R. J. SHELLEY, R. W. FIELD, Department of Chemistry,
   Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139;
   and J. L. KINSEY, Rice School of Natural Sciences, Rice University,
   Houston, Texas, 77005.

TC8. PRESSURE BROADENING OF THE ATOMIC IODINE \( 5^2P_{1/2} \) \( 5^2P_{3/2} \) TRANSITION.................................10 min.(10:24)
   D. CERNY, M. AUBERT-FRECON, R. BACIS, B. BUISSERY, Laboratoire de
   Spectrometrie Ionique et Moleculaire, 43 Bd du 11 November 1918,
   69622 Villeurbanne, France; and J. VERGES, Laboratoire AIM
   Cotton, CNRS 11, 91405 Orsay, France.

Intermission

TC9. INTERMEDIATE CASE LEVEL STRUCTURE IN INFRARED SPECTRA: EVIDENCE FOR BOTH
   ANHARMONIC AND CONTOHIS COUPLING IN THE C-H REGION OF 1-BUTYNE..................10 min.(10:50)
   A. M. DE SOUZA, DEVINDER KAUR, S. A. HAMMAD, G. A. BETHARDY,
   and D. DAVIDE PERRY, Department of Chemistry, University of Akron,
   Akron, Ohio, 44325.

TC10. A MODIFIED RRKM APPROACH TO THE VIBRATIONAL PRE-DISSOCIATION DYNAMICS
   OF THE S1 p-DIFLUOROBENZENE-Ar VAN DER WAALS COMPLEX..............................15 min.(11:02)
   H.-H. KEUN SHIEN-MING CHIN, S. C. PARMETER, Department of Chemistry,
   Indiana University, Bloomington, Indiana, 47405.

TC11. OBSERVATIONS OF ROTATIONALLY AND VIBRATIONALLY INELASTIC SCATTERING
   FROM AN EXCITED STATE POLYATOMIC: S1 GLYOXAL.................................15 min.(11:19)
   K. W. BUTZ, H. DU, C. S. PARMETER, Department of Chemistry, Indiana
   University, Bloomington, Indiana, 47405; and D. KRJANOVICH, IBM
   Almaden Research Center, 650 Harry Road, San Jose, California, 95120.
TC12. ENERGY DEPENDENCE OF THE INELASTIC COLLISION CROSS SECTION OF VIBRATIONALLY EXCITED I₂ (v = 35, 15) WITH He.................................15 min.(11:36)

K. W. BUTZ, H. DU, C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405; and D. J. KRAJNOVICH, IBM Almaden Research Center, 650 Harry Road, San Jose, California, 95120.

TC13. MEASUREMENTS OF VIBRATIONAL DEPHASING OF CO ADSORBED ON NaCl(100)..................15 min.(11:53)

HUGH H. RICHARDSON, Department of Chemistry, Ohio University, Athens, Ohio, 45701; HUAN-CHENG CHANG, and GEORGE E. EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.
TUESDAY, JUNE 14, 1988 -- 9:00 A.M.
Room 1008, Evans Chemical Laboratory

Chairman: RUSSELL H. BARNES, Battelle Memorial Institute, Columbus, Ohio.

TD1. HIGH RESOLUTION OPTICAL SPECTRA OF BENZOPHENONE UNDER HIGH PRESSURE..................15 min.(9:00)
I. Y. CHAN and W. M. CHUNG, Department of Chemistry, Brandeis University, Waltham, Massachusetts, 02254.

TD2. OPTICALLY DETECTED MAGNETIC RESONANCE OF Mn(IV) HEXAFLUORIDE IN Cs2GeF6
AND K2GeF6..................................................15 min.(9:17)
E. LIFSHITZ and A. H. FRANCIS, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

TD3. ANALYSIS OF THE MID-IR ELECTRONIC ABSORPTION SPECTRUM OF Fe2P3S6
AND Co2P3S6..................................................15 min.(9:34)
N. NAGASUNDARAM and A. H. FRANCIS, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

TD1. 7:14 WILL BE PRESENTED HERE (STELLA M. SUNG).................................15 min.(10:00)
TD2. 7:15 WILL BE PRESENTED HERE (M. SAWAMURA).................................15 min.(10:16)
TD3. 7:16 WILL BE PRESENTED HERE (R. B. ROSS).................................15 min.(10:32)
TD4. 7:17 WILL BE PRESENTED HERE (J. M. POWERS).................................15 min.(10:48)
TD5. 7:18 WILL BE PRESENTED HERE (SUSAN KRAFT).................................15 min.(11:04)
TD6. 7:19 WILL BE PRESENTED HERE (M. LARSSON).................................10 min.(11:15)
TD7. 7:23 WILL BE PRESENTED HERE (MICHAEL A. KAHLOW).............................10 min.(11:26)
TD8. 7:24 WILL BE PRESENTED HERE (C. F. CHALOWSKI).............................10 min.(11:37)
TD9. 7:25 WILL BE PRESENTED HERE (CARY F. CHALOWSKI).............................10 min.(11:48)
Recent Studies in High-Resolution Spectroscopy of Atmospheric Gases

Invited Paper

H. S. JPV, Institute of Atmospheric Physics, Academy of Sciences, Moscow, USSR.

New High-Resolution Spectra of O$_3$ in the 3-µm Region

M. A. H. Smith, Atmospheric Sciences Division, NASA Langley Research Center, Hampton, Virginia.

Line Intensities and Collision-Broadened Line Width Measurements in the v$_1$ Fundamental of 18O$_2$ at Atmospheric Temperatures

S. Chudamani and P. Varanasi, Laboratory for Planetary Atmospheres, State University of New York, Stony Brook, New York.

Line Width Variations in the Infrared Band of N$_2$O Perturbed by N$_2$

Cai Peipei, Shen Shangxiong, Yu Haiping, and I-Shan Cheng, Department of Physics, East China Normal University, Shanghai, People’s Republic of China.

Absolute Intensities in the v$_2$ Region of CO$_2$


Studies Concerning the Optimum Hamiltonian for Use in Large Amplitude, Direct Numerical Diagonalization Calculations

Richard B. Wattson, Visidyne, Inc., 10 Corporate Place, S. Bedford St., Burlington, Massachusetts, 01803.

Calculations of Energies and Intensities for the Asymmetric Species of CO$_2$

R. B. Wattson, A. Newburgh, R. Pavelle, Visidyne, Inc., 10 Corporate Place, S. Bedford St., Burlington, Massachusetts, 01803; and L. S. Rothman, Optics Division, Air Force Geophysics Laboratory, Hanscom AFB, Massachusetts, 01731.

CO$_2$ Spectroscopic Constants Determined by Global Least-Squares Fitting and Direct Numerical Diagonalization

Robert Hawkins, Laurence S. Rothman, Optics Division, Air Force Geophysics Laboratory, Hanscom AFB, Massachusetts, 01731; and Richard B. Wattson, Visidyne, Inc., 10 Corporate Place, S. Bedford St., Burlington, Massachusetts 01803.
F.11. SIMPLIFIED EXPRESSION FOR THE TOTAL INTERNAL PARTITION FUNCTION OF TEMPERATURE................................. 10 min. (4:39)

ROBERT R. GAMACHE, The Center for Atmospheric Research, University of Lowell, Lowell, Massachusetts, 01854; ROBERT HAWKINS, and LAURENCE S. ROHRMAN, Optics Division, Air Force Geophysics Laboratory, Hanscom AFB, Massachusetts, 01731.

F.12. TEMPERATURE DEPENDENCE OF LINE BROADENING OF CO2 LASER BAND ................. 10 min. (4:50)

CAL PEELER, SHAN SHANXION, XU JIDONG, and I-SHAN CHENG, Department of Physics, East China Normal University, Shanghai, 200062, People's Republic of China.
TUESDAY, JUNE 14, 1988 -- 1:30 P.M.
Room 1009, Physics Department

Chairman Before Intermission: L. H. COUDERT, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland.

Chairman After Intermission: C. DEMUYCK, Universite de Lille I, Laboratoire de Spectroscopie Hertzienne, Villeneuve d'Ascq, France.

TF1. MEASUREMENT OF THE STARK EFFECT IN A FLYGARE-BALLE MICROWAVE SPECTROMETER............15 min.(1:30)
T. EMILSSON and H. S. GUTOWSKY, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.

TF2. NOZZLE DESIGN FOR A FLYGARE-BALLE MICROWAVE SPECTROMETER.............................15 min.(1:47)
T. D. KLOTS, T. EMILSSON, and H. S. GUTOWSKY, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.

TF3. CHARGE REARRANGEMENT IN (HCN)2 AND (HCN)3 ..........15 min.(2:04)
R. S. RUOFF and H. S. GUTOWSKY, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.

TF4. INDIVIDUAL HYDROGEN-BOND LENGTHS IN HYDROGEN-BONDED TRIMERS........15 min.(2:21)

TF5. EMISSION FREQUENCY OF THE 496 um LINE IN CH3F AS A FUNCTION OF PRESSURE AND PUMP OFFSET BY INFRARED-SUMM DOUBLE RESONANCE TECHNIQUES............15 min.(2:38)
R. L. CROWNOVER, F. C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706; and D. D. SKATRUD, Army Research Office, Research Triangle Park, North Carolina, 27709.

TF6. A COLLISIONAL ENERGY TRANSFER MAP INCLUDING ÂK PROCESSES IN CH3F........15 min.(3:05)
HENRY EVERITT and FRANK C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

TF7. VERY LOW TEMPERATURE SPECTROSCOPY IN A COLLISIONALLY COOLED CELL: PRESSURE BROADENING STUDIES BETWEEN 4.2K AND 1.8K............................15 min.(3:22)
D. R. WILLEY, R. L. CROWNOVER, D. N. BITTNER, and F. C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

TF8. AN IAN FIT OF THE MICROWAVE SPECTRUM OF DIVINYL ETHER.............................15 min.(3:39)
L. H. COUDERT, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

TF9. TWO-DIMENSIONAL MICROWAVE FOURIER TRANSFORM SPECTROSCOPY............................15 min.(3:56)
B. VOGEILSANGER, M. ANDRIST, and A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.

TF10. ROTATIONAL SPECTRUM AND RING PUCKERING OF CYCLOBUTANE-1,1-d2........15 min.(4:13)
B. VOGEILSANGER, R. MEYER, A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland; and W. CAMINATI, Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale del Risorgimento 4, 1-40136 Bologna, Italy.

TF11. MICROWAVE SPECTRUM, CONFORMATIONAL ANALYSIS, AND BARRIERS TO INTERNAL ROTATION OF CIS-1-FLUORO-2-BUTENE..........................10 min.(4:30)
D. T. DURIG, Departments of Chemistry and Physics, University of the South, Sewanee, Tennessee, 37375; HOWARD Z. QIU, T. S. LITTLE, and J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

TF12. MICROWAVE SPECTRUM, BARRIERS TO INTERNAL ROTATION AND STRUCTURE OF METHYL FLUOROFORMATE..................10 min.(4:42)
C. L. TOLLEY, T. S. LITTLE, and J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.
TUESDAY, JUNE 14, 1988 -- 1:30 P.M.
Room 1005, Physics Laboratory

Chairman: PRABHAKAR MISRA, Department of Chemistry, Ohio State University, Columbus, Ohio.

TG1. THE X-Y BAND SYSTEM OF C2D2: IR CONSTANTS OF THE TRANSBENDING LEVELS ............ 10 min.(1:30)
    T. R. HUET, and M. HERMAN, Laboratoire de Chimie Physique Moléculaire - CP. 160, Université Libre de Bruxelles, Faculté des Sciences, 50, av. F. D. Roosevelt, B-1050 Bruxelles, Belgium.

TG2. THE X-Y BAND SYSTEM OF C2D2: ROVIBRONIC INFORMATION ON THE 3 STATE ............ 10 min.(1:41)
    T. R. HUET and M. HERMAN, Laboratoire de Chimie Physique Moléculaire - CP. 160, Université Libre de Bruxelles, Faculté des Sciences, 50, av. F. D. Roosevelt, B-1050 Bruxelles, Belgium.

TG3. HIGH RESOLUTION INVESTIGATION OF THE 3A_u STATE OF GLYOXAL .................... 10 min.(1:52)
    F. VANHORENBEKE, J. VANDER AUWERA, M. HERMAN, Laboratoire de Chimie Moleculaire - CP. 160, Université Libre Bruxelles, Faculté des Sciences, 50, av. F. D. Roosevelt, B-1050 Bruxelles, Belgium; and M. VERVLOET, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

TG4. ZEEMAX STUDIES OF MICROWAVE-OPTICAL DOUBLE RESONANCE SIGNALS IN THE 1A_1-1A_2 SYSTEM OF THIOFORMALDEHYDE .................... 15 min.(2:03)
    W. HÜTTER, Abteilung Chemische Physik, Universität Ulm, D-7900 Ulm, West Germany; J. C. PETERSEN, Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama, 35486; and D. A. RAMSAY, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

TG5. THE VIBRONIC SPECTRUM OF SELENOFORMALDEHYDE IN THE NEAR INFRARED .................... 10 min.(2:19)
    R. H. JUDGE, Department of Chemistry, University of Wisconsin-Parkside, Kenosha, Wisconsin, 53141; D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, Kentucky, 40506; and D. C. MOULE, Department of Chemistry, Brock University, St. Catharines, Ontario, Canada, L2S 3A1.

TG6. THE INTRASHELL ROTATION AND INVERSION MOTIONS OF THIOACETALDEHYDE IN ITS FIRST TRIPLET 3A_e ELECTRONIC STATE ............ 10 min (2:30)
    D. C. MOULE, Department of Chemistry, Brock University, St. Catharines, Ontario, Canada, L2S 3A1; Y. G. SMEYERS, and A. NINO, Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas, c/Serrano, 119, 28006 Madrid, Spain.

TG7. ON THE ASSIGNMENT OF THE EXCITED SINGLET STATES IN THE CO2 MOLECULE ............ 10 min.(2:41)
    P. J. KNOWLES, P. BOUSIS, University Chemical Laboratory, University of Cambridge, Cambridge, United Kingdom; and H. J. WERNER, Department of Chemistry, University of Bielefeld, Bielefeld, Germany.

TG8. CHEMOLUMINESCENCE SPECTRA OF SMALL MOLECULES CONTAINING SULFUR, SELENIUM, AND TELLURIUM .............................................. 15 min.(2:52)
    R. J. CLINSEK, Department of Chemistry, Tennessee Technological University, Cookeville, Tennessee, 38505.

   Intermission

TG9. STEADY STATE PRODUCTION OF THE HNCO IN THE GAS PHASE BY HYDROGEN ABSTRACTION FROM CYANAMIDE .................... 10 min.(3:20)
    P. E. FLEMING, C. W. MATHEWS, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and M. WINNEWISSER, Physikalisch-Chemisches Institut der Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-6300 Giessen, Federal Republic of Germany.

TG10. PICOSECOND ABSORPTION SPECTROSCOPY OF TRANSIENT CONDENSED PHASE RADICALS IN THE SPECTRAL REGION OF 200nm - 300nm .................... 15 min.(3:31)
    D. R. ANDERSON and J. B. HOPKINS, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70803.

TG11. HIGH RESOLUTION LASER SPECTROSCOPY OF AROMATIC IONS AND FREE RADICALS ............ 15 min.(3:47)
    JAMES M. WILLIAMSON, LIAN YU, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and STEPHEN C. FOSTER, Department of Chemistry, Florida State University, Tallahassee, Florida, 32306.
I. ANALYSIS OF ROTATIONALLY RESOLVED SPECTRA OF THE 5\(^{2}P_{3/2} - 5\(^{2}P_{5/2}\) BAND OF CYCLOPROPADIENYL RADICALS

IAI. C. BROWN, V. M. W. STEWART, and P. F. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210, and S. M. R. FOSTER, Department of Chemistry, Florida State University, Tallahassee, Florida, 32306.

II. rotational analysis of the 7\(^{2}S_{1/2} - 7\(^{2}P_{3/2}\) TRANSMISSION OF CH\(_2\)F\(_2\) AND CH\(_{2}\)F\(_{3}\)

MAHER, D., P. M. DAVIES, L. A. W. BOW, and S. M. R. FOSTER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210, and S. M. R. FOSTER, Department of Chemistry, Florida State University, Tallahassee, Florida, 32306.

III. LASER-INDUCED FLASHER SPECTROSCOPY OF NO\(_{2}\), EFFECTS OF ORBITAL ANGULAR MOMENTUM AND OBSERVATIONAL PARAMETERS

M. TOELLER, Laboratoire de Physique Université Laval, C.P. 1070, Quebec, Canada, G1K 7P4, and G. E. STERN, CNRS, France.

IV. LASER SPECTROSCOPY OF ALKALI EARTH MONOCARBOXYLATES AND MONOFORMAMIDES


V. THE STRUCTURAL ANALYSIS OF THE 5\(^{2}S_{1/2} - 5\(^{2}P_{3/2}\) TRANSITION OF CALCIUM BOROHYDRIDE

A. M. E. BORGEDER, F. G. PIANI, T. C. KELLER, and F. R. BERNATH, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.
EL-BAY, MH, P.O. Box 14, P.O.S., 1:30 P.M.

Intermission


TRIETEAU, JL, Laboratoire de Chimie Physique, Université de Lille, France.

Dyson, J.F., Chemistry Department, Berkeley, California.

Till, R., Laboratoire de Chimie Physique, Université de Lille, France.

SMYTH, R.G., Chemistry Department, University of Western Ontario, Canada.

Asymmetric Top Contour Simulation and Vibrational Spectra of Isopropyl Formate

R. S. Lee, J. Laane, Department of Chemistry, Texas A&M University, College Station, Texas, 77843; and B. J. van der Veken, Laboratory of Organic Chemistry, University of Antwerp, Universiteitsplein 1, 2018 Antwerp, Belgium.

Intermission

Dines, M., A.M. University, College Station, Texas, 77843.

Brazel, M., Department of Chemistry, Texas A&M University, College Station, Texas, 77843.

Applications of Molecular Mechanics to the Conformational Analysis of Ring Molecules

R. S. Lee, C. Cooper, and J. Laane, Department of Chemistry, Texas A&M University, College Station, Texas, 77843.

Rotary, Laboratory, University of Western Ontario, Canada.
VIBRATIONAL SPECTROSCOPY AND POTENTIAL ENERGY SURFACES FOR THE OUT-OF-PLANE MOTIONS OF CYCLOHEXENE AND SOME ANALOGUES

J. LAANE, M. M. TECKLENBURG, Department of Chemistry, Texas A&M University, College Station, Texas, 77843; and V. E. RIVERA-GAINES, Bristol-Myers USBNG, Evansville, Indiana 47721.
THE OVERTONE SPECTROSCOPY OF HYDROGEN PEROXIDE ON A MOLECULAR BEAM............................ 15 min (1:30)
C. DOUKETIS and J. P. REILLY, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

THE FUNDAMENTAL AND OVERTONE SPECTROSCOPY OF PYROLYSIS OF THE BULK GAS AND IN A MOLECULAR BEAM.................................................... 15 min (1:47)
C. DOUKETIS and J. P. REILLY, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

OBSERVATION OF A NEW RO-VIBRONIC BAND OF OOH FREE RADICAL GENERATED FROM H2O2 DECOMPOSITION ON GLASS SURFACES............................................. 15 min (2:04)
C. DOUKETIS and J. P. REILLY, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

VELOCITY SLIP IN ULTRA-COLD MOLECULAR BEAMS........................................................................ 15 min (2:21)
JAMES M. KILMASH, CLAYTON F. GIESE, and W. RONALD GENTRY, Chemical Dynamics Laboratory, University of Minnesota, 207 Pleasant Street, E.F., Minneapolis, Minnesota, 55455.

A-DOUPLING TRANSITION OF VITEL OXIDES MEASURED BY MOBF: CO.................... 15 min (2:38)
T. C. STEIMLE, W.-L. CHANG, and D. F. YACHMAN, Chemistry Department, Arizona State University, Tempe, Arizona, 85287.

ELECTRONIC PROPERTIES OF GAS-PHASE COPPER MONOSULFIDE.............................................. 10 min (2:50)
T. C. STEIMLE, W.-L. CHANG, and D. F. YACHMAN, Chemistry Department, Arizona State University, Tempe, Arizona, 85287.

INFRARED SPECTROSCOPY IN SLIT SUPERSONIC EXPANSION.................................................... 15 min (3:15)
C. M. LOVEJOY, A. McILROY, and D. J. NESBITT, Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado, 80309-0440.

EXTENDED INFRARED STUDY OF ArHF....................................................................................... 15 min (3:32)
C. M. LOVEJOY and D. J. NESBITT, Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado, 80309-0440.

J-DEPENDENT VIBRATIONAL PREDISSOCIATION IN NeHF.................................................. 15 min (3:49)
C. M. LOVEJOY and D. J. NESBITT, Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado, 80309-0440.

THE ROTATIONAL RKR METHOD............................................................................................... 15 min (4:06)

AN INTERMOLECULAR POTENTIAL SURFACE FOR Ar + HF(v=1) FROM HIGH RESOLUTION INFRARED MEASUREMENTS.................................................. 15 min (4:23)
1112. ABSOLUTE INFRARED ABSORPTION INTENSITIES FOR OH $X^2Π(v=1→0)$ .................................. 15 min. (4:40)

A. D. SCHIFFMAN, DAVID D. NELSON, and DAVID J. NESBITT.
Department of Chemistry and Biochemistry, University of Colorado; and Joint Institute for Laboratory Astrophysics, National Bureau of Standards, Boulder, Colorado, 80309.

1115. VIBRATIONAL MIXING AT THE C=H STRETCH EXCITED LEVEL IN SMALL HYDROCARBONS ......................................................... 15 min. (4:57)

A. MCILROY and D. J. NESBITT. Department of Chemistry and Biochemistry, University of Colorado; and Joint Institute for Laboratory Astrophysics, National Bureau of Standards, Boulder, Colorado, 80309.
WEDNESDAY, JUNE 15, 1988 -- 8:45 A.M.

Auditorium, Independence Hall

Chairman: WILLIAM KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts.

WA1. ELECTRONIC VIBRATIONS..................35 min.

DUDLEY HERSCHBACH, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

WA2. SPECTRUM OF THE WATER DIMER: A GROUP THEORETICAL AND MULTIDIMENSIONAL TUNNELING APPROACH TO THE DATA...............................35 min.

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

Intermission

WA3. THE VIBRATIONAL DEPENDENCE OF CENTRIFUGAL DISTORTION CONSTANTS -- THE LIMIT OF USEFUL PERTURBATION THEORY?.................................35 min.


WA4. A NEW APPROACH FOR HIGH RESOLUTION VIBRATIONAL SPECTROSCOPY ON SOLVATED IONIC SPECIES IN THE GAS PHASE.........................35 min.

YUAN T. LEE, Department of Chemistry, University of California, Berkeley, California, 94720.
WEDNESDAY, JUNE 15, 1988 -- 1:30 P.M.

Auditorium, Independence Hall

Chairperson: ROMOLA D'CUNHA, Bhabha Atomic Research Centre, Trombay, Bombay, India 400 085.

WE1. C_{60} .............................................................. 30 min.

R. E. SMALLEY, Department of Chemistry, Rice University, Houston, Texas 77251.

WE2. THE SPECTRA OF KrH AND KrD ......................... 30 min.

G. HERZBERG, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR6.

WE3. INFRARED SPECTROSCOPY OF RECENT COMETS ............ 30 min.

M. MUMMA, Planetary Systems Branch, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771.

Intermission

WE4. STAR FORMATION SEEN WITH HIGH RESOLUTION INTER- STELLAR SPECTROSCOPY ......................... 30 min.

GISBERT WINNEWISER, I. Physikalisches Institut, Universitat zu Koln, Koln, West Germany.

WE5. DYNAMICAL MOLECULAR STRUCTURE STUDIED BY HIGH RESOLUTION SPECTROSCOPY ................. 30 min.

EIZI HIROTA, Institute for Molecular Science, Myodiaji, Okazaki, Japan.

PLEASE NOTE:

This session will be held in Independence Hall Auditorium.
THURSDAY, JUNE 16, 1988 -- 8:30 A.M.
Room 1153, Physics Laboratory

Chairman Before Intermission: R. SOORYAKUMAR, Department of Physics, The Ohio State University, Columbus, Ohio.

Chairman After Intermission: PETER M. FELKER, Department of Chemistry and Biochemistry, University of California-Los Angeles, Los Angeles, California.

RA1. 10 YEARS OF HIGH RESOLUTION NONLINEAR RAMAN SPECTROSCOPY........Invited Paper..................30 min.(8:30)
H. W. SCHROTTNER, Sektion Physik, Ludwig-Maximilians-Universität München, München, West Germany.

RA2. FOURIER TRANSFORM (INTERFEROMETRIC) NONLINEAR SPECTROSCOPIES..........................15 min.(9:03)
PETER M. FELKER, Department of Chemistry and Biochemistry, University of California-Los Angeles, Los Angeles, California, 90024-1569.

RA3. FTIR STUDIES OF WOOD CHEMISTRY..........................................................10 min.(9:19)
Y. L. OWEN, Department of Chemistry, Brigham Young University, Provo, Utah, 84602; W. B. BARKER, and H. WEST, Department of Wood Science, University College of North Wales, Bangor, United Kingdom.

RA4. BEN' STRETCH INTERACTIONS IN THE CH OVERTONE SPECTRUM OF ACETYLENE............15 min.(9:30)
BRIAN C. SMITH and JOHN S. WINN, Department of Chemistry, Dartmouth College, Hanover, New Hampshire, 03755.

RA5. ANALYSIS OF WEAKER BANDS OF ACETYLENE IN THE 1.1 μm REGION....................5 min.(9:46)

RA6. SPECTROSCOPIC CONSTANTS OF CS2 DERIVED FROM THE 2 μm SPECTRAL REGION........10 min.(9:52)
D. CHRIS BENNER, V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; GUY GUELACHVILI, Laboratoire d'Infrarouge, Université de Paris-Sud, CNRS, Orsay, France; and K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

RA7. INFRARED DIODE LASER SPECTROSCOPY OF NaCl........................................10 min.(10:03)
H. UEHARA, K. HORII, K. NAKAGAWA, T. KONNO, Department of Chemistry, Josai University, Keyakidai, Saitama 350-02, Japan; and T. FUJIMOTO, Research Institute for Catalysis, Hokkaido University, Kita-Ku, Sapporo 060, Japan.

Intermission

RA8. INFRARED SPECTRUM OF THE v3 BAND OF C2H5 AND ISOTOPIC SPECIES........................15 min.(10:30)
M. F. JAGOD, B. D. REHFUSS, T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637; M. W. CROFTON, Lawrence Livermore National Laboratory, Livermore, California, 95440; and F. SCAPPINI, Istituto di Spettroscopia Molecolare del C.N.R., Bologna, Italy.

*An elaborate celebration of the 100th Birth Centenary which is also the Diamond Jubilee Year of the discovery of Raman Effect is planned for November 1988 in Calcutta, India, where Professor Raman conducted his original research.
RA10. ASYMMETRIC STRETCHING BAND OF BRIDGED BRIDGED ACETYLENE

M. W. Crofton, Lawrence Livermore National Laboratory, Livermore, California, 94550; M. F. Jagod, B. D. Rehfuss, and T. Oka, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

RA11. OBSERVATION OF HOT BANDS OF H\textsuperscript{+} USING AN EXTENDED DIFFERENCE FREQUENCY SPECTROMETER

M. G. Bawendi, B. D. Rehfuss, and T. Oka, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

RA12. IS THE DISSOCIATIVE RECOMBINATION OF H\textsuperscript{+} REALLY SLOW?

A NEW SPECTROSCOPIC MEASUREMENT OF THE RATE CONSTANT

T. Amano, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, KIA ORB.

RA13. A SEARCH FOR THE C-H (BRIDGE) STRETCH VIBRATION-ROTATION BAND OF C\textsubscript{2}H\textsubscript{4}

T. Amano, N. Moazzenz-Ahmad, and A. R. W. McKellar, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, KIA ORB.

RA14. FIR LASER SIDEBAND SPECTROSCOPY OF H\textsubscript{2}O

P. Verhoef, J. J. Ter Meulen, A. Dymanus, W. Leo Meerts, Fysisch Laboratorium, Toernooiveld, 6525 ED Nijmegen, The Netherlands; and D. B. McLay, Department of Physics, Queen's University, Kingston, Canada.
THURSDAY, JUNE 16, 1988 -- 8:30 P.M.
Room 101P, Physics Laboratory

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

RR1. DISSOCIATION OF H$_2$ IN A FAST BEAM: OPTICAL TRANSLATIONAL SPECTROSCOPY......... 10 min. (8:30)
S. C. LAPERRIERE, M. LARZILLIÈRE, J. TREMBLAY, J. P. MOREAU, and A. ALTAFFÉ, Département de Physique, CRM-LEPM, Université Laval, Quebec, Quebec, Canada, G1K 7P4; also for M. LARZILLIÈRE - Laboratoire de Spectrométrie Ionique et Moléculaire, CNRS, Université Lyon-L 09022 Villeurbanne, France.

RR2. FOURIER TRANSFORM SPECTROSCOPY ANALYSIS OF THE Al-COMPLEX VISIBLE EMISSION SPECTRA OF H$_2$ - EXPERIMENTAL RESULTS AND THEORETICAL INTERPRETATION......... 10 min. (8:41)
A. ALTAFFÉ, M. LARZILLIÈRE, J. TREMBLAY, and S. C. LAPERRIERE, Département de Physique, CRM-LEPM, Université Laval, Quebec, Quebec, Canada, G1K 7P4; also for M. LARZILLIÈRE - Laboratoire de Spectrométrie Ionique et Moléculaire, CNRS, Université Lyon-L 09022 Villeurbanne, France.

RR3. THE NUMBER OF QUASIBOUND LEVELS BEHIND A ROTATIONAL BARRIER........ 10 min. (8:52)
DAVID L. HUESSTM, Chemical Physics Laboratory, SRI International, Menlo Park, California, 94025.

RR4. A DOUBLE-RESONANCE STUDY OF PREDISSOCIATION OF THE 1/2$^+$ STATE OF H$_2$................. 15 min. (9:03)
S. J. LENNO, D. L. HUESSTM, H. HELM, Molecular Physics Department, SRI International, Menlo Park, California, 94025; N. BÆHRE, and S. E. KILDING, Institute of Physics, University of Aarhus, 8000 Aarhus C, Denmark.

RR5. LASER SPECTROSCOPIC INVESTIGATION OF THE VAN DER WAALS MOLECULE Xakr........ 15 min. (9:19)
J. KAPETANAKIS, V. SCHMIDTLOCH, E. ZANGER, and D. ZIMMERMANN, Institut für Strahlungs-und Kernphysik, TU Berlin, Hardenbergstr. 36, 12099 Berlin 12, Germany.

RR6. ORANGE BANDS OF CaO:ODOR SPECTROSCOPY AND ELECTRONIC STRUCTURE MODEL........ 15 min. (9:35)
DAVID P. BALDWIN and ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

RR7. DYNAMICS OF Ck + PULSED OPTICAL-DOUBLE RESONANCE EXCITATION OF THE E$^2$$_g$-$A^2$$_e$$_e$ - $X^2$$_e$$_g$ TRANSITION IN CdF...................... 15 min. (9:51)
J. E. MERPHY, M. C. McCARTHY, J. M. BERG, and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

Intermission

RR8. HIGH RESOLUTION LASER SPECTROSCOPY OF NIOBIUM NITRIDE, THE ORANGE, YELLOW AND NEAR INFRARED BANDS...................... 15 min. (10:20)
Y. AZUMA, J. A. BARRY, G. HUANG, A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Z6; and J. O. SCHMÖDER, Institut für Molekülphysik, Freie Universität Berlin, Arnimallee 12, D-1000 Berlin 33, Germany.

RR9. HIGH RESOLUTION LASER SPECTROSCOPY OF MANGANESE OXIDE, MnO.................. 15 min. (10:36)
Y. AZUMA, T. CHANDRABHAR, and A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Z6.

RR10. FIRST OBSERVATION OF BOUND-CONTINUUM TRANSITIONS IN THE LASER INDUCED A$_1^2$$_g$ - $X^2$$_e$$_g$ FLUORESCENCE OF K$_2$........... 10 min. (10:52)
V. ZAFIROPOULOS, A. M. LYRA, W. C. SWALLEY, Iowa Laser Facility, University of Iowa, Iowa City, Iowa, 52242-1294; and W. T. LUE, Department of Chemistry, National Kaohsiung Normal University, Kaohsiung 80224, Taiwan, Republic of China.

RR11. POLARIZATION OF ATOMIC POTASSIUM FLUORESCENCE EXCITED BY LASER PHOTODISSOCIATION OF K$_2$.......................... 15 min. (11:03)
V. ZAFIROPOULOS, X. ZENG, A. M. LYRA, P. KLEBER, K. SANDO, and W. C. SWALLEY, Iowa Laser Facility, University of Iowa, Iowa City, Iowa, 52242-1294.
RB12. LASER INDUCED FLUORESCENCE OF Cs, BY ARGON ION LASER LINES IN THE PRESENCE OF NOBLE BUFFER GASES

J. J. Hsi, Department of Chemistry, Tamkang University, Tamsui, Taipei Hsien, Taiwan, 25137; CHONGYE WANG, and R. A. BERNHEIM, 152 Davey Laboratory, Pennsylvania State University, University Park, Pennsylvania, 16802.

RB13. THE ISOTOPIC BEHAVIOUR OF BORN-OPPENHEIMER BREAKDOWN EFFECTS: APPLICATION OF A LEAST-SQUARES PROCEDURE TO THE HCl ISOTOPOMERS

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

RB14. PARITY SELECTED EXCITATION SPECTROSCOPY OF ArCl2

THURSDAY, JUNE 16, 1988 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chairman: ROGER E. MILLER, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina.

RC1. VIBRATION-ROTATION SPECTRUM OF CARBONYL SULFIDE DIMER. ......................... 15 min. (8:30)
R. W. RANDALL, J. M. WILKIE, C. E. JAMES, B. J. HOWARD, Physical Chemistry Laboratory, Oxford University, Oxford, OX1 3QZ, England; and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

RC2. VIBRATION-ROTATION SPECTRUM OF CARBON DIOXIDE-ACETYLENE. ...................... 15 min. (8:46)
DIANA G. PRICHARD, R. N. NANDI, J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627; and B. J. HOWARD, Physical Chemistry Laboratory, Oxford University, Oxford, OX1 3QZ, England.

RC3. VIBRATION-ROTATION SPECTRUM OF ACETYLENE-NITROGEN. .......................... 15 min. (9:02)
R. N. NANDI, DIANA G. PRICHARD, and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

RC4. VIBRATION ROTATION SPECTRUM OF ACETYLENE-CARBON MONOXIDE. .................. 15 min. (9:16)
MARK D. MARSHALL, Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002; DIANA G. PRICHARD, and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

RC5. STRUCTURAL STUDY OF THE H2O-H2O-CO2 TRIMER. .................................. 15 min. (9:34)
K. I. PETERSON, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island, 02881; R. D. SUENRAM, and F. J. LOVAS, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

Intermission

RC6. ROTATION SPECTRUM AND STRUCTURE OF CO2-CO2-H2O. .................................. 15 min. (10:00)
K. I. PETERSON, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island, 02881; R. D. SUENRAM, and F. J. LOVAS, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RC7. HYPERFINE STRUCTURE AND TUNNELING MOTIONS IN HYDRAZINE. ..................... 15 min. (10:16)
L. H. COUDERT and J. T. HOUGEN, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RC8. QUADRUPOLE HYPERFINE SPLITTING IN THE J=1-0 ROTATIONAL TRANSITION OF CCl3F. 15 min. (10:32)
M. D. MARSHALL, Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002; H. O. LEUNG, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138; and R. D. SUENRAM, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RC9. MICROWAVE SPECTRUM OF THE OZONE-WATER COMPLEX. ............................. 15 min. (10:48)
R. D. SUENRAM, F. J. LOVAS, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899; J. GILLIES, and C. W. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12181.

RC10. ELECTRIC DIPOLE MOMENTS OF HCl- AND HCN-HYDROCARBON COMPLEXES. .......... 15 min. (11:04)
A. WEBER, G. T. FRASER, and R. D. SUENRAM, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RC11. DETERMINATION OF THE STRUCTURE OF H2-CO2. ........................................ 15 min. (11:20)
T. A. BLAKE, S. E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457; R. D. SUENRAM, and F. J. LOVAS, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RC12. DETERMINATION OF THE STRUCTURE OF Ar H2CO. ...................................... 15 min. (11:36)
S. E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457; R. D. SUENRAM, F. J. LOVAS, and G. T. FRASER, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RC13. Σ6 WILL BE PRESENTED HERE (R. C. COHEN) ........................................ 10 min. (11:52)

RC14. Σ7 WILL BE PRESENTED HERE (R. C. COHEN) ........................................ 10 min. (12:03)
THURSDAY, JUNE 16, 1988 -- 8:30 A.M.
Room 1008, Evans Chemical Laboratory

Chairman Before Intermission: MARLIN D. HARMONY, Department of Chemistry,
University of Kansas, Lawrence, Kansas.

Chairman After Intermission: W. CAMINATI, Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Bologna, Italy.

RD1. A PROGRAM FOR FITTING SPECTRA WITH INTERACTING VIBRATIONS AND SPINS...........10 min.(8:30)
H. M. PICKETT, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

RD2. PYRROLE, Ar: ITS MICROWAVE SPECTRUM, STRUCTURE, DIPOLE MOMENT, 14N QUADRUPOLE COUPLING AND BINDING ENERGY.......................15 min.(8:42)
ROBERT K. Rohn, Department of Chemistry, University of Connecticut, Storrs, Connecticut, 06268; K. W. HILLIG, II, and ROBERT L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

RD3. THE MICROWAVE SPECTRUM OF 13C SUBSTITUTED METHYL CYANIDE FOR THE FREQUENCY RANGE 17-95 GHz..........................................................10 min.(8:59)
J. A. ROBERTS and H. TAM, Department of Physics, North Texas State University, Denton, Texas, 76203.

RD4. ROTATIONAL SPECTRUM OF 1,3-BUTADIENE-1,1-d4............................10 min.(9:11)
W. CAMINATI, Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy; and
A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.

RD5. TORSIONAL MOTIONS IN METHYLGLYCOLATE........................................10 min.(9:23)
W. CAMINATI, Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy; H. ROYSENSTEIN, and R. MEYER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.

RD6. MOLECULAR STRUCTURE AND TAUTOMER EQUILIBRIUM OF GASODES 1,2,3-TRIAZOLE STUDIED BY MICROWAVE SPECTROSCOPY, ELECTRON DIFFRACTION AND AB INITIO CALCULATIONS..............................................15 min.(9:35)
M. BECTRUP, Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark; C. J. NIELSEN, C. E. SJÖGREN, Department of Chemistry, University of Oslo, P. O. Box 1033, Blindern, N-0315 Oslo 3, Norway; L. NYGAARD, G. O. SØRENSEN, Chemical Laboratory, University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark; and S. SAMDAL, Oslo College of Engineering, Cort Adelers gate 30, N-0254 Oslo 2, Norway.

Intermission

RD7. STRUCTURAL DETERMINATIONS USING SCALED MOMENTS OF INERTIA.............15 min.(10:05)
RAJIV J. BERRY and MARLIN D. HARMONY, Department of Chemistry, University of Kansas, Lawrence, Kansas, 66045.

RD8. ROTATIONAL SPECTRUM, RING PUCKERING, AND NH INVERSION OF 3-PYRROLINE........15 min.(10:22)
J. DOMMEN, R. MEYER, A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland; and
W. CAMINATI, Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale del Risorgimento 4, I-40136 Bologna, Italy.

RD9. TUNNELING MOTION IN ArH3+ AND ISOTOPOMERS FROM THE ANALYSIS OF THEIR ROTATIONAL SPECTRA..............................................15 min.(10:39)
M. BOGEY, H. BOLVIN, C. DEMUYNCK, J. L. DESTOMBES, Laboratoire de Spectroscopie Hertzienne, Université des Sciences et Techniques de Lille-Flandres-Artois, UFR de Physique, Villeneuve d'Ascq, France; and
B. P. YAN ELJOCK, Department of Structural Chemistry, University of Utrecht Padualaan 1 - 3584 CH Utrecht, The Netherlands.

RD10. INFRARED DIODE LASER SPECTRA OF MaD, CaH and CaD (X 2e+)..............10 min.(10:56)
B. DEMUYNCK, C. DEMUYNCK, and J. L. DESTOMBES, Laboratoire de Spectroscopie Hertzienne, Université des Sciences et Techniques de Lille-Flandres-Artois, UFR de Physique, Villeneuve d'Ascq, France.
THURSDAY, JUNE 16, 1988 -- 1:30 P.M.
Room 1133, Physics Laboratory

Chairman: Mark D. Marshall, Department of Chemistry, Amherst College, Amherst, Massachusetts.

**REI. MICROEAVE SPECTRUM OF THE \( \text{N}_2\cdot\text{H}_2\text{O} \) COMPLEX.**

T. D. Lowy, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138; M. D. Marshall, Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002; R. D. Stephan, and F. J. Lovas, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

**RE2. ROTATIONAL SPECTRA AND STRUCTURES OF THE \( \text{H}_3S\cdot\text{H}_2\text{O} \) AND \( \text{H}_2S_2 \) COMPLEXES.**

F. J. Lovas, R. D. Stephan, and L. H. Coutert, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

**RE3. STUDIES OF ISOTOPICALLY ENRICHED WATER DIMER SPECIES.**


**RE4. VIBRATIONAL SPECTROSCOPY OF SOLID-LIKE CLUSTERS OF HYDROGEN CYANIDE.**

D. S. Anfin and G. E. Eng, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

**RE5. VIBRATIONAL PREDISSOCIATION STUDIES OF \( \text{Cs}^+(\text{MeOH})_n \) AND \( \text{Cs}^+(\text{EtOH})_n \) SOLVATED ION CLUSTERS.**

Wen-Long Liu and James M. Lisby, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801.

**RE6. SOLVATION OF ALKALI IONS WITH NON-POLAR SOLVENTS.**

Jeffrey A. Braven and James M. Lisby, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801.

**RE7. 18-IR DOUBLE RESONANCE SPECTROSCOPY: A STUDY OF THE TORSIONAL VIBRATIONS OF CYCLIC (HF).**

Kirk D. Kolodbrander and James M. Lisby, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801.

Intermission

**RE8. THE PHOTODETACHMENT SPECTRA OF NEGATIVE CLUSTER IONS OF WATER.**

G. H. Lee, J. G. Eaton, H. W. Sarkas, K. H. Bowen, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218; C. Ludewigt, and H. Haberland, Department of Physics, Universität Freiburg, Freiburg, Germany.

**RE9. THE PHOTODETACHMENT SPECTRA OF HOMEMEOUS ALKALI METAL CLUSTER ANIONS: \( \text{Na}^+ \cdot \text{K}^+ \cdot \text{Rb}^+ \cdot \text{Cs}^+ \) n=2-5:**


**RE10. PHOTODETACHMENT STUDIES OF HETEREOUS ALKALI METAL DIMER AND TRIMER ANIONS.**


**RE11. PRODUCTION AND PHOTODETACHMENT STUDIES OF \( \text{Li}_2^- \).**


**RE12. THE PHOTODETACHMENT SPECTROSCOPY OF HYDRATED AND DEUTERATED NITRIC OXIDE ANIONS.**


**RE13. THE STRUCTURE AND DYNAMICS OF \( \text{Ne}_2\cdot\text{Cl}_2 \).**


**RE14. \( \Sigma \) WILL BE PRESENTED HERE (G. A. Blake).**

**RE15. \( \Sigma \) WILL BE PRESENTED HERE (J. V. Cole).**
THURSDAY, JUNE 16, 1988 -- 1:30 P.M.
Room 1009, Physics Laboratory

Chairman Before Intermission: J. WORMHOLDT, Center for Chemical and Environmental Physics, Aerodynamic Research, Billerica, Massachusetts.

Chairman After Intermmission: R. H. TIPPING, Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama.

RF1. (2,1 = 1,0) TRANSITIONS AND OVERLAP PARAMETERS FOR H2-Ar MIXTURES..........................15 min.(1:30)
C.T.W. HSIEH and S. PADDI REDDY, Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland, Canada, A1B 3X7.

RF2. INFRARED SPECTRUM OF SOLID HYDROGEN: THEORY OF THE INTEGRATED ABSORPTION COEFFICIENTS OF W(J=6) TRANSITIONS.................................10 min.(1:46)
T. K. BALASUBRAMANIAN, R. D'SOUZA, Spectroscopy Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay 400 085, India; and K. VARABARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

RF3. ABSOLUTE RO-VIBRATIONAL INTENSITIES FOR THE Δν = 1 VIBRATIONAL BANDS OF 32S16O................15 min.(1:57)
C. CHACKERIAN, NASA-Ames Research Center, Moffett Field, California, 94035; G. GUELACHVILI, Laboratoire d'Infrarouge, CNRS, Université de Paris-Sud, 91405 Orsay, France; A. LOPEZ-PINEIRO, Departamento de Quimica Fisica, Facultad de Ciencias, Universidad de Extremadura, Badajoz, Spain; and R. H. TIPPING, Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama, 35487.

RF4. TWO-TONE FREQUENCY-MODULATION SPECTROSCOPY: MEASUREMENT OF HIGH OVERTONE INTENSITIES OF HBr......................................................10 min.(2:13)
C. B. CARLISLE, SRI International, 333 Ravenswood Avenue, Menlo Park, California, 94025; T. F. GALLAGHER, Department of Physics, University of Virginia, Charlottesville, Virginia, 22901; and R. H. TIPPING, Department of Physics and Astronomy, University of Alabama, Tuscaloosa, Alabama, 35487.

RF5. HIGH RESOLUTION OBSERVATIONS OF STARS, PLANETS AND THE SUN USING AN FTS/POSTDISPERSER..................................................15 min.(2:24)

RF6. DETERMINATION OF THE ORTHO-PARA RATIO AND NUCLEAR SPIN TEMPERATURE FROM HIGH RESOLUTION WATER FLUORESCENCE SPECTRA OF COMETS HALLEY AND WILSON.............15 min.(2:40)
W. E. BLASS, Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee, 37996-1200; M. J. MUMMA, Planetary Systems Branch, NASA Goddard Space Flight Center, Greenbelt, Maryland, 20771; H. A. WEAVER, Space Telescope Science Institute, 3700 San Martin Drive, Baltimore, Maryland, 21218; H. P. LARSON, Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona, 85721; and S. DRAPATZ, Max Planck Institute, Federal Republic of Germany.

RF7. AIR-BROADENED HALFWIDTHS AND PRESSURE SHIFTS IN THE v3 BAND OF 13CH3..................10 min.(2:56)
V. MALATHY DEVI, D. CHRIS BENNER, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; MARY ANN H. SMITH, and CURTIS P. RINSLAND, Atmospheric Sciences Division, Mail Stop 401A, NASA Langley Research Center, Hampton, Virginia, 23665-5225.

Intermission

RF8. AIR-BROADENED AND NITROGEN-BROADENED HALFWIDTH COEFFICIENTS AND PRESSURE SHIFTS IN THE v2 BAND SPECTRAL REGION OF 12CH2.........................10 min.(3:20)
D. CHRIS BENNER, V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; Mary Ann H. SMITH, and C. P. RINSLAND, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665.

RF9. TUNABLE DIODE LASER MEASUREMENTS OF INTENSITIES AND COLLISION-BROADENED LINE WIDTHS IN THE v3 AND v6 FUNDAMENTALS OF 13CH3D AT LOW TEMPERATURES.................15 min.(3:31)
S. CHUDAMANI and P. VARANASTI, Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York, 11794-2300.
INTENSITY AND LINE WIDTH MEASUREMENTS IN THE $v_2$-FUNDAMENTAL OF $^{13}$CH$_4$ AT
PLANETARY ATMOSPHERIC TEMPERATURES.................................................................10 min.(3:47)

K. VARANASI and S. CHIDAMANI, Laboratory for Planetary Atmospheres
Research, State University of New York, Stony Brook, New York.

MEASUREMENT OF INTENSITIES AND COLLISION-BROADENED LINE WIDTHS IN THE
$v_2$-FUNDAMENTAL OF $^{12}$CH$_4$ AT LOW TEMPERATURES...........................................15 min.(3:58)

K. VARANASI and S. CHIDAMANI, Laboratory for Planetary Atmospheres
Research, State University of New York, Stony Brook, New York.

PRESSURE SHIFT MEASUREMENTS ON THE INFRARED LINES OF $^{12}$CH$_4$, $^{13}$CH$_4$, $^{12}$CH$_3$D
AND $^{13}$N$_2$ AROUND 7.85 $\mu$m USING A TUNABLE DIODE LASER.................................10 min.(4:14)

K. VARANASI and S. CHIDAMANI, Laboratory for Planetary Atmospheres
Research, State University of New York, Stony Brook, New York.

INFRARED BAND STRENGTH MEASUREMENTS OF CF$_2$ AND CH$_3$.................................10 min.(4:25)

J. WORMHoudt and K. McCurdy, Center for Chemical and Environmental
Physics, Aerodyne Research, 45 Manning Road, Billerica, Massachusetts.

THEORETICAL PREDICTION OF FAR WING INFRARED LINESHAPES................................15 min.(4:36)

R. C. Brown and J. WORMHoudt, Center for Chemical and Environmental
Physics, Aerodyne Research, 45 Manning Road, Billerica, Massachusetts.

1821.
THEORETICAL STUDIES OF THE SPECTROSCOPY OF FIRST-ROW MOLECULES...Invited Paper...30 min. (1:30)
C. W. REISCHL, S. J. LANGHOFF, B. PARTIDGE, and P. B. TAYLOR.
NASA Ames Research Center, Moffett Field, California, 94035.

REFLECTION SYMMETRIES OF LINEAR-MOLECULAR SYMMETRIC LEVELS.................. 15 min. (2:03)
J. E. S. C. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

ON THE ES OF SMALL CARBON CLUSTERS.................................................. 10 min. (2:19)
R. W. BIEHL, Department of Chemistry, John Carroll University, Cleveland, Ohio, 44118.

AB INITIO CALCULATIONS ON Ag, Au, AND AgAu INCLUDING POLARIZATION
FUNCTIONS AND EXTENDED ELECTRON CORRELATION................................. 15 min. (2:30)
R. B. ROSS and W. C. FERMER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

VIBRATIONAL-ROTATIONAL ANALYSIS OF THE HYDROGEN PEROXIDE CATION FROM
AN AB INITIO POTENTIAL ENERGY AND DIPOL MOMENT SURFACES...................... 15 min. (2:46)
SUSAN KRAFT, Citron Aromatic Inc., 120 Veterans Boulevard, Carlstadt, New Jersey, 07072; OSCAR C. HESBERG, and WALTER C. FERMER, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

AN AB INITIO STUDY OF OS AND OH ABSORPTION ON Fe AsIAL.................................. 15 min. (3:15)

AB INITIO CALCULATIONS OF POLARIZABILITIES INCLUDING RELATIVISTIC EFFECTS
FOR ELEMENTS OF GROUPS 1A AND 1B................................................... 15 min. (3:31)
J. M. BAEKS, R. B. ROSS, and W. C. FERMER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

CHARGE STABILIZATION OF EXCITED ELECTRONIC STATES OF CN.......................... 15 min. (3:47)
C. L. WING and J. HELLWIG, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

AN APPROXIMATE AB INITIO THEORY OF LARGE MOLECULAR SYSTEMS.................... 15 min. (4:03)
C. Y. LEE, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

ELECTRONIC STATES OF Na, AND Na; CALCULATED PE SURFACES AND MOLECULAR
STRUCTURES................................................. Late Paper.............................. 10 min. (4:19)
C. H. JACOB, Laboratoire de Chimie Quantique, Université Louis Pasteur,
4 Rue Blaise Pascal, 67000 Strasbourg, France; M. BROYER, and P. LABASTIE,
Laboratoire de Spectroscopie Ioniq e et Moléculaire, Université de Strasbourg I, 43 Bd du 11 Novembre 1918, 67002 Strasbourg, France.

EMISSION SPECTRUM OF SUPERSONICALLY COOLED BENZYL RADICAL....................... Late Paper.............................. 10 min. (4:31)
P. G. LANDER, Air Force Aeronautics Laboratory/YSX, Edwards Air Force Base, California, 93523; and J. L. SELKO, Department of Chemistry, University of Redlands, Redlands, California, 92373.

FLUORESCENCE SPECTROSCOPY OF PREASSOCIATED LEVELS OF ELECTRONICALLY EXCITED
S................................. Late Paper.............................. 10 min. (4:44)
M. C. HEAVEN and M. C. HEAVEN, Department of Chemistry, Emory University,
Atlanta, Georgia, 30322.

FLUORESCENCE STUDIES OF THE COLLISION DYNAMICS OF Br,(B)......................... Late Paper.............................. 10 min. (4:52)
M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, Georgia, 30322; F. A. DOROG, G. P. FERRAR, and L. HANKO, AFML, First Air Force, New Mexico, 87117.
TO ALL THOSE PRESENTING PAPERS:

Please use 2" x 2" (5 cm x 5 cm) slides and give them to the projectionist at the beginning of the session.

Overhead projectors are available in each of the rooms where the sessions are held. If you plan to use them, please advise your projectionist at the start of the session so he or she can be ready to have equipment moved around as needed.

Thank you.
THURSDAY, JUNE 16, 1984 -- 1:30 P.M.
Room 1008, Evans Chemical Laboratory

Chairman Before Intermission: T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois.

Chairman After Intermission: PRASAD POLVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee.

RH1. ON THE HARMONIC FORCE FIELD OF n-BUTANE ...........................................10 min.(1:30)

RH2. ON THE LIMITS OF THE CONCEPT OF TRANSFERABILITY OF VIBRATIONAL PARAMETERS.......15 min.(1:42)
WILLIS B. PERSON and K. KUBULAT, Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

RH3. THE THEORY OF VIBRATIONAL CIRCULAR DICHROISM: ALTERNATIVE REPRESENTATIONS
OF ATOMIC POLAR AND AXIAL TENSORS..........................................................15 min.(1:59)
P. J. STEPHENS, K. J. JALKANEN, Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482; R. D. AMOS, N. C. HANDY, Department of Theoretical Chemistry, Cambridge, University, Cambridge, United Kingdom; P. LAZZERETTI and R. ZANASI, Dipartimento di Chimica, Universita Di Modena, 41,100 Modena, Italy.

RH4. MEASUREMENT OF VIBRATIONAL CIRCULAR DICHROISM SPECTRA USING DISPERSIVE
INSTRUMENTATION.................................................................................15 min(2:16)
P. DEVLIN and P. J. STEPHENS, Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482.

RH5. VIBRATIONAL CIRCULAR DICHROISM OF B-LACTONES.......................................15 min.(2:33)
K. J. JALKANEN, F. DEVLIN, P. J. STEPHENS, Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482; T. POLONSKI, Department of Organic Chemistry, Technical University 80-952, Gdansk, Poland; R. D. AMOS, and N. C. HANDY, Department of Theoretical Chemistry, Cambridge University, Cambridge, United Kingdom.

RH6. VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF MOLECULES CONTAINING SECOND-ROW
ELEMENTS..................................................................................................15 min.(2:50)
R. BURSI and P. J. STEPHENS, Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482.

Intermission

RH7. VIBRATIONAL SPECTRA OF TETRAFLUOROOXIRANE-16O AND -18O................................15 min.(3:20)
NORMAN C. CRAIG, DIANE GESTY, and ALLEN G. KASTELLE, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074.

RH8. VIBRATIONAL SPECTRA OF I-CHLOROCYCLOBUTENE............................................10 min.(3:37)
NORMAN C. CRAIG and STEVEN S. BORICK, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074.

RH9. VIBRONIC STATES OF PuF6 IN THE NEAR IR AND VISIBLE SPECTRAL REGIONS..........15 min.(3:49)
S. J. DAVID and K. C. KIM, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545.

RH10. INTEGRATED INTENSITIES OF CO2 AND SF6 VIBRATIONAL BANDS FROM 1800 TO 5000 CM^-1
AS A FUNCTION OF DENSITY AND TEMPERATURE........................................15 min(4:06)
MICHAEL E. THOMAS and MILTON J. LINEVSKY, Applied Physics Laboratory, The Johns Hopkins University, Laurel, Maryland, 20770.

RH11. STUDY OF ZEOLITE FRAMEWORK STRUCTURE AND ITS FORCE FIELD BY VIBRATIONAL
SPECTRA.................................................................................................15 min.(4:23)
HU JIEHAN and NI JIANYI, Dalian Institute of Chemical Physics, Dalian, Liaoning, People's Republic of China.
FRIDAY, JUNE 17, 1988 -- 8:30 A.M.
Room 1153. Physics Laboratory

Chairman: PAUL BALOG, Battelle Memorial Institute, Columbus, Ohio.

FAI. FOURIER TRANSFORM INFRARED SPECTROSCOPY OF NITRIC OXIDE IN ELECTRIC AND MICROWAVE DISCHARGES.........................10 min.(8:30)

FA2. FOURIER TRANSFORM DETECTION OF THE $v_3$ FUNDAMENTAL OF THE N$_3$ RADICAL.............10 min.(8:41)

FA3. DIODE LASER SPECTROSCOPY OF ALKALI HALIDES........................................15 min.(8:52)
C. R. BRAZIER, M. DOCAY, and P. F. BERNATH, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

FA4. PROGRESS ON NH$_3$: MORE ROTATIONAL ASSIGNMENTS, A HAMILTONIAN FOR BAND ORIGINS, AND MODELING OF NH STRETCH INTRAMOLECULAR DYNAMICS..........................10 min.(9:08)
STEPHEN L. COY, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138; and KEVIN K. LEHMANN, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

FA5. INVESTIGATION OF HOT BAND TRANSITIONS OF NH$_3$ IN THE 10 $\mu$m REGION.............15 min.(9:19)
R. D'CUNHA, K. SINGH, and V. B. KARTHA, Spectroscopy Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay-400 085, India.

FA6. THE $s_2v_2 + av_3$ HOT BAND IN $^{14}$NH$_3$ AND $^{15}$NH$_3$.................................................. 5 min.(9:35)
R. D'CUNHA and M. N. DEO, Spectroscopy Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay-400 085, India.

FA7. INTERPRETATION OF HIGH RESOLUTION FOURIER TRANSFORM SPECTRA OF $^{14}$NH$_3$ AT 2-3 $\mu$m.........................................................10 min.(9:41)
Y. TU, K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210; S. URBAN, Czechoslovak Academy of Sciences, J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Dolejsova ul. 3 182 23 Praha 8, Czechoslovakia; and G. GUELACHVILI, Laboratoire d'Infrarouge, CNRS, Universite Paris-Sud, 91405 Orsay, France.

Intermission

FA8. HIGH RESOLUTION SUPersonic BEAM INFRARED SPECTRA OF ACETYLENE TETRAMER..........15 min.(10:05)
G. BRYANT, Australian National University, Canberra, Australia; R. O. WATTS, and D. F. EGGER HS Department of Chemistry, University of Washington, Seattle, Washington, 98195.

FA9. THE STRUCTURE AND TUNNELING MOTION OF ACETYLENE DIMER STUDIED BY FREE-JET INFRARED ABSORPTION SPECTROSCOPY IN THE 14 $\mu$m REGION......................15 min.(10:21)
YASUSHIRO OSHIMA, KOZO KUCHITSU, Department of Chemistry, Faculty of Science, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan; YOSHIIYASU MATSUMOTO, and MICHIO TAKAMI, The Institute of Physical and Chemical Research(RIKEN), Wako, Saitama, 351-01, Japan.

FA10. INFRARED DIODE LASER SPECTROSCOPY OF THE BF$_3$ VAN DER WAALS COMPLEXES WITH RARE GASES.........................................................15 min.(10:37)
YOSHIIYASU MATSUMOTO, MICHIO TAKAMI, The Institute of Physical and Chemical Research(RIKEN), Wako, Saitama, 351-01, Japan; YASUSHIRO OSHIMA and KOZO KUCHITSU, Department of Chemistry, Faculty of Science, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.

FA11. FAR-INFRARED SPECTRA OF HCl - RARE GAS VAN DER WAALS MOLECULES..................5 min.(10:53)

FA12. INFRARED SPECTRA OF HYDROGEN - RARE GAS VAN DER WAALS MOLECULES..............15 min.(10:59)
FA13. INFRARED SPECTRA OF HYDROGEN DIMERS ..................................................15 min.(11:15)


FA14. FAR-INFRARED SPECTRUM OF THE HCl DIMER ............................................15 min.(11:31)


FA15. CALCULATION OF THE TUNNELLING SPLITTING IN SEVERAL ROTATIONAL STATES FOR (HF) ............................................................................................................15 min.(11:47)


FA16. WILL BE PRESENTED HERE (C. CHAPADOS) ..........................................................10 min.(12:03)
THE MICROWAVE SPECTRUM OF DIFLUOROMETHANAMINE, CF₂NH.............................10 min.(8:30)
FR.2. THE SUBMILLIMETER-WAVE SPECTRUM OF THE 12CH₃O AND THE 13CH₃O RADICALS..............15 min.(10:15)
FR.3. MICROE WAVE SPECTRUM AND STRUCTURE OF CYCLOBUTADIENE OZONIDE.......................10 min.(10:30)
FR.4. THE COMPLETE CHLORINE NUCLEAR QUADRUPOLE COUPLING TENSOR IN CHLOROTRIFLUOROETHYLENE...........15 min.(11:01)
FR.5. THE COMPLETE CHLORINE NUCLEAR QUADRUPOLE COUPLING TENSOR IN CHLOROTRIFLUOROETHYLENE...........15 min.(11:01)
FB11. THE MICROWAVE SPECTRUM OF KR\textsuperscript{PF\textsubscript{3}}.................................15 min.(11:18)
K. W. HILLIG, II, M. S. LABARGE, E. BITTNER, R. C. TAYLOR,
R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan,
Ann Arbor, Michigan, 48109-1055; and R. BOHN, Department of

FB12. Σ\textsubscript{4} WILL BE PRESENTED HERE (R. H. PETRIMICH)........................................15 min.(11:35)
FRIDAY, JUNE 17, 1988 -- 8:30 A.M.
Room 1005, Physics Laboratory

Chairman: P. J. STEPHENS, Department of Chemistry, University of Southern California, Los Angeles, California.

FC1. CONFORMATIONAL STUDY OF 1,2-AMINO ALCOHOLS BY VIBRATIONAL CIRCULAR DICHROISM.....15 min.(8:30)
N. RAGUNATHAN, L. A. NAFIE, and T. B. FREEDMAN, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-1200.

FC2. CIRCULAR DICHROISM IN THE FAR INFRARED AND MILLIMETER WAVELENGTH RANGE:
NEW TECHNIQUES.................................................................15 min.(8:47)
P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

FC3. ON HF CIRCULAR DICHROISM MEASUREMENTS IN THE 50-100 CM^-1 RANGE................10 min.(9:04)
P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

FC4. NEW DEVELOPMENTS IN RAMAN OPTICAL ACTIVITY.................................10 min.(9:16)
P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

FC5. AB INITIO VIBRATIONAL PROPERTIES OF LARGE OPTICALLY ACTIVE MOLECULES:
GLUCOSE ET AL.............................10 min.(9:28)
P. K. BOSE and P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

FC6. RAMAN OPTICAL ACTIVITY SPECTROMETER..............................................10 min.(9:40)
M. VAVRA and T. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

Intermission

FC7. VIBRATIONAL CIRCULAR DICHROISM OF S-2,2'-DIMETHYL-6,6'-DIAMINOBIPHENYL........10 min.(10:05)
C. N. SU, M.-C. TISSOT, and T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

FC8. VIBRATIONAL ANALYSIS AND VCD OF TRANS-1,2-DICYANOCYCLOPROPANE................10 min.(10:17)
ADEL A. EL-AZHARY and TIMOTHY A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

FC9. VIBRATIONAL CIRCULAR DICHROISM OF 1,3-DIDEUTERIOALLENE, CALCULATIONAL RESULTS....15 min.(10:29)
A. ANNAMALAI, U. NARAYANAN, M.-C. TISSOT, T. A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680; K. J. JALKANEN, and P. J. STEPHENS, Department of Chemistry, University of Southern California, Los Angeles, California, 90089.

FC10. COLLECTION OF ROA SPECTRA USING LINEAR INCIDENT POLARIZATION..................15 min.(10:46)
K. M. SPENCER, T. B. FREEDMAN, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-1200.

FC11. VIBRATIONAL CIRCULAR DICHROIS STUDIES OF EPHEDRINE AND RELATED MOLECULES......15 min.(11:03)
T. B. FREEDMAN, N.-S. LEE, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-1200.

FC12. Z9 WILL BE PRESENTED HERE (G. M. ROBERTS).................................................15 min.(11:20)

FC13. Z10 WILL BE PRESENTED HERE (M. DIEM).........................................................15 min.(11:37)
Y SESSION

The following papers arrived after the typing of the program was completed and the program was on its way to the printers. They have been scheduled for presentation in the sessions indicated below.


22. LOW FREQUENCY INTERMOLECULAR VIBRATIONS IN VARIOUS BINARY COMPLEXES FROM Near infrared SPECTROSCOPY. G. Miller, K. R. Hills, and R. E. Miller, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27599.

23. SUP-DOPPLER RESOLUTION INFRARED SPECTROSCOPY of WATER DIMER. Z. S. Huang and R. E. Miller, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27599.


26. TUNABLE FAR INFRARED LASER SPECTROSCOPY OF VAN DER WAALS AND HYDROGEN BONDED CLUSTERS FORMED IN A PLANAR SUPERSONIC JET. K. Busarov, K. B. Laughlin, R. C. Cohen, Y. T. Lee, R. J. Saykally, Department of Chemistry and Lawrence Berkeley Laboratories, University of California, Berkeley, California, 94720; and G. A. Blake, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, 91125.

27. TUNABLE FAR INFRARED LASER SPECTROSCOPY OF VAN DER WAALS BONDS; TUNNELING-ROTATIONAL AND VIBRATION-ROTATION SPECTRA of Ar-H2O. R. C. Cohen, K. L. Busarov, K. B. Laughlin, M. Havenith, Y. T. Lee, R. J. Saykally, Department of Chemistry and Lawrence Berkeley Laboratories, University of California, Berkeley, California, 94720; and G. A. Blake, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, 91125.


30. VIBRATIONAL CIRCULAR DICHLORISM OF OLIGO-NUCLEOTIDES: EXPERIMENTAL DATA AND CALCULATIONS. M. Goluotta and M. Diem, Department of Chemistry, City University of New York, Hunter College, New York, New York, 10021.
II SESSION

PLEASE NOTE: The following papers arrived after the program was sent to the printers. The sessions in which they are scheduled for presentation are indicated in the right-hand margin.

21. THE OVERTONE SPECTROSCOPY OF HYDROGEN PEROXIDE ON A MOLECULAR BEAM. 15 min. (TI1)
   C. DOUKETIS and J. P. REILLY, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

22. THE FUNDAMENTAL AND OVERTONE SPECTROSCOPY OF PYRROLE IN THE WTG GAS AND
    IN A MOLECULAR BEAM. 15 min. (TI2)
   C. DOUKETIS and J. P. REILLY, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

23. OBSERVATION OF A NEW RO-VIBRONIC BAND OF OOH FREE RADICAL GENERATED
    FROM H2O DECOMPOSITION ON GLASS SURFACES. 15 min. (TI3)
   C. DOUKETIS and J. P. REILLY, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

24. VELOCITY SLIP IN ULTRA-COLD MOLECULAR BEAMS. 15 min. (TI4)
   JAMES M. WILKINSON, CLAYTON F. GIESE, and W. RONALD GENTRY,
   Chemical Dynamics Laboratory, University of Minnesota,
   207 Pleasant Street, S.E., Minneapolis, Minnesota, 55455.

25. A-DOU BILING TRANSITIONS OF METAL OXIDES MEASURED BY MODR: CuO. 10 min. (TI5)
   T. C. STEIMLE, W.-L. CHANG, and D. F. NACHMAN,
   Chemistry Department, Arizona State University, Tempe, Arizona, 85287.

26. ELECTRONIC PROPERTIES OF GAS-PHASE COPPER MONOSULFIDE. 10 min. (TI6)
   T. C. STEIMLE, W.-L. CHANG, and D. F. NACHMAN,
   Chemistry Department, Arizona State University, Tempe, Arizona, 85287.

27. INFRARED SPECTROSCOPY IN SLIT SUPERSONIC EXPANSION. 15 min. (TI7)
   C. M. LOVEJOY, A. L. LAROY, and D. J. NESBITT,
   Joint Institute for Laboratory Astrophysics, National
   Bureau of Standards and University of Colorado, Boulder, Colorado, 80309-0440.

28. EXTENDED INFRARED STUDY OF ArHF. 15 min. (TI8)
   C. M. LOVEJOY and D. J. NESBITT, Joint Institute for
   Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado, 80309-0440.

29. J-DEPENDENT VIBRATIONAL PREDISSOCIATION IN NeHF. 15 min. (TI9)
   C. M. LOVEJOY and D. J. NESBITT, Joint Institute for
   Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado, 80309-0440.

30. THE ROTATIONAL RRK METHOD. 15 min. (TI10)
    DAVID J. NESBITT and MARK S. CHILD, Joint Institute for
    Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado, 80309-0440.

31. AN INTERMOLECULAR POTENTIAL SURFACE FOR Ar + HF(v=1) FROM HIGH
    RESOLUTION INFRARED MEASUREMENTS. 15 min. (TI11)
    DAVID J. NESBITT, CHRISTOPHER M. LOVEJOY, and MARK S. CHILD,
    Joint Institute for Laboratory Astrophysics, National Bureau
    of Standards and University of Colorado, Boulder, Colorado, 80309-0440.

32. ABSOLUTE INFRARED ABSORPTION INTENSITIES FOR OH X2Π(v=1-0). 15 min. (TI12)
    ARAM SCHIFFMAN, DAVID D. NELSON, and DAVID J. NESBITT,
    Department of Chemistry and Biochemistry, University
    of Colorado, and Joint Institute for Laboratory Astrophysics,
13. VIBRATIONAL MIXING AT THE C-H STRETCH EXCITED LEVEL IN SMALL HYDROCARBONS..........................15 min.(TI13)
   A. McILROY and D. J. NESBITT, Department of Chemistry and Biochemistry, University of Colorado, and Joint Institute for Laboratory Astrophysics, National Bureau of Standards, Boulder, Colorado, 80309-0440.

14. RESTRICTED HARTREE-FOCK WAVEFUNCTIONS AND EXCITATION ENERGIES OF ALOXY RADICALS..............15 min.(TD'1)
   STELLA M. SUNG and RUSSELL M. Pitzer, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

15. AN AB INITIO STUDY OF CS AND H ADSORPTION ON Be METAL..............................................................15 min.(TD'2)

16. AB INITIO CALCULATIONS ON Ag, Au, and AgAu INCLUDING POLARIZATION FUNCTIONS AND EXTENDED ELECTRON CORRELATION..........................15 min.(TD'3)
   R. B. ROSS and W. C. ERMLER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

17. AB INITIO CALCULATIONS OF POLARIZABILITIES INCLUDING RELATIVISTIC EFFECTS FOR ELEMENTS OF GROUPS IA AND IB..................................................15 min.(TD'4)
   J. M. POWERS, R. B. ROSS, and W. C. ERMLER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

18. VIBRATIONAL-ROTATIONAL ANALYSIS OF THE HYDROGEN PEROXIDE CATION FROM AB INITIO POTENTIAL ENERGY AND DIPOLE MOMENT SURFACES..............15 min.(TU'5)
   SUSAN KRAFT, Citroil Aromatic, Inc., 320 Veterans Boulevard, Carlstadt, New Jersey, 07072; and HSUCHIN C. HSIEH and WALTER C. ERMLER, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

19. EXPERIMENTAL AND THEORETICAL ANALYSIS ON DOUBLY CHARGED MOLECULAR IONS: N_2^2+ AND CO^2+.................................................................10 min.(TD'6)
   G. KINDVALL, M. LARSSON, B. J. OLSSON, and P. SIGRAY, Research Institute of Physics, Frescativagen 24, S-104 05, Stockholm, Sweden.

20. FOURIER TRANSFORM SPECTROSCOPY OF ^7Li_2: THE 1^3_p-1^3_g TRANSITION...........................................10 min.(MF16)
   R. BACIS, F. MARTIN, Laboratoire de Spectrometrie Ionique et Moleculaire, Universite Claude Bernard-Lyon I, 69622 Villeurbanne, France; C. LINTON, GUO BUIJIN, C. H. CHENG, and E. STAD, Physics Department, University of New Brunswick, P.O. Box 4400, Fredericton, N.B., Canada E3B 5A3.

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

22. INFRARED MATRIX ISOLATION STUDIES OF THE 1:1 MOLECULAR COMPLEXES OF THE HYDROGEN HALIDES, AND CIF WITH 18-CROWN-6 AND RELATED CYCLIC POLYETHERS......................................................10 min.(MH16)
   BRUCE S. AULT and HEBI BAI, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

23. ULTRAFAST TRANSIENT SOLVATION OF POLAR DYE MOLECULES IN SIMPLE POLAR SOLVENTS..............................10 min.(TD'7)
   MICHAEL A. KAHLON, TAI JONG KANG, WLODZIMEIRZ JARZEB, and PAUL F. BARBARA, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455.
47

4. AB INITIO CI STUDY OF THE MAGNETIC CIRCULAR DICHLORISM SPECTRUM OF ACETYLENE FOR THE X — C(*) Bu AND X — C(Pu) ELECTRONIC TRANSITIONS...........10 min.(TD'8)

C. F. CHABALOWSKI, U.S. Army Ballistic Research Laboratory, SLCBR-IB-I, Aberdeen Proving Ground, Maryland, 21005-5066;
J. O. JENSEN, Chemical Research, Development, and Engineering Center, Aberdeen Proving Ground, Maryland, 21010-5423;
and D. R. YARKONY, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218.

725. THEORETICAL STUDY OF THE RADIATIVE LIFETIME FOR THE SPIN-FORBIDDEN TRANSITION X — C(*) + a C(*) IN He2* USING AB INITIO STATE AVERAGED MCSCF PLUS CI METHODS..........................10 min.(TD'9)

CARY F. CHABALOWSKI, U.S. Army Ballistic Research Laboratory, SLCBR-IB-I, Aberdeen Proving Ground, Maryland, 21005-5066;
D. R. YARKONY, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218; B. H. LENGSFIELD, Lawrence Livermore National Laboratory, P.O. Box 803, Livermore, California, 94550; and J. O. JENSEN, Chemical Research, Development, and Engineering Center, Aberdeen Proving Ground, Maryland, 21010-5423.
Phase-coherent molecular motion is initiated whenever a sufficiently short (i.e., femtosecond) laser pulse passes through most media. Optical absorption leads to coherent wavepacket propagation on excited state surfaces, while impulsive stimulated scattering (ISS) leads to coherent motion in electronic ground states. This motion can then be monitored (or altered) with subsequent femtosecond pulses. Collective vibrational motion in solids and liquids, local intermolecular vibrations, and even many intramolecular vibrations have been time-resolved. If the motion under observation is involved in a chemical or structural rearrangement, then the rearrangement process may be observed in real time. In crystalline solids, structural phase transitions and oriented bimolecular reactions have been examined. Molecular dynamics in simple liquids and structural relaxation in viscoelastic fluids have also been characterized. Unimolecular dissociation in the liquid phase is under study.

In simple liquids, elementary molecular orientational and translational motions are vibrational (not diffusional) in character. Through ISS, time-domain characterization of librational frequencies and their inhomogeneities has been carried out in pure and mixed liquids at various temperatures. As in any vibrational spectroscopy, the results yield information about dynamics (in this case, molecular orientational dynamics) and also (effective) potentials. Configuration-averaged intermolecular "force constants" are determined.

In excimer-forming molecular crystals, the process of excimer formation (an oriented bimolecular reaction) can be initiated phase-coherently and then time resolved. Results in pyrene and \( \alpha \)-perylenes crystals, in which the excited-state reaction path is closely related to a single lattice phonon coordinate, will be presented.

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Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
First order optical design via ray transfer matrices can be combined with the first order expression for throughput or etendue, leading to a simple method of design of an efficient optical system from beam splitter to detector.

Address of Olson: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland 20894

ULTRA-HIGH RESOLUTION WITH A BOMEM SPECTROMETER

J.W.C. JOHNS

A relatively simple modification to a Bomem DA3.002 FT spectrometer has increased the maximum optical retardation to 4.54 m. The FWHM of the instrument function has thus been reduced to 0.0014 cm\(^{-1}\) which allows the observation of Doppler limited spectra to about 10 mm. The modification also changes the way in which the dynamic alignment has been implemented and this results in some other improvements.

The performance of the instrument, which has now been in operation for about six months, will be discussed.

Address: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

SELECTIVE FOURIER TRANSFORM SPECTROSCOPY OF RADICALS

M. Elhanine, R. Farenq and G. Guelachvili

Two types of selective detection of paramagnetic species, based on Zeeman effect, have been examined with both Fourier transform and diode laser spectrometers.

A magnetic modulation requires both a constant and a periodic magnetic fields; however a variation of the magnetic field in a plasma induces, in addition to Zeeman modulation, a non selective modulation concentration.

This effect is avoided with a polarization modulation which needs a polarizing system and a constant magnetic field only.

We present here experimental results obtained using these technics.

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HIGH PRECISION IN SPECTROSCOPY: THE STATE OF THE ART AND ITS EXPECTED LIMITATIONS

L. HENRY and A. VALENTIN

Systematic comparison of spectra obtained with grating, Fourier transform, tunable diode lasers and saturated absorption spectrometers gives strong experimental support for precision and accuracy of line parameters.

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ANALYSIS OF FERMI RESONANCES AND LOCAL MODES IN CH₂CL₂ AND CD₂CL₂ USING AN INTERNAL COORDINATE HAMILTONIAN

L. HALONEN

A curvilinear internal coordinate Hamiltonian is used to analyse Fermi resonances between CH₂CL₂ stretching and CH₂ (CD₂) scissoring vibrations in CH₂CL₂ and CD₂Cl₂. The Hamiltonian is constructed by expanding the matrix elements and the potential energy function in terms of the Morse variational y = 1 - exp (-\alpha r). For the stretches and the curvilinear internal bending coordinate for the scissoring vibration. The important local mode and Fermi resonance terms are retained in the final Hamiltonian. The eigenvalues are obtained variationally using a symmetrized Morse oscillator basis set for the stretching vibrations and a harmonic oscillator basis set for the scissoring vibration. The least squares method is used to optimize the potential energy parameters. The observed vibrational levels of CH₂Cl₂ and CD₂Cl₂ are reproduced well with a single potential energy surface.

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ROTATIONAL PARTITION FUNCTIONS FOR SYMMETRIC-TOP MOLECULES

ERVIN S. MCDOWELL

It has recently been shown that improved closed-form expressions for the rotational partition functions of linear and spherical-top molecules allow one to obtain these with high accuracy over a wide temperature range without having to calculate and sum explicitly the rotational energy levels. This work has been extended to symmetric-top molecules, with particular attention to (1) a new treatment of the quantization correction which converges more rapidly at all temperatures; (2) corrections for the effect of nuclear-spin statistics at very low temperatures; and (3) corrections for centrifugal distortion of the rotating molecules at high temperatures.

The derived form of the rotational partition function is

\[ Q = \exp(-\beta(\omega^2/2)) \sum_{m=-l}^{+l} \frac{1}{(1+\rho_0 + \rho_0^2 + \ldots)} \frac{1}{(1+\rho_0 + \rho_0^2 + \ldots)} \]

where \( \beta = \frac{\hbar^2}{kT} \), \( m = \frac{\hbar}{\gamma} \) for prolate tops or \( \frac{\hbar}{\gamma} \) for oblate tops; and for XY molecules \( \sigma = (2I_x + 1)\sigma/\gamma \), where \( I_x \) is the nuclear spin of the Y nuclei and \( \sigma \) is the classical symmetry number. Here the first five factors are the high-temperature quantum-mechanical partition function, with an improved series development to account for quantization. The factor \( 1+\delta \) accounts for nuclear-spin statistics, and is given by

\[ \delta = \exp(-\beta m^2)/\gamma \exp(\pi m^2/54)/(2I_x + 1)^2 \]

The final factor gives the centrifugal distortion correction in the form derived by Wilson, where in terms of the usual spectroscopic distortion constants \( D_J, D_K, D_K' \), the parameters are

\[ \rho_0 = -\frac{(8+2m-4m^2+3m^3)D_J + m(2-2m+3m^2)D_K + 3m^3D_K'}/12B, \]
\[ \rho_1 = \frac{(8+4m+3m^2)D_J + m(2+3m)D_K + 3m^2D_K'}/4B. \]

The accuracy of this expression will be demonstrated with calculations on \( \text{NH}_3, \text{CH}_2, \text{CH}_2^\prime \), and \( \text{CHD}_2 \).


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CALCULATION OF THE VIBRATIONAL ENERGY LEVELS OF TRIATOMIC MOLECULES

VIKTOR SZALAY

The vibrational energy levels of a number of triatomic molecules, HCN, HNC, C_3, CH_2, and H_2O have been calculated from their ground electronic state potential energy surfaces. The calculations were carried out with a new method developed for molecules with large-amplitude internal motions in Ref. (1). This new method allowed us to use a wide variety of potential surfaces, from the most complicated Sorbie-Murrell type surface of the HCN--HNC isomerization reaction^2 to the simple Hoy-Mills-Strey potential of H_2O^3 with minor changes in the computer program. The results are discussed and compared to those of the variational and nonrigid-bender^4 calculations. The Schrodinger equation of the effective bending Hamiltonian of triatomic molecules has been solved by combining the power and advantages of the variational method and of the discrete variable representation^5.

1. V. Szalay, J. Mol. Spectrosc. in press.

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DEGENERATE AND STRONGLY INTERACTING VIBRATIONAL STATES OF POLYATOMIC MOLECULES: THE PROBLEMS IN ROTATIONAL ANALYSIS AND DETERMINATION OF SPECTROSCOPIC CONSTANTS

V. G. TYUTEREEV

The problem of processing of experimental vibration-rotation spectra in the case of strongly interacting vibrational states are discussed. Among these two aspects of convergence problems are considered in more details: a) convergence properties of expansions of effective Hamiltonians; b) convergence properties of least square fits.

In order to improve convergence properties of a Hamiltonian more flexible developments may be applied. Nonpolynomial hamiltonians /1/ and interacting-state models are discussed in this context. A quality of a fit and extrapolation properties are improved, however, in many cases correlations between parameters and their ambiguities become more pronounced /2/ if interacting bands are treated together.

The subject is to study the following question. How to obtain simultaneously good fit of experimental data and unambiguous physically meaningful values of spectroscopic parameters?


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PERTURBATIONS OF THE DOMINANT APPROXIMATION IN SPHERICAL-TOP MOLECULES

B. J. KROHN AND J. K. G. WATSON

Observed systematic shifts of individual rotational lines within the fine-structure J-manifolds of fundamental bands have prompted a detailed analysis of tensor interactions between sublevels in the (v=1, J) excited state. Perturbation theory through third order yields algebraic expressions for transition wavenumbers. These formulas give wavenumbers in terms of diagonal tensor functions (the $F^+-$ and $F^+$ coefficients of Moret-Bailly /2/ and the $\xi$-coefficients of Ozier /3/) and rational functions of J and R. In most cases the accuracy is sufficient to fit diode spectra, and diagonalization of large matrices is thereby avoided.

Properties of clustered tensor functions lead to a qualitative description of the shifted lines. Expansions of these functions in terms of "cluster" quantum numbers (R,K) /4/ have been developed to give order-of-magnitude comparisons of contributions to the wavenumber shifts.

Fits of the formulas to the $u_1$ and $u_4$ spectra of $SiF_4$ are examined to test the accuracy, reliability, and convergence of perturbation theory.


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This paper is concerned with the rovibronic energy levels and intensities of rovibronic transitions in complexes formed from a rare gas atom and an open-shell diatomic molecule in a $^3\Sigma$ or a $^1\Sigma$ electronic state. Previously, Mills et al. have discussed pure rotational spectra of ArNO for the $^1\Sigma$ case.

The model system used in this work is an ArOH Van der Waals complex, where the OH internuclear axis can be at any angle ($\theta$) relative to the line connecting the Ar atom to the center of mass of the OH. The electronic states under consideration are the X $^3\Sigma$ and the A $^1\Sigma$ states of the OH radical. Such a model can be represented as an asymmetric rotor possessing electron-spin angular momentum and electronic orbital angular momentum.

The components of the rotational angular momentum are most naturally defined in the principal axis system of the triatomic ArOH complex. On the other hand, the components of the electronic orbital angular momentum are most naturally defined in the OH diatomic axis system. The components of the electron-spin angular momentum can be defined either in the OH axis system or in the principal axis system of ArOH.

We have derived matrix elements of the total rovibronic Hamiltonian, taking into account, as did Mills et al., the spin-orbit coupling, the spin-rotation interaction, and a quenching parameter, which allows the degeneracy of the $^3\Sigma$ and $^1\Sigma$ orbitals existing in the diatomic radical to be split upon complex formation. We have also derived the electric dipole transition moment matrix elements for rovibronic transitions of the type $^3\Sigma \rightarrow ^1\Pi$ and $^3\Pi \rightarrow ^1\Sigma$, respectively, where the $^3\Sigma$ and $^3\Pi$ labels describe electronic states in the diatomic radical. Results of calculations show that the "goodness" of various quantum numbers and the type of the rovibronic transitions (a,b or c-type) depend on the angle ($\theta$).

Both the theory and examples of calculated spectra with different values of the various parameters will be presented.


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RENNER-TELLER ROVIBRONIC SPECTRUM OF THE HCS RADICAL

AND THE ROVIBRATIONAL SPECTRUM OF HCS$^-$

P. Rosmus, J. Senekowitsch, S. Carter, H.-J. Werner and N.C. Handy

Using highly correlated electronic wavefunctions, the three-dimensional potential energy, electric dipole and electronic transition moment functions have been calculated for the first two electronic states of the HCS radical. Both states form a Renner-Teller pair, the lower has a bent equilibrium structure, the upper is linear. The results of the electronic structure calculations have been used in solutions of the nuclear motion problem. The standard perturbation theory results for the rovibrational levels will be compared with the variational rovibrational and rovibronic Renner-Teller results. In the calculation of the radiative transition probabilities between the rovibronic states contributions from the electric dipole moment functions of both electronic states as well as the electronic transition moment function have been considered. The rovibronic spectrum of the hitherto unknown HCS radical will be predicted. For the HCS$^-$ ion the rovibrational terms and radiative transition probabilities will be predicted. In these calculations the rotational-vibrational coupling has been fully accounted for.

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BOUND ROVIBRATIONAL STATES OF HeN$_2^+$

S.Miller, J.Tennyson, B.Follmeg, P.Rosmus and H.-J.Werner

The two-dimensional electronic ground state interaction potential of the He...N$_2^+$ system has been calculated from highly correlated electronic wavefunctions. The potential has a minimum about 140 cm$^{-1}$ below the dissociation limit and is deep enough to give rise to a cluster-like, bound structure with considerable number of rovibrational states. The well depth is almost independent of the N$_2^+$...He angle, which leads to large amplitude bending motions. Rovibrational calculations have been performed for J=0, 1 and 2. Values for the rotational constant B, the fundamental stretching frequency $\nu_s$, and its first and second overtone, the rotational constant $C_n$ in each $n\nu_s$ manifold, have been obtained from the energy levels computed. It is found that $B = 1.879$ cm$^{-1}$, $1\nu_s = 55.231$ cm$^{-1}$, $2\nu_s = 83.404$ cm$^{-1}$, $3\nu_s = 92.491$ cm$^{-1}$, $C_\nu = 0.477$ cm$^{-1}$, $C_1 = 0.370$ cm$^{-1}$, and $C_2 = 0.254$ cm$^{-1}$.

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SPECTROSCOPY AND PHOTOPHYSICS OF REFRACTORY MOLECULES AT LOW TEMPERATURE. THE GREEN SYSTEMS OF ZrS

B. SIMARD, S.A. MITCHELL, AND P.A. HACKETT

The diatomic molecule ZrS has been observed by laser induced fluorescence in a supersonic molecular beam following reaction of laser-vaporised zirconium atoms with 2% carbonyl sulfide (OCS) added into a flow of He carrier gas. Two band systems have been observed in the 413-700 nm region. The R-heads of their band origins lie at 20218.9 and 20208.3 cm\(^{-1}\). The former is tentatively ascribed to the \(E' E'\) transition; the latter remains unassigned but is shown to borrow all of its intensity from the former through a simple intensity borrowing mechanism. A vibrational analysis leads to the following molecular constants for the ground state: \(\omega_e = 548.4\) cm\(^{-1}\), \(\omega_{eX} = 1.6\) cm\(^{-1}\). Frank-Condon factors for several vibronic transitions are also reported. Intrinsic radiative lifetimes of several vibrational levels of both upper states have been measured, and confirm that the two states perturb each other. A limited deperturbation analysis has been carried out. Vibrational constants, mixing coefficients, interaction matrix elements and other spectroscopic parameters are reported.

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NEW INFRARED ELECTRONIC SPECTRA OF C\(_2\) AND SiC


Two new low-lying electronic states of C\(_2\), B'A\(_{1u}\) and B'\(\Sigma^+\)\(_{1u}\), were discovered by Fourier transform emission spectroscopy. The B'A\(_{1u}\)-A'\(\Pi_{1u}\) and B'\(\Sigma^+\)-A'\(\Pi_{1u}\) transitions occur prominently in the infrared emission spectrum of C\(_2\) recorded with the Fourier transform spectrometer associated with the National Solar Observatory at Kitt Peak. The C\(_2\) spectra were excited in an electrodeless microwave discharge of argon and allene.

The 0-0 band of the d'E'-b'\(\Pi\) transition SiC was observed\(^1\) near 6000 cm\(^{-1}\) by Fourier transform emission spectroscopy. The d'E'-b'\(\Pi\) transition of SiC corresponds to the B'\(\Sigma^+\)-A'\(\Pi_{1u}\) transition of C\(_2\). There are no previous spectroscopic observations of the SiC molecule.


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HIGH RESOLUTION LASER SPECTROSCOPY OF OH

D.J. RODGERS AND P.J. SARRE

The first observation of transitions in the $c^3\Pi - b^1\Sigma^+$ system of the OH$^+$ molecule has been achieved by fast-ion-beam laser photofragment spectroscopy. The spectrum was recorded by monitoring $O^+$ photofragment ions which are produced by predissociation of the $c^3\Pi$ state by repulsive $^1\Sigma^-$ and $^3\Sigma^-$ states.

Five vibrational bands have been recorded, with P, Q and R branch structure and molecular parameters have been determined. The rotational constant for the v=0 level of the $b^1\Sigma^+$ state agrees well with that obtained by Merer et. al. [1] from an analysis of perturbations in the $A^1\Pi - X^1\Sigma^-$ emission spectrum.

Molecular parameters for the $b^1\Sigma^+$ and $c^3\Pi$ states are in good agreement with those obtained from ab-initio calculations of the potential energy curves [2].


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ELECTRONIC SPECTROSCOPIC STUDIES AT BHABHA ATOMIC RESEARCH CENTRE

T.K. BALASUBRAMANIAN AND S.L.N.G. KRISHNAMACHARI

At the Spectroscopy Division of Bhabha Atomic Research Centre, there is an ongoing programme of research relating to the study of the electronic spectra of diatomic molecules and radicals. A 10.6 m Ebert grating spectrograph set up some years ago in the laboratory and a few other smaller grating and prism spectrographs are being used to carry out systematic investigations on several molecules which include some hydrides and a host of heavier ones like AlO, NS, S$_2$ ... to name a few. A flash photolysis set up coupled to a suitable spectrograph has helped to obtain and identify new radicals like NOCS, NOCO etc. Identification of new electronic states or new electronic transitions and the characterization of the new radicals are the main objectives of these studies.

The rotational intensity distribution in the spectra of some of the molecules have been investigated from the theoretical and experimental standpoints. From this, important conclusions could be drawn regarding the nature of the electronic states.

The fluorescence spectra of I$_2$ and Na$_2$ excited by Ar$^+$ and He-Ne laser lines have been studied leading to useful conclusions on the electronic transition moment functions in the related transitions.

Results of these studies will be highlighted in the talk.

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MAGNETIC DIPOLE TRANSITIONS IN DIATOMIC MOLECULES: SOME NEGLECTED ASPECTS
T.K. BALASUBRAMANIAN AND V.P. BELLARY

A diatomic molecule in the vibronic state \( | \tilde{E};v \rangle \) has a dominant magnetic moment given by \( \frac{1}{2} e\mu B \langle \tilde{E} \rangle \) which due to which weak rotational transitions within this state are possible. Magnetic dipole transitions of this kind are known in the \( X^3 \Sigma^- \) state of \( \text{O}_2 \). Extending the results to other electronic states, expressions for the intensity factors are derived for rotational transitions in \( 1 \Sigma \) and \( 3 \Sigma \) states. A noteworthy feature is that both parallel and perpendicular moments can contribute to the rotational intensities.

An allied aspect, perhaps more interesting, is that the magnetic moment in the state \( | \tilde{E};v \rangle \) has no dependence on the internuclear distance. Thus in a given electronic state rotation-vibration transitions of magnetic dipole origin seem forbidden notwithstanding the occurrence of pure rotational transitions. Nevertheless one could invoke indirect mechanisms that can impart non-zero intensities to ro-vibrational transitions. In the simplest case of a \( \Sigma (\Lambda \neq 0) \) state centrifugal distortion is one such mechanism. In states of higher multiplicity other mechanisms are conceivable.

Possible application of these results will be indicated.

\[ ^1 \text{L.R. Zink and M. Mizushima, J. Mol. Spectrosc. 125, 154 (1987).} \]

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ON THE WIGNER - WITMER CORRELATION RULES IN DIATOMIC MOLECULES
T.K. BALASUBRAMANIAN AND V.P. BELLARY

The rules for building the manifold of electronic states of a diatomic molecule from those of the separated atoms were originally given by Wigner and Witmer. Most of these rules seem intuitively plausible and their validity is readily demonstrated. An exception is the derivation of the terms for a homonuclear diatomic molecule from the separated atoms in identical atomic states. Here the answer to the important question of the \( u \) or \( g \) character of the resulting molecular state is not so obvious. In the original paper this point has been settled by resorting to group theoretical arguments.

We have been able to show that the same results could be obtained by invoking a simple model which reduces the problem to one akin to the Heitler-London treatment of the \( \text{H}_2 \) molecule. In the limit of strong spin-orbit coupling in the atoms, the model can be extended readily to derive Hund's case (c) molecular states.

\[ ^1 \text{E. Wigner and E.E. Wittmer, Z. Physik 51, 859 (1928).} \]
\[ ^2 \text{G. Herzberg, Molecular Spectra and Molecular Structure Vol.1 (Spectra of Diatomic Molecules) Van Nostrand, New York (1950).} \]
\[ ^3 \text{L.D. Landau and E.M. Lifshitz, Quantum Mechanics , Pergamon Press, London (1965).} \]

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THE ELECTRONIC SPECTRUM OF MANGANESE MONOHYDRIDE

W. J. BALFOUR, B. LINDGREN AND S. O'CONNOR

The electronic spectrum of MnH has been examined in thermal emission from Mn/H₂ mixtures in a King furnace using both photographic and Fourier transform techniques. Two systems have been studied at high resolution: an infrared system centered near 847 nm and a visible system in the blue near 480 nm. Rotational analysis of the 847 nm system shows it to be due to a \(^3\Sigma - ^1\Sigma\) transition. The 480 nm spectrum, which is extremely complex with dense rotational structure, arises from a \(^3\Pi - ^1\Sigma\) transition. The two systems have the same lower electronic state. While the MnH spectra appear relatively free of local perturbations the corresponding MnD spectra show a number of branch irregularities. Branches in both systems are broadened to differing extents through nuclear hyperfine coupling.

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UV ABSORPTION SPECTROSCOPY OF SUPERSONIC JET-COOLED MOLECULES; THE SCHUMANN-RUNGE BANDS OF OXYGEN

K. YOSHINO, A. S.-C. CHEUNG, W. H. PARKINSON and D. E. FREEMAN

We have developed instrumentation which uses the technique of supersonic jet expansion of a gas through a small orifice to produce cold gas-phase molecules. The absorption spectrum of oxygen in the wavelength region 170-180 nm has been investigated at very low temperature with a 6.65 m vacuum spectograph/spectrometer with a resolution of 0.0006 nm. The supersonic jet (SSJ) is crossed with a focused continuum uv radiation from a hydrogen discharge lamp. The light transmitted through the molecular beam is refocused on the entrance slit of the 6.65 m vacuum spectograph. The cooling effects are easily demonstrated by intensity distribution of rotational lines. The rotational intensity peak in the SSJ spectrum are lines with N=1 or 3 which indicates the rotational temperature of the supersonic cooled gas is around 25K.

This work is supported by the Smithsonian Institution, SS52-2-85.

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LEVEL SHIFTS IN THE $B^3E_u$ STATE OF MOLECULAR OXYGEN

R.S. FRIEDMAN AND A. DALGARNO

The $B^3E_u$ state of molecular oxygen (the upper state of the Schumann-Runge band system) is predissociated by several repulsive continuum states including the $^1Π_u$, $^3Π_u$, $^5Π_u$, and $2^2E_u$ states. In an extension of the work of Julienne and Krauss, who first showed that the $^3Π_u$ state is the dominant perturbative state, we have determined an empirical representation for the $^1Π_u$ state which yields a smooth deperturbation in the second vibrational energy differences of the three isotopic molecules $^{16}O_2$, $^{18}O_2$, and $^{16}O^{18}O$. The $^5Π_u$ state is found to cross the $B^3E_u$ state at 1.880 Å with a slope at the crossing point of 40000 cm$^{-1}$ Å$^{-1}$ and the coupling strength between the $^3Π_u$ and $B^3E_u$ states is 65 cm$^{-1}$.

This work is supported by NSF Grant ATM-87-13204 to Harvard University.


BAND OSCILLATOR STRENGTHS OF THE SCHUMANN-RUNGE ABSORPTION BANDS OF MOLECULAR OXYGEN

R.S. FRIEDMAN

Band oscillator strengths of the Schumann-Runge ($B^3E_u - X^3E_g$) absorption bands of $^{16}O_2$, $^{18}O_2$, and $^{16}O^{18}O$ have been theoretically determined and are compared to the Harvard-Smithsonian experimental values. A slight increase in the magnitude of the theoretical electronic transition moment results in satisfactory agreement between theory and experiment for all three species.

This work is supported by NSF Grant ATM-87-13204 to Harvard University.

ROTATIONAL STRUCTURE OF THE LOW LYING ELECTRONIC STATES OF SAMARIUM MONOXIDE

GUO BUJIN AND C. LINTON

High resolution laser excitation spectra have been obtained for several transitions involving three of the lowest lying states of SmO. Very careful wavelength selected detection enabled us to eliminate unwanted overlapping transitions and to obtain separate spectra for the individual $e,f$ parity components of an $O = 1-1$ transition. The rotational structure has been assigned for six isotopic species and the molecular constants computed using a simultaneous least squares fit to all the transitions. Some parity and isotope dependent perturbations were observed in the [16.9] state. The results of the analysis will be presented and the rotational constants, $Ω$-doubling, isotope effects and the interpretation of perturbations will all be discussed.

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LASER SPECTROSCOPY OF THULIUM MONOXIDE

C. LINTON AND D.N. HEUFF

High resolution excitation spectra have been obtained for six electronic transitions of TmO. Analysis of resolved fluorescence and excitation spectra have enabled us to assign four low lying electronic states and provide energy linkages between them. The excitation spectra show well resolved rotational and hyperfine structure (I=0.5 for Tm) and some transitions show large D-doubling. Several transitions are complicated by perturbations.

The results of the preliminary analysis will be presented. The electronic state assignments and energy linkages will be discussed and compared with predictions of Ligand Field Theory calculations.

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LONG WAVELENGTH VIBRONIC TRANSITIONS OF $^{79}$BrCl AND $^{81}$BrCl

B. McFEETERS, L. HANKO, G.P. PERRAM, AND E.A. DORKO

A technique was developed by which the vibronic spectrum of bromine monochloride was observed from laser induced fluorescence at long wavelengths. An RCA C31034 PMT was used to detect short wavelength emissions (650-890nm) and an ADC cooled germanium infrared detector was used to detect long wavelengths (800nm-1.1μ). The vibrational band heads were spectrally resolved with a resolution of 0.2nm at 650-890nm and 1.0nm at 800nm-1.1μ. This resolution allowed the separation and characterization of the bandheads for the two bromine isotopes.

The signal from the ADC detector was passed through a lock-in amplifier. A computer controlled data acquisition system allowed the signal from the lock-in to be averaged at each spectral point for 100-400 signals. This technique increased signal to noise substantially and allowed the observation of previously unreported transitions so that band heads could be readily reported. These studies allowed the extension of the spectral observations of Coxon (1) on BrCl. The newly observed transitions ranged from v'=3→v''=5 to v'=0→v''=19. Molecular constants were calculated from the values for the band head positions by means of a merging technique (2). The calculated constants were compared with those reported by Coxon (1) for shorter wavelength transitions. The correspondence between the constants will be discussed.


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AB INITIO ANALYSIS OF PERTURBED ROTATIONAL LEVEL STRUCTURE IN EXCITED STATES OF HeD

M.C. VAN HEMERT AND S.D. PEYERIMHOFF

The bound excited states of the HeH molecule are known to have strong interaction with the repulsive ground state through the radial component of the nuclear kinetic energy operator. Apart from this interaction that leads, as in the case of ArH(I), to predissociation of the vibrational levels, there is also interaction between the bound states, as was found in recent emission spectroscopy experiments for HeD(2).

It will be demonstrated that also in the case of bound-bound interaction, radial coupling is the source of the perturbations. A two-states coupled equations formalism, using matrix elements resulting from large scale ab initio MRDCI calculations, is shown to give a quantitative explanation of the perturbed level structure in the HeD C,D-A emission.


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THE COMET-TAIL AND BALDET-JOHNSON SYSTEMS OF $^{13}$C$^{18}$O$^{+}$

S. PADDI REDDY AND C. V. V. PRASAD

The emission spectra of the comet-tail ($A^{2}E_{1} - X^{2}Z^{+}$) and the Baldet-Johnson ($B^{2}E^{+} - A^{-1}$) bands of the molecular ion $^{13}$C$^{18}$O$^{+}$, excited in the cathode glow of a hollow-cathode discharge tube of special design, and occurring in the spectral regions 3700 - 4225 Å and 3620 - 6165 Å, respectively, were observed for the first time. The rotational structure of seven bands of the A-X system involving $v' = 0$ to 5 and $v'' = 0$ to 2 and that of three (1-0, 0-0, and 0-1) bands of the B-X system were photographed in the 2nd and/or 3rd orders of 2 m and 3.4 m grating spectographs. All the twelve branches of each of the bands of both systems (except only six branches for the 0-1 and 0-2 bands of the A-X system arising from $^{2}S_{1/2} - X^{2}Z^{+}$) were rotationally analyzed. The molecular constants obtained from the analysis of the wavenumber data of the individual bands of both systems were merged together and a unique set of constants for the $X^{2}Z^{+}$, $A^{2}E_{1}$ and $B^{2}E^{+}$ states of $^{13}$C$^{18}$O$^{+}$ was obtained.

Research supported in part by NSERC Grant No. A-2440.

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FOURIER TRANSFORM SPECTROSCOPY OF $^7$Li$_2$: THE $^1\Sigma^+_u^-$-$^3\Pi_u^-$ TRANSITION

R. BACIS, F. MARTIN, C. LINTON, GUO BUJIN, C.H. CHENG AND E. STAD

Fluorescence resulting from excitation of $^7$Li$_2$ by the 476.5 nm line of an Argon ion laser has been detected at very high resolution using a Fourier Transform spectrometer at Orsay. A very rich, complex spectrum is obtained in the 8000-10000 cm$^{-1}$ region. By comparing results of a preliminary rotational analysis with ab-initio calculations, the spectrum has been assigned to the $^1\Sigma^+_u^-$-$^3\Pi_u^-$ transition, and is the first triplet system of Li$_2$ to be observed at high resolution. The results of a global fit to the 31 analyzed bands will be presented and rotational constants, dissociation energies, potential curves and Franck-Condon Factors will be discussed and compared with ab-initio calculations.

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THE OBSERVATION OF CS$_2$ CONTINUUM-LIKE EMISSION IN A SUPERSONIC JET

D. GIBLIN, S. J. McNICHOL, AND S. J. SILVERS

When CS$_2$ is excited in the 280 - 340 nm region, its dispersed fluorescence displays both discrete and continuum-like components. Our bulb studies have shown that the continuum is enhanced by collisions, but persists in the low pressure limit where collisions during the excited state lifetime are unlikely.

This work in a supersonic jet confirms that continuum emission persists under essentially collision-free conditions. The continuum emission is identified both by dispersing the fluorescence and by observing its long (relative to the discrete emission) lifetime. The amount of continuum compared to discrete emission is monitored as the excitation wavelength is scanned through the region of the T and V systems bands. Continuum emission is excited almost everywhere; an apparent continuum in excitation corresponds to the one seen in emission. In the region of excitation bands the discrete and continuum emissions do not track each other; the continuum/discrete ratio varies with J.

The origin of CS$_2$ continuum-like emission is discussed using a model proposed by Hardwick$^1$ to explain similar emission for NO$_2$.


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PHOTO-ASSISTED FRAGMENTATION SPECTROSCOPY BY NEUTRALIZATION-REIONIZATION MASS SPECTROSCOPY$^1$ SUSAN F. SELGREN AND GREGORY I. GELLENE

A new technique whereby the high resolution absorption spectrum of unusual radicals in a high velocity beam can be obtained by monitoring photo-induced changes in their neutralization-reionization mass spectra will be described. Very recently obtained absorption spectra for the H$_3$ radical will be presented as evidence of the feasibility of the technique. Application of this technique toward the observation of the electronic spectra of the hypervalent radicals NH$_4$, H$_3$O, and H$_2$F will be discussed.

$^1$This work was supported by Finnigan MAT through the ASMS research award program.

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EXCITATION AND DISPERSED FLUORESCENCE SPECTRA OF THE ETHOXY FREE RADICAL

STEPHEN C. FOSTER, PRABHAKAR MISRA, T.-Y. LIN, CRISTINO P. DAMO, CHRISTOPHER C. CARTER, AND TERRY A. MILLER

Alkoxy free radicals are well known chemical intermediates in combustion processes and atmospheric reactions. Our laboratory has studied a number of these radicals: methoxy, ethoxy, iso-propoxy, and ethynyloxy. Typically, these are produced in situ by excimer laser photolysis of the appropriate precursor in a pulsed or cw supersonic free jet expansion. Ultra-high resolution spectra of the $A - X$ transition of ethoxy, $C_2H_5O$, have been obtained with our argon-ion pumped ring dye laser system with pulse amplification; rotational resolution is significantly better than spectra obtained previously with our YAG-pumped dye laser. Wavelength-resolved spectra have also been obtained using an excimer-pumped dye laser with an optical multichannel analyzer. Details of the rotational and vibrational analyses of the ethoxy free radical will be presented.

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IONIC CLUSTERS [(NO)\textsuperscript{n}, (C\textsubscript{6}F\textsubscript{5})\textsuperscript{R,} R=He, Ne or Ar] IN A SUPersonic JET

S.-Y. KUNG, RICHARD A KENNEDY, DAVID A. DOLSON, AND TERRY A. MILLER

An apparatus which combines the ability to take laser induced fluorescence (LIF) and time-of-flight (TOF) mass spectra has recently been put into operation in our laboratory. We have performed initial experiments on cluster species involving NO\textsuperscript{+} and C\textsubscript{6}F\textsubscript{5}\textsuperscript{+}.

Resonantly enhanced multiphoton ionization of NO produces cleanly NO\textsuperscript{+} in a supersonic jet expansion. Sampling of the expansion through a skimmer with a TOF mass spectrometer reveals that cluster species containing as many as 15 NO's and 20 Ar's can be grown from the isolated NO\textsuperscript{+} seed.

For the van der Waals molecules (C\textsubscript{6}F\textsubscript{5})\textsuperscript{R,}, the TOF mass spectrometry is combined with laser induced fluorescence (LIF) measurements prior to skimming the expansion. Features in the LIF spectra can thus be correlated to the species present in the jet as determined directly by the TOF analysis.

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PHOTOPHYSICS OF AZULENE FROM S\textsubscript{1} MANIFOLD

SUDHIR S. KULKARNI AND JONATHAN E. KENNY

Absorption spectra of azulene from S\textsubscript{1} manifold are obtained in a pulsed planar supersonic jet. Line profiles of single vibrational levels, starting from S\textsubscript{1} origin up to 2417 cm\textsuperscript{-1} excess energy, are obtained and homogeneous linewidth contributions are extracted using proper deconvolution procedures. Lifetimes as well as internal conversion rates from single vibrational levels are calculated. Internal conversion rates appear to increase as a function of excess energy. Internal conversion processes from the S\textsubscript{1} and S\textsubscript{2} state are compared.

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PRERESONANCE RAMAN INTERFERENCE IN LINEAR POLYENES

J. SITAINBUCH and J. E. LEROU

In centrosymmetric chromophores, such as linear polyenes, approximately half of the electronic excited state manifold is inaccessible from the ground state by conventional absorption spectroscopy because of parity selection rules. However, the presence of such "hidden" excited states can sometimes be inferred from preresonance Raman excitation profiles. As the excitation radiation is tuned through the appropriate energy range vibronic coupling between the state of interest and nearby "allowed" electronic states will produce interference effects in the ground state scattering intensity.

We have used this method in conjunction with two-photon excitation data for a diphenyldecapentaene (DPDP) to locate the lowest-lying excited gerade singlet state (\(A_g\)) of DPDP. Excitation was supplied by an Ar-pumped tunable dye laser in the wavelength region covered by coumarin 480 and stilbene 420. The excitation spectrum was determined point-by-point from the ratio of the scattered intensity of the DPDP C=C symmetric stretch (1565 cm\(^{-1}\)) to that of a cyclohexane solvent made at 1446 cm\(^{-1}\). The technique has been applied to other polyenes, and results for all systems investigated to date will be described.

R. R. Birge and H. L. Fang, private communication.

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CHARACTERIZATION OF EXCITED ELECTRONIC STATES OF LIGAND-BRIDGED Ru(II) BIMETALLIC COMPLEXES BY RESONANCE RAMAN SPECTROSCOPY

C. TURRO, P. J. WAGNER, and G. E. LEROI

Various polypyridyl organometallic complexes of Ru(II) and other d\(^{6}\)-transition metals have been subjects of recent study. Interest in these systems stems from the possible application of their metal-to-ligand charge transfer (MLCT) excited states in energy conversion processes.

We have prepared and investigated spectroscopically (bpy\(_2\))\(_2\)Ru(II)(bpm), (phen)_2Ru(II)(bpm), [(bpy)_2Ru(II)]\(_2\)(bpm), and [(phen)_2Ru(II)]\(_2\)(bpm), where bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, and bpm = 2,2'-bipyrimidine. The monometallic complexes show intense absorption in the blue region of the spectrum, whereas the lowest energy MLCT absorption band of the bimetallic complex is red shifted. The bimetallic complexes have many MLCT transitions in the visible region. Resonance Raman spectroscopy has been utilized to characterize and assign these transitions.


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FLUORESCENCE EXCITATION SPECTROSCOPY OF p-C₆H₄Cl₂ AND p-C₆D₄Cl₂ IN A SUPERSONIC FREE JET EXPANSION  W. D. SANDS AND R. MOORE

The spectra of p-C₆H₄Cl₂ and p-C₆D₄Cl₂ have been assigned over the range of 0 - 2500 cm⁻¹. The spectra are dominated by totally symmetric vibrations and vibronically allowed b₃g vibrations. Overtones of several out of plane bending modes are observed. The S₁ frequencies are markedly reduced from S₀ values, indicating that the molecules are significantly less rigid in S₁. Isotopic frequency shift ratios due to chlorine and deuterium/hydrogen substitution are in good agreement with those derived from ab initio calculations of vibrational frequencies and normal modes.

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ULTRA HIGH-RESOLUTION ELECTRONIC SPECTROSCOPY IN MOLECULAR BEAMS. THE S₁-S₀ TRANSITION OF 1-FLUORONAPHTHALENE  D. F. PLUSQUELLIC, W. A. MAJEWSKI, AND D. W. PRATT

The past few years have witnessed major advances in the resolution of spectroscopic experiments carried out in UV, visible, and infrared regions of the electromagnetic spectrum. In this report, we describe the first test of our new "laser spectrograph", consisting of a tunable, single-frequency dye laser operating in the UV, a molecular beam machine, and a sophisticated data acquisition system. Linewidths of less than 5 MHz have been achieved in the S₁-S₀ fluorescence excitation spectrum of 1-fluoronaphthalene, at ca. 310 nm, permitting tests of the instrumental bandwidth and sensitivity as well as a determination of the beam rotational temperature and velocity distribution. Complete resolution of the rotational structure in different vibronic bands also makes possible measurements of the inertial constants of both S₁ and S₀ states and the orientation of the optical transition moment relative to the inertial frame. Future applications of this instrument to problems in chemical dynamics will be discussed.

*Work supported by NSF, WPATC, and the University of Pittsburgh.

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CONFORMATIONAL CHANGE ON ELECTRONIC EXCITATION. THE LOWEST EXCITED TRIPLET AND SINGLET STATES OF ACETOPHENONE AND 2-METHYLPYRAZINE

J. L. TOMEER, S. YAMAUCHI, AND D. W. PRATT*

Several recent studies have shown that the conformational preferences of methyl groups adjacent to double bonds in the ground states of organic molecules are reversed on electronic excitation.1 In this report, we describe the results of phosphorescence and fluorescence excitation experiments in a supersonic jet that were designed to explore the origins of these effects. S1 acetophenone exhibits the expected change, with the methyl group being staggered with respect to the carbonyl bond rather than eclipsed, as in the ground state. But T1 acetophenone exhibits no such change, a fact that can be attributed to subtle differences in the orbital character of the two excited states. In contrast, both S1 and T1 2-methylpyrazine have methyl group conformations that are identical to the ground state. Analyses of these results, in terms of the usual potential functions for hindered methyl rotors, provide considerable insight into the electronic factors that are responsible for these effects.

*Work supported by NSF.


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ROTATIONALLY RESOLVED PHOSPHORESCENCE EXCITATION SPECTRUM OF p-BENZOQUINONE IN A SUPersonic JET. ORBITAL SYMMETRY OF THE LOWEST TRIPLET STATE

J. R. JOHNSON, S. YAMAUCHI, AND D. W. PRATT*

We report the first study of the lowest triplet state of p-benzoquinone (pBQ) with both vibrational and rotational resolution, using the technique of phosphorescence excitation spectroscopy in a supersonic jet. The strongest band in the spectrum, at ca. 535 nm, has previously been assigned as the origin of the 3AGamma → 1AGamma electronic transition.1 The rotational structure of this band will be presented and shown to be inconsistent with assignment of AGamma orbital symmetry to the lowest triplet state. A resolution of this problem will be proposed, leading to a mutually consistent interpretation of the properties of triplet pBQ in the gas and condensed phase, and its geometry, vibrational frequencies, and electronic character.

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HIGH RESOLUTION ABSORPTION SPECTRUM OF THE MOLECULAR EIGENSTATES OF PYRAZINE

W.M. VAN HERPEN, P.A.M. UIJT DE HAAG and W. LEO MEERTS

The pyrazine molecules serves as a prototype of an intermediate case molecule in the theory of intramolecular radiationless transitions. The main attention is focused on the fluorescence decay of the first excited singlet \( ^1B_3u \) electronic state. For a recent review see [1] and the references therein.

The high resolution absorption spectrum of the P, Q and R branches of the 0-0 electronic transition of pyrazine was recorded with a bolometer in a supersonic molecular beam and a single mode, frequency doubled ring dye laser. A residual Doppler linewidth of 50 MHz was achieved. Simultaneously with the absorption spectrum the laser induced fluorescence spectrum was observed. A comparison is made between excitation and absorption intensities of the molecular eigenstate spectra. It is concluded that substantial differences exist between both spectra.


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INTERSYSTEM CROSSING IN NAPHTHALENE AT ROTATIONAL RESOLUTION

P. UIJT DE HAAG and W.LEO MEERTS

Due to intersystem crossing the \( S_1 \) state of naphthalene is coupled to a manifold of triplet states. Therefore part of the excited singlet state molecules will end in the triplet state. We have measured simultaneously the laser induced fluorescence and phosphorescence spectra of several vibronic bands of the \( S_1 \rightarrow S_0 \) transition in naphthalene in a molecular beam. The phosphorescence was detected by colliding the molecules after excitation on a cold copper surface further downstream.

With this set-up, in combination with a single frequency laser rotational resolution was achieved. The resulting spectra correspond to an asymmetric rotor, for which all lines could be identified. We found the intersystem crossing rate to be independent of the rotational quantum numbers and depending on the vibrational state.

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INFRARED SPECTRUM AND STRUCTURE OF THE $\text{AlC}_2\text{H}_4$ MOLECULE IN SOLID ARGON

Laurent Manceron and Lester Andrews

$\text{AlC}_2\text{H}_4$, aluminum monoethylene, has been synthesized by cocondensation of Al atoms and ethylene molecules in solid argon. Analysis of the isotopic shifts (using $\text{C}_2\text{H}_4$, $\text{C}_2\text{D}_4$, $^{13}\text{C}_2\text{H}_4$ and $\text{CH}_2\text{CD}_2$) for the 7 observed fundamentals, shows that the metal forms a symmetrical $\pi$ complex of $C_2v$ symmetry. A normal-coordinate analysis for the Al block motions estimates the perturbations of the $\text{C}=$ and $\text{CH}_2$ bending and stretching force constants, and allows quantitative comparisons with other metal complexes of transition metals and lithium with ethylene. If these complexes present structural similarities and comparable perturbations of the $\text{C}=$ bond, $\text{AlC}_2\text{H}_4$ presents two noteworthy characteristics: i) a relatively large Al-C force constant and ii) the relative intensities of the observed fundamentals are very different from other $\pi$ complexes. This second point is analysed through estimates of some of the electro-optical parameters of $\text{AlC}_2\text{H}_4$, linked to the variation of charge flow between the metal center and the $\pi$ bond through $\text{CC}$ distance or $\text{CH}_2$ bond angle variations. Comparison with the same parameters in $\text{LiC}_2\text{H}_4$ reveals a significant difference. This fact might be more indicative of differences in the nature of the bonding between the metals and the $\text{C}=$ double bond, than is a simple comparison of the vibrational frequencies or even $\text{C}=$ force constant perturbations.

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MATRIX REACTIONS OF OXYGEN ATOMS WITH $P_4$. INFRARED SPECTRA OF $P_4\text{O}$, $P_2\text{O}$, $P\text{O}$ and $P\text{O}_2$

Lester Andrews and Robert Withnall

Oxygen atoms (160 and 180) were reacted with $P_4$ molecules using ozone photolysis and discharge of oxygen as sources, and the products were trapped in solid argon at 12K. The major product $P_4\text{O}$ exhibited a strong terminal $P=\text{O}$ stretching mode at 1241 cm$^{-1}$, a $P-P=O$ deformation mode at 243 cm$^{-1}$, and four $P-P$ stretching modes near $P_4$ values, all of which characterize a $C_3v$ species. Two new molecular species probably arise from energized $P_4\text{O}$ before relaxation by the matrix: the first absorbed at 1197 cm$^{-1}$, photolysed with red light, and is probably $P_2\text{O}$; the second absorbed at 856 and 553 cm$^{-1}$, increased with short wavelength radiation, and is most likely due to the $C_2v$ bridge-bonded $P_4\text{O}$ structural isomer. Higher discharge power gave O atoms and vacuum ultraviolet radiation; these conditions favored the bridge-bonded $P_4\text{O}$ species and the simple oxides $P\text{O}$ and $P\text{O}_2$, which were observed at 1218 and 1319 cm$^{-1}$, respectively. The matrix efficiently quenched the large exothermicity ($130 \pm 10$ kcal/mole) for the $P_4 + \text{O}$ reaction and allowed the lowest oxide of phosphorus $P_4\text{O}$ to be trapped for the first time as a molecular species.

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INFRARED SPECTROSCOPY AND PHOTOCHEMISTRY ON SALT FILMS

O. BERG AND G.E. EWING

Sublimation as alkali metal halides in vacuo produces well-defined crystals of colloidal scale. Such films have high specific surface areas and are transparent from the infrared through the ultraviolet. Thus they are useful as substrates for the spectroscopic study of adsorbed species. We are currently exploring the photochemical behavior of small molecules adsorbed on sodium chloride. Sub-monolayer coverages of carbon monoxide, when irradiated with ultraviolet light, produce carbon dioxide and carbon monoxide cation; in the presence of sulfur, carbonyl sulfide is formed. We will discuss the role of the substrate in these reactions, and evaluate sodium chloride as a medium for modifying and trapping surface reactants. We will also make analogies between salt film and matrix isolation spectroscopy for the study in small molecule photochemistry.


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"ISOELECTRONIC" TRANSITION-METAL DIATOMIC MOLECULES: ScNi, ScPd, YNi, YPd

R. J. VAN ZEE AND W. WELTNER, JR.

ESR spectra of three of these molecules were observed in solid argon matrices at 4 K; results on ScNi have been reported earlier. They were all found to have 2E ground states, as the simplest theory predicts for molecules having the same number of d + s valence electrons. g-tensors and hyperfine coupling constants with 45Sc, 89Y, and 105Pd nuclei were determined. The 2E ground state of YPd found here is among the three lowest states calculated by Shim and Gingerich.


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S = 4 and S = 5 SPIN STATES OF THE "ANTIFERROMAGNETIC" Mn2 MOLECULE

M. CHEESEMAN, R. J. VAN ZEE AND W. WELTNER, JR.

Mn2 has been shown to be a van der Waals molecule with the two Mn atoms (3d54s2) antiferromagnetically coupled (J = -10 cm⁻¹) to form a 1Eg lowest state. Mn2 can be formed in solid methane or cyclopropane at 12 K without reacting, and warming successively populates the higher S = 1, 2, 3, 4, 5 spin states. These hydrocarbon matrices allowed higher temperatures to be reached than in rare-gas matrices with still resolvable spectra so that ESR transitions in S = 4 and S = 5 could be observed and analyzed. The derived g and D values corroborate the earlier application of the Judd-Owen theory.


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ESR OF TRANSITION METAL DIATOMIC IONS: Mn₂

R. J. VAN ZEE, M. CHEESEMAN, AND W. WELTNER, JR.

The molecular cation $^{55}$Mn⁺ has been generated in an argon matrix at 4 K by simultaneous laser vaporization of manganese metal and open tube argon discharge photoionization. Its ESR spectrum contains many fine structure lines, each apparently split by hyperfine interaction into 11 lines spaced 25 G apart, identifying two equivalent $^{55}$Mn($I = 5/2$) nuclei. Tentatively, it is a high-spin $^{1^2}$I molecule with a zero-field splitting parameter, $D$, of about 0.06 cm⁻¹. This contrasts sharply with Mn₂ which has an "antiferromagnetic" $^{3^2}$I ground state, but also a much weaker bond than Mn₂.

1 Similar to the procedure pioneered by L. B. Knight, Jr., Acc. Chem. Res. 19, 313 (1986).

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FTIR ISOTOPIC STUDY OF THE C₃H RADICAL IN AN ARGON MATRIX AT 9 K

JIUNWEOI HUANG and W.R.M. GRAHAM

The rotational spectrum of C₃H observed in two astronomical sources and in the laboratory showed that it has a linear structure with a $^2Π$ ground state. Ab initio calculations by Green¹ support this model. In a previous IR study,² bands at 1834 and 1826 cm⁻¹ obtained by the vacuum uv photolysis of methylacetylene and allene were assigned to an antisymmetric C-C stretch mode of C₃H, and the same mode of C₃D was also reported. In the present FTIR study using the photolysis of methylacetylene and its deuterated counterparts, vibrational frequencies in addition to those reported earlier by Jacox and Milligan, have been observed. The analysis for C₃H and C₃D will be reported.


Supported by the Welch Foundation

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HIGH RESOLUTION, HIGH DILUTION SPECTRA OF OCS IN Ar, N₂, AND Xe
VALERIE I. LANG AND JOHN S. WINN

We have used high resolution (0.01 cm⁻¹) FTIR spectroscopy to measure the spectrum of OCS isotopomers in natural abundance in Ar, Xe, and N₂ matrices at dilutions as high as 1:96,000 in the 2000 cm⁻¹ region (the nominal CO stretch region). Over the temperature range 10 - 30 K, we find very different behavior to the positions of the absorptions and their widths. Most striking is a narrowing of widths with increasing temperature in Ar, but a broadening in N₂. At these dilutions, the true "matrix isolation limit" to the spectra can be attained: viz., single sharp (FWHM ~0.04 cm⁻¹) features for each isotopomer. Annealing induces irreversible changes that are sensitive probes of the solute-solvent interactions. A potential energy model for these interactions will be discussed that can rule out certain assignments to new features and illuminate the origin of the shift in absorption frequency when OCS is taken from the gas phase to the matrix phase. The model also allows identification of the origin of the two features seen in Xe spectra as two readily identifiable matrix sites.

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SPATIALLY-RESOLVED MATRIX ISOLATION ACTION SPECTRA OF Cr(CO)₆
VALERIE I. LANG AND JOHN S. WINN

We have used the technique of spatially-resolved matrix isolation spectroscopy to elucidate the photochemical action spectrum of the Cr(CO)₆ - Cr(CO)₅ - Cr(CO)₄ photochemical system in an Ar matrix. In this technique, we exploit the fact that each position on a matrix isolation sample is potentially the site of a different experiment. Here, we labeled each position parametrically with a unique photolysis wavelength produced by passing a continuum source through a simple quartz prism. The dispersed lamp spectrum was spayed across the matrix, and a spatially uniform probe beam at one wavelength imaged through the matrix onto a linear photodiode array detector allowed us to observe the changes in species' concentrations at all photolysis wavelengths in a single experiment. In the Cr(CO)₆ system, we were able to elucidate the photodissociation and photoreversion spectra of the three principle species in spite of the fact that the absorption spectra were highly overlapped. The low energy absorption band of Cr(CO)₄ was identified in this way for the first time.

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Current Address of Lang: Jet Propulsion Labs, 183-301, 4800 Oak Grove Drive, Pasadena, CA 91109
THE EFFECT OF HYDROGEN BONDING ON THE VIBRATIONAL SPECTRUM OF t-HOCO TRAPPED IN SOLID Ar AND CO

MARILYN E. JACOX

The OH stretching, in-plane OH deformation, and torsional fundamentals of t-HOCO, previously reported in a study of the vacuum-ultraviolet photolysis of H2O in a CO matrix, experience large shifts upon removal of the hydrogen-bonding perturbation by isolation of t-HOCO in solid argon. Because of these large shifts, a Fermi resonance perturbation of the C=O stretching fundamental is altered, resulting in a substantial matrix dependence for the isotopic shift in this fundamental of t-DOCO. t-HOCO affords an unusual opportunity to study the effect of hydrogen bonding at either end of the molecule. Infrared spectral data for OC· · ·H-O=C=O, isolated t-HOCO, and H-O=C=O···HF will be compared.

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INFRARED SPECTRA OF H2O AND D2O ON SODIUM CHLORIDE FILMS

J. Reynolds, K. Pensak, B. Stone, and C.A. Baumann

The infrared spectrum of water vapor adsorbed on sodium chloride films at 77 and 89 K has been observed and characterized. H2O exhibits broad bands at 3300 cm⁻¹ and 1650 cm⁻¹, which, upon annealing, resolve into a quartet and a doublet, respectively. The annealing process also resolves structure on the wings of these bands, indicative of combinations between the normal modes of the molecule with vibrations of the molecule against the surface. The infrared spectrum of D2O consists of unstructured bands at 2350 cm⁻¹ and 1165 cm⁻¹, with no apparent structure on the wings.

*Supported by PRF

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SPECTRA AND ISOTHERMS OF NITROSOTRIFLUOROMETHANE (CF$_3$NO) ON SODIUM CHLORIDE FILMS* 

J. Reynolds, K. Miller, K. Pensak, and C. A. Baumann

The UV-visible and infrared spectra of CF$_3$NO have been obtained on sodium chloride films at 77 and 89 K. From band shifts in the mid-IR, we have determined the mode of adsorption to be one in which the C-N axis is normal to the (100) face exposed at the surface, with the fluorines atop a sodium ion. The spectroscopically obtained isotherms were used in the calculation of the low-coverage limit to the heat of adsorption ($q_0 = -18\pm2$ kJ mol$^{-1}$).

At high coverages, multilayer adsorption was noted: spectral features attributed to the 'glassy liquid' phase observed by Gordon and coworkers were seen in the visible and infrared.

*Supported by PRF


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INFRARED SPECTROSCOPY OF CO ON NaCl(100) 

H.-C. Chang, H.H. Richardson, and C.E. Ewing

Vibrational spectra of CO physisorbed on NaCl(100) single crystal surfaces mounted in an ultrahigh vacuum chamber were obtained using a Fourier transform infrared interferometer. Structures of CO from a monolayer to thin slabs of multilayers have been explored. By probing with polarized light, monolayer CO molecules are shown to be adsorbed perpendicularly to the surface$^1$. Polarized multilayer spectra show that CO molecules stacked above the monolayer are also aligned but in arrangements consistent with the bulk crystal structure of $\alpha$-CO. This structure is a consequence of the near perfect match of the $\alpha$-CO lattice constant and that of the NaCl(100) substrate. Features of both longitudinal and transverse modes of multilayer CO were observed and the results imply that these two modes have different damping constants and consequently different vibrational relaxation times. The dependence of absorption profiles on sample thickness was also examined systematically. Theoretical formalism to account for the frequency shift, band splitting and broadening will be discussed.


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ELECTROSTATIC MODELING OF HCN ADSORBED ON NaCl(100)

D.S. Anex

The electrostatic contributions to molecular orientation, binding energy, and vibrational frequency shift (C-H stretching motion) have been calculated for HCN molecules adsorbed on the (100) face of NaCl. A large set of electrostatic moments, polarizabilities, and hyperpolarizabilities were used with the model for the electrostatic potential above the surface taking into account the continuous distribution of charge within the crystal. The present results are compared to previous calculations and experiments involving HCN adsorbed on NaCl films.


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INFRARED SPECTRAL ANALYSIS OF THE PRODUCTS AND MECHANISM OF THE LASER-INITIATED OXIDATION OF SIMPLE HYDROCARBONS, Bruce S. Ault

The matrix isolation technique has been coupled with excimer laser technology for the identification and characterization of intermediates of the reactions of oxygen atoms with acetylene and propyne. 193 nm laser irradiation of argon matrices containing O2 leads to the production of O atoms, which subsequently react with the trapped alkyne. Two sets of products are observed, one coming from the reaction of a single O atom with the alkyne, and the second set requiring two O atoms. Irradiation of matrices containing N2O as a "single O atom" photolytic source allow distinction between these two sets. Similar results were obtained with both in situ and in vivo irradiation. The results for O + CyH4 are interpreted in terms of an undetected ethylidene intermediate.

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INFRARED MATRIX ISOLATION STUDIES OF THE 1:1 MOLECULAR COMPLEXES OF THE HYDROGEN HALIDES, AND ClF WITH 18-CROWN-6 AND RELATED CYCLIC POLYETHERS Bruce S. Ault and Heli Bai

Twin jet deposition has been employed with conventional matrix isolation for the study of isolated complexes of crown ethers with small neutral guests. For each system, from 1,4 dioxane to 18-crown-6, a single 1:1 complex was isolated. The dominant spectral feature of the complex was the stretching mode of the diatomic acid, shifted to lower energies from the parent position. For example, the complex of HF with 18-crown-6 absorbs at 3290 cm⁻¹, while the complex of ClF with 18-crown-6 absorbs at about 665 cm⁻¹. In addition, considerable broadening of the absorption was noted, compared to complexes of these acids with single-oxygen donors. The shifts observed here are quite similar to those observed for single O-atom donors, suggesting that the cooperativity observed for crown ether complexes of metal cations is not important for the current complexes.

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OPTOTHERMAL-INFRARED AND PULSED-NOZZLE FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY OF RARE GAS-CO$_2$ COMPLEXES

C. T. FRASER, A. S. PINE, AND R. D. SUENRAM

Sub-Doppler infrared spectra of Ne-CO$_2$, Ar-CO$_2$, and Kr-CO$_2$ have been recorded near 3613 and 3713 cm$^{-1}$, in the region of the $2v_2 + v_3/2 + v_3 + v_3$ Fermi diad of CO$_2$, using an optothermal molecular-beam color-center laser spectrometer. In addition, pulsed-nozzle Fourier-transform microwave spectra are reported for the ground vibrational states of the complexes. The infrared and microwave spectra are consistent with T-shaped complexes as shown originally by Steed, Dixon, and Klemperer$^1$ for Ar-CO$_2$. The infrared band origins for the Ar and Kr complexes are red shifted, from that of free CO$_2$, by 1.09 and 0.95 cm$^{-1}$ for Ar-CO$_2$ and by 1.97 and 1.76 cm$^{-1}$ for $^{84}$Kr-CO$_2$. For Ne-CO$_2$, blue shifts of 0.15 and 0.19 cm$^{-1}$ are observed. The lower Fermi components are free of perturbations, whereas the upper components of Ar-CO$_2$ and Kr-CO$_2$ are perturbed. For Ar-CO$_2$ the perturbation is strong, shifting the positions of the observed Q-branch lines of the $K_a=1-0$ subband by as much as 500 MHz.


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VIBRATIONAL PREDISSOCIATION IN THE CO$_2$ DIMER AND TRIMER AND RARE GAS-CO$_2$ COMPLEXES

A. S. PINE AND G. T. FRASER

Vibrational predissociation linewidths for the CO$_2$ dimer and trimer and the Ne-CO$_2$ and Ar-CO$_2$ complexes have been resolved using a bolometer-detected (optothermal) molecular-beam color-center laser spectrometer. Observations were made on the pair of vibrations near 3715 and 3613 cm$^{-1}$ corresponding to the $v_1 + v_3/2 + 2v_2 + v_3$ Fermi diad of CO$_2$. Homogeneous linewidths of from -0.5 to -22 MHz (FWHM) were measured for these related complexes, with Ne-CO$_2$ exhibiting both the broadest and the sharpest lines for the upper and lower bands respectively. Ar-CO$_2$ and (CO$_2$)$_2$ showed mode-independent intermediate predissociation rates while only the lower band of (CO$_2$)$_3$ could be found. The results indicate that V-V energy transfer processes are the dominant predissociation channels with symmetry selection or propensity rules and specific resonances playing a role.

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VIBRATIONAL, ROTATIONAL, AND TUNNELING DEPENDENCE OF VIBRATIONAL PREDISSOCIATION IN THE HF DIMER

A. S. PINE AND G. T. FRASER

As observed previously\textsuperscript{1-3}, there is a marked vibrational dependence to the vibrational predissociation rate in the HF dimer with the "free"-H stretching mode, \(\nu_1\), much longer lived than the "bound"-H stretching mode, \(\nu_2\). Using an optothermal (bolometer-detected) crossed molecular-beam color-center laser spectrometer, we have achieved sufficient resolution to measure the narrow homogeneous linewidths for the \(\nu_1\) band with high precision (± 0.5 MHz). We observe a substantial \(K\), but negligible \(J\), dependence for the \(\nu_1\) predissociation linewidths, and a smaller, but statistically significant, dependence on the tunneling state. For the symmetric lower tunneling level of \(\nu_1\), the \(K=0\) predissociation linewidths are almost twice as broad as the \(K=0\). The widths for the antisymmetric tunneling level are roughly 50\% greater than for the symmetric level for \(K=0\) and about 20\% for \(K=1\). We also report improved measurements of the broader \(\nu_2\) band predissociation linewidths with reduced spectral congestion and blending\textsuperscript{1,2} afforded by the low effective temperatures of the adiabatic expansion.


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OPTOTHERMAL SPECTROSCOPY OF HF COMPLEXES WITH CO\textsubscript{2}, OCS, AND NO

G. T. FRASER AND A. S. PINE

The H-F stretching bands of the HF van der Waals complexes with CO\textsubscript{2}, OCS, and NO have been recorded with an optothermal (bolometer-detected) molecular-beam color-center laser spectrometer. As with the CO\textsubscript{2} complex observed previously,\textsuperscript{1} the OCS species has a low frequency mode associated with a large amplitude bending-rotation motion of a quasilinear molecule. The H-F stretching bands are red shifted from the isolated monomer by 52.10 and 57.48 cm\(^{-1}\) for CO\textsubscript{2} and OCS\textsubscript{2} respectively, while the low frequency mode "hot" bands are further red shifted by 2.69 and 2.46 cm\(^{-1}\) respectively. The spectrum of the NO complex is complicated by the presence of the unpaired electron in the ground state and has not yet been interpreted. Vibrational predissociation linewidths for the three species are in the range of 100-200 MHz (FWHM).


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A sub-Doppler infrared spectrum of \((\text{HCCN})_2\) has been obtained in the region of the acetylene \(\text{C} = \text{H}\) stretching fundamental using an optothermal molecular-beam color-center laser spectrometer. Microwave spectra were obtained for the ground vibrational state using a pulsed-nozzle Fourier-transform microwave spectrometer. In the infrared spectrum both a parallel and perpendicular band are observed with the parallel band being previously assigned to a T-shaped complex by Prichard et al. and the perpendicular band to a \(C_2\) complex by Bryant et al. The parallel band exhibits three \(K_a = 0\) and three asymmetry-doubled \(K_a = 1\) series. The transitions show a clear intensity alternation with \(K_c\), with two of the \(K_a = 0\) series missing every other line. In addition, the perpendicular band has the same ground-state combination differences as the parallel band. To explain these anomalies in the spectrum, we invoke a model consisting of a T-shaped equilibrium configuration with interconversion tunneling between four isoenergetic hydrogen-bonded minima. In this picture, the parallel and perpendicular bands arise from excitation of the acetylene units parallel and perpendicular to the hydrogen bond. The observation of rotation-inversion transitions in the microwave spectrum, in addition to the pure rotation transitions of Prichard et al., verifies the model. The measured microwave splittings yield a tunneling frequency of 2.2 GHz for \(K_a = 0\) which is consistent with a \(-33 \text{ cm}^{-1}\) barrier separating the four minima.


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LASE.-INDUCED FLUORESCENCE MOLECULAR-BEAM OBSERVATIONS OF THE HYPERFINE STRUCTURE IN THE NO, SPECTRUM AT 593.5 nm AND 585.1 nm

A.G. ADAM, M.C.L. GERRY, A.J. MERER, I. OZIER and D.M. STEUNENBERG

While testing a wavelength calibration system for molecular beam work in the visible region we have measured the hyperfine structures of the K=0 bands at 593.5 nm and 585.1 nm in the spectrum of jet-cooled NO2 (bands 99 and 115 of Smalley et al.). Linewidths of 10 MHz were obtained typically; for the strongest lines these could be reduced to 2 MHz by a Lamb-dip technique to resolve closely spaced components. The calibration system allowed the hyperfine splittings of a rotational line to be measured to ±1 MHz, while giving agreement to ±10 MHz between ΔF"(N) combination differences measured from the optical spectrum and calculated from the microwave spectrum. The N, J, and F assignments could then be made unambiguously without the need for wavelength-resolved fluorescence.

Values for the electron spin-rotation, Fermi contact and (I,S) dipolar parameters were obtained for the 2B2 upper levels with N=1,3,...,9. Good agreement was obtained with literature values where they exist. We find that the spectrum in this region consists of individual subbands which can each be approximately described by a single set of constants, though the density of local perturbations requires that the structure of each N' level be treated separately. It seems that the apparently contradicting descriptions of the spectrum given by Lehmann et al. and Demtroder et al. are not inconsistent with each other, but represent different viewpoints of the same perturbed system.


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MOLECULAR BEAM OBSERVATIONS OF HYPERFINE TRANSITIONS IN KOH

J. CEDERBERG, D. PIQUES, D. NITZ, D. OLSON

We have used a molecular beam electric resonance spectrometer to measure radio-frequency transitions in KOH. Both pure hyperfine transitions (arising primarily from the potassium nuclear quadrupole interaction) and transitions between the I doublet states have been observed. The spectrum indicates that the hydrogen spin-rotation interaction is opposite in sign to that of fluorine in KF, and smaller in magnitude by about a factor of ten. Further work is continuing so that we can present a more detailed analysis of the spectrum.

Work supported by a Northwest Area Foundation Grant of the Research Corporation and NSF RUI Grants # PHY-8319293 and PHY-8617538.

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OBSERVATION OF \((\text{H}_2\text{O})_2\) K-1 TRANSITIONS OF E SYMMETRY AND DISCUSSION OF NUCLEAR HYPERFINE SPLITTINGS

A. Hu and T.R. Dyke

We have recently observed a-type microwave and radiofrequency spectra from K-1 levels of E symmetry for \((\text{H}_2\text{O})_2\). As anticipated from group theoretical arguments and similar to K-O E-type spectra which we observed earlier, these transitions do not exhibit the tunneling doubling found in the a-type spectra for nondegenerate tunneling levels.

Rotational constants and K-type doublings were determined from several transitions of low J, which were obtained by molecular beam electric resonance spectroscopy. The relatively strong intensity of these lines correlates with the K=0 E states lower in energy with respect to the proton acceptor 180° rotation tunneling motion. The large K-doubling, which is 259 92 MHz for the J=1 state, is also in reasonable agreement with a prediction by L.H. Coudert and J.T. Hougen for these levels. Nuclear hyperfine splittings were observed for these transitions, in addition to those for the K=0 states of E symmetry. These splittings will be discussed in terms of the proton spin-spin interaction and the structure of the dimer.


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ROTATIONAL SPECTRA OF CARBOXYLIC ACID DIMERS

W. KRESA AND A. BAUDER

Rotational transitions of the dimers HCOOH•••CF₃COOH and CH₃COOH•••CF₃COOH have been observed in a pulsed molecular beam with a Fabry-Perot cavity spectrometer. The monomer units are connected with two hydrogen bonds forming a planar eight-membered ring. Transitions with J between 6 and 15 have been assigned over 8 - 12 GHz. The K structure of the nearly prolate symmetric rotors was completely resolved. No splittings were found for hydrogen tunneling between the equivalent positions in the two hydrogen bonds. The internal rotation splittings of the CF₃ groups were too small to be observed. Only the internal rotation of the CH₃ group led to splittings of the order of 1 - 40 MHz.

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LOW FREQUENCY INTERMOLECULAR VIBRATIONS IN VARIOUS BINARY COMPLEXES FROM NEAR INFRARED SPECTROSCOPY

D. Dayton, K.W. Jucks, and R.E. Miller

Fundamental intramolecular vibrational spectra have been used in conjunction with combination and hot bands to obtain intermolecular vibrational frequencies for (HCN), and HCN-HF in both the ground and excited intramolecular vibrational states. These spectra were recorded in the UNC-CH opto-thermal molecular beam apparatus at sub-Doppler resolution. Comparisons are made between these accurate values and those obtained from L-type doubling. Recent ab-initio calculations are also available for (HCN), for comparison.

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SUB-DOPPLER RESOLUTION INFRARED SPECTROSCOPY OF WATER DIMER

Z.S. Huang and R.E. Miller

The opto-thermal detection method has been used in conjunction with an F-center laser to obtain rotationally resolved infrared spectra of the water dimer under jet cooled conditions. The most intense sub-band observed to date is K=0→1 which shows three strong Q branches associated with different tunneling states. Assignment and fitting of these spectra is underway.

The observed transitions are broader than the instrumental linewidth due to vibrational predissociation. Transitions associated with the different tunneling states are found to have different linewidths, indicating that vibrational symmetry may play an important role in determining the rate of dissociation.

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ANALYSIS OF THE \( v_5 \) BAND IN CH\(_2\)DF, AND ASSIGNMENT OF SOME SMMW LASER LINES

D.F. Eggert, W. Lewis-Bevan, M.C.L. Gerry, T.S. Tobin and T.W. Daley

A sample of CH\(_2\)DF was prepared in high isotopic purity and the IR spectrum was run on a Bomem instrument at 0.005 cm\(^{-1}\) resolution. The \( v_5 \) band has strong A-type transitions that could be assigned for \( J \) values up to 31; for many lower \( J \) some \( K \)’s up to 10 were also found. There are numerous B-type transitions as well, though with lower intensity. The analysis was based on the A-type transitions and gave a reasonable fit with inclusion of some sextic distortion constants. There is a \((K, K+2)\) Coriolis resonance of \( K_0 = 10 \) in this band with \( K_0 = 8 \) in the \( v_3 \) band whose center is some 117 cm\(^{-1}\) higher; the rotational levels cross at about \( J = 14 \). The molecular constants will be compared with those for the \( \text{-symmetrical} \) isotopic molecules, with adjustment for isotopic relationships.

This sample was also optically pumped with a CO\(_2\) laser, and five SMMW laser lines were found. The IR measurements permit assignment of two; however, the other three present more of a problem.

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THE INFRARED SPECTRUM OF AMINODIFLUOROBORANE, NH\(_2\)BF\(_2\): PARTIAL ASSIGNMENT OF THE FUNDAMENTALS AND ANALYSIS OF THE 2\(^1\)o BAND NEAR 1608 cm\(^{-1}\)

A. Lewis-Bevan, H.M. Jemson and M.C.L. Gerry

The infrared spectrum of gas phase aminodifluoroborane, NH\(_2\)BF\(_2\), has been observed for the first time. A partial assignment to the fundamental vibrations has been made. The 2\(^1\)o band has been recorded at high resolution, and the rotational and centrifugal distortion constants of NH\(_2\)BF\(_2\) have been obtained in both the ground and 2\(^1\) level. A small rotational perturbation in the 2\(^1\) level has been attributed to a perpendicular Coriolis interaction. Using a newly written least squares fitting program, spectroscopic constants of the unseen level have been evaluated, including its band origin, and the Coriolis coupling coefficient. Possible identities of the unseen level are suggested.

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HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CHF₂: THE νg BAND AT 1435 cm⁻¹
R. D'CARIA, P. K. WAHL, V. B. KARTHA, AND A. WEBER

Fourier transform infrared spectra of methylene fluoride were recorded with the NBS BOMEM DA 002 spectrometer with an apodized resolution of 0.004 cm⁻¹. Detailed assignments up to J = 25 have been made for the νg parallel A type band centered at 1435 cm⁻¹. Watson's A type reduced Hamiltonian in the 1² representation was used to obtain upper state molecular parameters. These reproduce the observed data to within the limits of the experimental accuracy. The details of the analysis will be presented.

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INFRARED-INFRARED FOUR-LEVEL DOUBLE RESONANCE IN NH₃
Masao Matsuo, Dong K. Lee, and R. H. Schwendeman

Infrared-infrared four-level double resonance has been observed in NH₃ by using a CO₂ laser as a pumping source and an infrared microwave sideband laser system as a probing source. The horizontally-polarized pumping beam is introduced into the sample cell through Brewster angle windows while the vertically-polarized probing beam is directed through the cell and onto a detector by reflection off the same windows. The probing beam is 700 MHz amplitude modulated and processed by phase-sensitive detection. By using a double-modulation scheme in which the pumping beam is chopped and the output of the phase-sensitive detector is processed by a second similar instrument, the effects of pumping can be separated from the linear absorption.

The aA(2,0) transition in the ν₁ band of ¹⁴NH₃ has been pumped while transitions in the 2ν₁ = 2a + ν₂ = 1 hot band have been probed. A general increase in intensity of all of the hot band transitions is observed as a result of the pumping. In addition, a narrow transferred spike in the velocity distribution is observed in a ΔK=0 four-level double resonance, whereas a broader velocity-conserving effect is seen in a ΔK=3 four-level double resonance. In many other transitions there is no evidence of a transferred spike. The pressure and power dependence of these observations will be described and discussed.

¹This research was supported by the U.S. National Science Foundation.

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LINEAR AND NONLINEAR SPECTROSCOPY BY USE OF MICROWAVE MODULATION SIDERBANDS IN THE CO LASER REGION

Jing-Jung Hae and R. H. Schwendeman

The analysis of infrared microwave sideband laser spectra of the \( \nu_2 \) band of CD\(_3\)I at 1090 cm\(^{-1}\), for which a preliminary report was given at this meeting last year, has been completed with the determination of improved molecular constants for the \( \nu_2 = 1 \) state. Approximately 150 transitions have been fit to a set of constants that can predict transitions for \( J < 30 \) and \( K_a, K_c < 9 \) to an absolute accuracy of approximately 10 MHz. The transitions for \( K_a \), \( -9 \sim \) show evidence for a resonance.

An infrared radio-frequency double resonance effect has been observed by pumping an \( R \)-band transition in the \( \nu_2 \) band of H\(_2\)CO with the infrared microwave sideband laser system operating at fixed resonant frequency and recording the infrared transmission as a function of radio frequency. Double resonance effects were observed when the \( RF \) frequency coincided with the splittings of the connected symmetry doublets.

This research was supported by the U.S. National Science Foundation.

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HIGH RESOLUTION INFRARED STUDY OF THE \( \nu_2 \) BAND OF CD\(_3\)I

Han-G. Cho and R. H. Schwendeman

The infrared spectrum of the \( \nu_2 \) band of CD\(_3\)I near 949 cm\(^{-1}\) has been studied by means of an infrared microwave sideband laser spectrometer. Frequencies of transitions have been obtained by fitting the spectral lines to a Gaussian lineshape. Quadrupole hyperfine spectra have been resolved for several transitions even in the Doppler limit. New molecular constants and the results of an analysis of the Coriolis interaction with the \( \nu_2 \) state will be presented and compared to previous results.

This research was supported by the U.S. National Science Foundation.

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STARK EFFECT OBSERVATIONS WITH IR LASER SIDE BANDS

W.A. Kreiner, G. Maquerl, H. Prinz, W. Hohe

Linear Stark effect has been resolved on several ro-vibrational transitions in the $v_4$ fundamental of $^{13}$CO$_4$. Tunable sidebands of a CO$_2$ laser were used to saturate single $m$-components. The vibration induced dipole moment $P$ has been determined for different values of the quantum number $R$; similar observations on the silane isotopomer $^{29}$SiH$_4$ are presented.

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COLOR CENTER LASER SPECTROSCOPY OF C$_2$H AND $^{13}$C$_2$H

J. W. Stephens, M. L. Richnow, and R. F. Curl

Transient absorption spectra of C$_2$H and $^{13}$C$_2$H in the region 3250 to 3600 cm$^{-1}$ have been obtained using ArF excimer laser flash photolysis of acetylene and color center laser probing 0.6 μsec after the flash. The principal aim of the work was to observe and identify the CH stretching fundamental. Therefore, approximately 20 Torr of H$_2$ was added to provide efficient relaxation of the C$_2$H produced to the ground vibrational state. For the color center probe beam a 2 meter long multiple reflection (“White”) cell was configured so as to overlap the photolysis region of the excimer. IR path lengths of 40 meters were typical.

Several new bands of C$_2$H and $^{13}$C$_2$H have been observed and fitted. Bands originating from both the ground state and excited vibrational states were observed for both species. These include three C$_2$H bands of $^2\Sigma^+-^2\Pi$ symmetry, three $^{13}$C$_2$H bands of $^2\Sigma^+-^2\Pi$ symmetry, and one $^{13}$C$_2$H band of $^2\Pi^--^2\Sigma^*$ symmetry. Three of the $^{13}$C$_2$H bands have been assigned as analogues of $^{12}$C$_2$H bands observed here and in previous works. The assignment of the CH stretch is still uncertain, however two of the three $^2\Pi^--^2\Sigma^*$ ground state C$_2$H bands are possible candidates.

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INFRARED-RADIOFREQUENCY DOUBLE RESONANCE SPECTROSCOPY OF CHF USING A COLOR CENTER LASER

C. J. PURSELL, W. C. HO, F. SCAPPINI, and T. OKA

The color center laser is continuously tunable between 2.3 - 3.3 μm with single mode power between 1 - 15 mW. This relatively high power makes infrared-radiofrequency double resonance spectroscopy possible [1].

We have used this technique to study the A₁₋A₂ splitting of CHF in the ν₄ (J, K=1, l=1 and J, K=2, l=-1) state. This splitting can be represented by

\[ \Delta \nu = \frac{(J+K)!(J-K)!}{(J+1)!(J-1)!} \left( q + q_J(J+1) + q_{JJ}(J+1)^2 + \ldots \right) \]

where the second and third terms are centrifugal distortion terms. We determined \( q = 16.0 \pm 0.5 \) kHz, \( q_J = 3.5 \pm 0.2 \) kHz for \( K=1, l=1 \); and \( q = 6.8883(27) \) kHz, \( q_J = 4.6124(6) \) kHz for \( K=2, l=-1 \).

We also measured the electric dipole moment of CHF in the ν₄ state using this technique. By applying a Stark field perpendicular to the RF radiation, we could observe the splitting between M-components in the ground and ν₄ states. Using the ratio of this splitting (when \( J'' = K'' \) and \( J' = K' \)) the dipole moment can be calculated according to

\[ \mu' = \mu'' \frac{\Delta \nu'}{\Delta \nu''} \]

which is independent of the Stark field. We determined \( \mu' = 1.8332(23) \) D, which is calculated using the ground state dipole moment, \( \mu'' = 1.8585(5) \) D, accurately determined by molecular beam electric resonance [2].

This study was conducted as a preliminary experiment for the planned IR-RF and IR-MW double resonance spectroscopy of molecular ions, which is in progress and will also be discussed.


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THE INFRARED SPECTRUM OF THE FOUR LOWEST FUNDAMENTAL BANDS OF NITRIC ACID

A. G. MAKI, W. B. OLSON, R. ESCRIBANO, A. GOLDMAN, J. B. BURKHOLDER, AND C. H. HOWARD

High resolution infrared spectra have been measured and analyzed for the four lowest frequency fundamental bands of nitric acid (HNO₃). The two in-plane vibrations, ν₆ at 646.83 cm⁻¹ and ν₇ at 580.30 cm⁻¹, are found to be nearly 100% A-type bands and the intensity of ν₇ has been measured relative to that of ν₆. The two out-of-plane fundamentals, ν₈ and ν₉, have band-centers at 763.15 cm⁻¹ and 458.23 cm⁻¹ respectively. The R-branch of ν₈ is considerably stronger than the P-branch and appropriate Herman-Wallis-like constants were determined in order to allow one to accurately calculate the spectra. All of the four lowest fundamental bands are easily fit with quartic centrifugal distortion constants that are nearly the same as in the ground state, but the sextic constants are in some cases quite different.

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A FORBIDDEN BAND IN THE FAR INFRARED SPECTRUM OF H$^{13}$CO

M. WINNEWISSER, D. WAGNER AND B. P. WINNEWISSER

The far infrared spectrum of H$^{13}$CO exhibits a widely spread set of perpendicular transitions in the manifold of the quasilinear bending mode, $v_b$, and the combination manifold $v_b - n\nu_4$, where $v_b$ is the skeletal bending mode. We have analyzed the spectrum of the $\mathrm{^{13}C}$-substituted species, and found a Q branch without any P or R branches and a P, R subband without any Q branch. Neither of these features are observed in the spectrum of the parent species. They have been assigned to the vibrational transitions $(v_b, n\nu_4) = (02) \nu_4 - (11) \nu_4$ and $(C2U, n\nu_4) = (11) \nu_4$, respectively. These transitions are only allowed due to a Coriolis interaction between the levels $(02) \nu_4$ and $(10) \nu_4$, which was observed as a relatively weak interaction in the parent species.

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THE LOWEST SKELETAL BENDING MODE OF N$_2$O IN THE GAS PHASE

F. DELUCIA, M. WINNEWISSER, B. P. WINNEWISSER AND G. FAWELKE

The search for the lowest bending mode of N$_2$O has been intensified due to the need for atmospheric monitoring of all of the species involved in the atmospheric nitrogen oxide chemistry. We have succeeded in recording absorption due to this lowest mode in the far infrared region. Both low resolution and high resolution spectra were recorded. So far only the low resolution data has yielded useful information. The band is extremely weak and very broad, and inevitable decomposition leads to strong absorption due to NO, which severely limits the possibility of locating rotational structure due to N$_2$O. However, the information obtained about the shape and location of the band should allow testing of models for the internal rotation/bending/end-over-end rotation dynamics of N$_2$O.

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HIGH RESOLUTION INVESTIGATION OF CH$_3$CHO IN THE INFRARED

I. KLEINER, M. GODFROID, H. HERMAN

H. D. MARSHALL, J. W. C. JOHNS, A. R. W. McKELLAR

The v4 infrared band of CH$_3$CHO, C-O stretch centered around 1743 cm$^{-1}$ (1), is studied at high resolution. Different experimental approaches were carried out at Ottawa, including Fourier Transform Spectroscopy, frequency modulation diode laser absorption in a supersonic jet, Stark modulation diode laser absorption and CO laser Stark spectroscopy. These various complementary experiments appear justified by the extreme line density encountered on the FT spectrum. At the same time, a computer program package is developed at Brussels, based on the internal axis method (IAM) procedure described in (2,3) and used by Liang et al. (4) for the analysis of the millimeter-wave spectrum of acetaldehyde. This program should solve properly the rotation-torsion Hamiltonian and provide the eigenvalues needed for the spectral assignments. Preliminary results will be presented.


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MOLECULAR BEAM SPECTRUM OF THE PERTURBED C-H STRETCHING REGION OF FLUOROFORM
A. S. PINE, G. T. FRASER, AND J. PLIVA

The highly perturbed C-H stretching fundamental band v1 of CHF3 has thus far defied analysis even as its overtones received attention in studies of intramolecular vibrational relaxation. The spectrum of the fundamental region remains complex at Doppler-limited resolution, and we have obtained a Doppler-free spectrum in an adiabatically cooled molecular beam at 4 K using a scanning color center laser with bolometric detection of the optically excited molecules. This has enabled us to make definite assignments of the observed lines. Under these conditions, the central Q-branch, which dominates the spectrum at room temperature, almost vanishes, while the bulk of the intensity is equally shared by two "sidebands" with Q-branches symmetrically displaced by +5 cm⁻¹ from the suppressed central Q-branch. This peculiar structure is due to a close anharmonic resonance between the fundamental v1 species and the combinations v4⁺v5⁺v6 (A1·A2) located only 1.45 cm⁻¹ above v1, whose origin is at 3033.52 cm⁻¹. The coupling constant of the resonance is k1456/2ν2 = 3.67 cm⁻¹. Additional severe perturbations by the E components of v4⁺v5⁺v6 and v2⁺v4⁺v6 have been identified in the spectrum.

Since the v1 vibration is known to be in global Fermi resonance with the overtone 2ν4⁰, we have also recorded the 2680 - 2815 cm⁻¹ region, containing the 2ν4 and 2ν4² bands, under Doppler-limited conditions using a difference-frequency laser spectrometer. This has yielded much improved spectroscopic constants, in particular for the strongly perturbed 2ν4² state.

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PHOTOFRAGMENTATION OF JET-COOLED ACETIC ACID

S. S. HUNNICUP, L. D. WAITS, AND J. A. GUEST

Acetic acid cooled in a free jet expansion photodissociates following n→n* excitation at 218 nm. The nascent internal energy distribution of the OH X 2Π product is determined by laser fluorescence excitation. These results will be used to gain insight into the photochemical details of this simple acid. A comparison to related experiments on jet-cooled formic acid will also be presented.

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PHOTOFRAGMENTATION OF KETENE AT THE SINGLET THRESHOLD

I-CHEL CHEN, WILLIAM H. GREEN, JR. and C. BRADLEY MOORE

Ketene (CH₂CO) in a supersonic free jet was photodissociated by a tunable pulsed laser in the frequency range just above the threshold for production of singlet methylene, CH₂ (a²Π). CH₂ was detected by laser-induced fluorescence (LIF). The appearance threshold and yield curve of individual CH₂ rotational states were obtained by scanning the photolysis laser frequency with a fixed LIF probe laser frequency. The dissociation occurs on the ground electronic state potential energy surface. The threshold for CH₂CO → CH₂ + CO is found to be 30 116.2 ± 0.4 cm⁻¹. By varying the delay between the photolysis and probe pulses, a lower bound of 7 x 10⁻³ s was set for the dissociation rate on the triplet surface at the singlet energy threshold. The yield curves, or photofragment excitation (PHOFEX) spectra, exhibit sharp steps spaced by the CO rotational term values. The experimental data provide a rigorous test of theoretical models of photofragment dynamics. The data clearly show that nuclear spin is conserved through the photodissociation. PHOFEX curves calculated from Phase Space Theory (PST) are in excellent agreement with the experiment and show that there is no barrier along the reaction coordinate. The singlet/triplet branching ratio as a function of photolysis laser frequency is inferred from PST fits to the PHOFEX data. The data show that the only dynamical constraints on product state rotational energy distributions are conservation of energy, angular momentum, and nuclear spin.

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PICOSECOND RAMAN INVESTIGATIONS OF THE VIBRATIONAL ENERGY DEPENDENCE OF INTER-LIGAND ELECTRON TRANSFER IN TRANSITION METAL COMPLEXES

L. K. Orman and J. B. Hopkins

Two color picosecond Raman spectroscopy has been utilized to measure the vibrational energy dependence of electron transfer. Above the classical barrier to inter-ligand electron transfer, vibrational relaxation completely quenches electron transfer from the excited vibrational states. Below the barrier the first direct measurements of inter-ligand electron hopping are reported in the excited electronic state of D_3 symmetry complexes of polypyrrolidyl Ru(II). It was found that the rate of inter-ligand electron transfer from the thermalized vibrational states varied between >10^{11} sec^{-1} and < 10^{7} sec^{-1} depending on the chemical nature of the complex.

The observed kinetics are rationalized in terms of recent electron transfer theory which describe the reaction dynamics through Franck-Condon factors weighted by the density of product vibrational states. Results for five complexes will be presented.

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INVESTIGATION OF THE RESPONSE OF THE NO/NO2/N2O4 SYSTEM TO AN INTENSE OPTICAL PERTURBATION

M Van Roozendael, Y De Wilde, P Miller and M Herman

An Argon ion laser is used to perturb the NO/NO2/N2O4 chemical system. The perturbation is monitored, in different experiments, with the Laser Induced Fluorescence (1), the Infrared Optical Double Resonance (2) and the OptoAcoustic experimental techniques. It appears that the absorption of visible laser light in NO2 induces some non radiative processes, which in turn result into a temperature increase. That variation has two main contributions to the evolution of the system: through the Boltzmann distribution of population and through the chemical equilibrium connecting NO2 and N2O4. Evidence for the first effect will be given and it is hoped that the occurrence of the second - chemical - effect will also be demonstrated, either experimentally or through simulations.


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HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF THE SINGLET MOLECULAR OXYGEN-IODINE REACTION AND POPULATIONS OF THE B O* AND A 1u STATES THROUGH NON LINEAR INVERSION OF EMISSION SPECTRA

D CERNY, R BACIS, and J VERGES

The dissociation of molecular iodine I_2 by metastable oxygen O_2 (1Δ_g) is poorly understood. It leads to the dissociation of I_2. Knowledge of this process is important to assessing the ultimate efficiencies of high-power Chemical Oxygen Iodine Lasers. In our analysis O_2 (1Δ_g) is obtained from a microwave discharge in oxygen. The flow of less than 10% of O_2 (1Δ_g) is mixed with pure iodine. The reaction gives a flame emitting from 3700 cm^{-1} to 20000 cm^{-1}. We observe this flame along the axis with a high resolution Fourier Transform spectrometer. The 10000 - 20000 cm^{-1} emission is due to the B O* → X O* transition and allows to determine the populations of the B O* rovibrational levels. The Infra-Red region comes from A 1u → X O* from which we obtain the A 1u populations. We have set a general program that gives from non linear least squares fits the rovibrational populations and their statistical errors. A 1u serves as a reservoir with a non Boltzmann vibrational distribution and B O* has a maximum population around v = 30 - 35. The rotational distribution in A 1u or B O* is Boltzmann and corresponds to 370 ± 20 K. We will give our main results. Our general fitting method will be presented and statistical or systematic errors discussed.

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LASER EXCITED SPECTRA OF THE SINGLET MOLECULAR OXYGEN-IODINE REACTION AND POPULATIONS OF INTERMEDIATE STATES

P. CROZET, R BACIS, A BOUVIER, A J BOUVIER and S CHURASSY

As reported in the previous paper the mechanism of dissociation of I_2 by O_2 (1Δ_g) is poorly known. It is a multi-step process. In order to find the intermediate states of I_2 involved we have systematically explored excitation spectra of the flame with a dye laser pumped by a copper vapour laser. Moreover some high resolution spectra have been obtained in the 810 - 830 nm range with a styryl dye pumped by an Ar^+ laser. From inversion of the excitation spectra we have found that high vibrational levels of the I_2 ground state until v ~ 45 are involved. These vibrational populations vary with the region of the flame explored. With a frequency doubled dye laser we succeeded to detect a relatively high population of the A'2u state through A'2u → D'2g excitation. Unfortunately the D'2g state is spectroscopically too poorly known to obtain reliable inversion of the spectra.

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J-REORIENTATION IN THE H\(_2\CO\) A \(\text{A}_2\) \(\text{A}_1\) V,=1, J=1, K=0, ROTATIONAL LEVEL

S. HALLE, S.L. COY, J.L. KINSEY, R.J. SILBEY AND R.W. FIELD

We report measurements of the rate of depolarization of a single rotational level of formaldehyde in the absence of an external field. The level in question is \(\text{A}_1\) \(\text{A}_2\) \(\nu\),=1, \(J\),=1, \(K\),=0. Previous rotational state-to-state measurements in the \(\text{H}_2\CO\) \(\text{A}_1\) state by Transient Gain and Transient Polarization Spectroscopies suggested a remarkable resistance to depolarization, even for \(\Delta J = \pm 1, \pm 2\) rotationally inelastic processes, and a strong propensity for electric a-dipole collision-induced inelastic transitions. At zero electric field, elastic depolarization within \(J\),=1 are dipole forbidden; however, M-changing transitions could occur via two-step \(1\nu\),\(\rightarrow(0\nu\), or \(2\nu\),\(\rightarrow1\nu\), processes. The transient response within the \(1\nu\), level is monitored by various PUMP and PROBE polarization schemes. The transient gain data are fitted by various master equation models which provide information about the direct vs. sequential nature of the depolarization process.

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PRESSURE BROADENING OF THE ATOMIC IODINE \(5\text{P}_{1/2} - 5\text{P}_{3/2}\) TRANSITION

D. CERNY, M. AUBERT-FRECON, B. BACIS, B. BUSSERY and J. VERGES

The pressure broadening of the hyperfine lines of the \(2\text{P}_{1/2} - 2\text{P}_{3/2}\) atomic iodine transition is of importance in the chemically pumped iodine laser.

The hyperfine lines are observed in emission with a high resolution Fourier Transform spectrometer after dissociation of \(I_2\) by the 496.5 nm Ar\(^+\) lines. Pressure broadening of 1.95 MHz/torr, 3.9 MHz/torr and 193 MHz/torr were observed by collision with Argon, Oxygen and Iodine respectively.

We have tried to calculate theoretically these enlargements by a semi-classical method. Relaxation cross-sections are calculated between hyperfine levels of the I atom, in the first-order Born approximation. The interaction potential is a second order long-range potential, described as a multipolar expansion between \(O_2\), \(Ar\) or \(I_2\) and \(I\) atom and calculated from molecular or atomic polarisabilities.

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A MODIFIED RRKM APPROACH TO THE VIBRATIONAL PREDISSOCIATION DYNAMICS OF THE S1 p-DIFLUOROBENZENE-Ar VAN DER WAALS COMPLEX

HYE-KEUN O, MENG-CHII SU AND C.S. PARMENTER

The vibrational predissociation (VP) dynamics of the S1 pDFB-Ar vdW complex have been characterized by an adaptation of RRKM theory. Several calculations based on Fermi's Golden Rule have been used by others to model the VP dynamics of diatomic-rare gas vdW complexes. Those methods, however, have not been successful in fitting an extensive set of VP data1 for the pDFB-Ar vdW complexes. Recently, Kelley and Bernstein2 applied RRKM theory with the assumption of an energy gap law to VP in s-tetrazine-Ar. Although the method worked well for that case, we find that it does not predict the results of pDFB-Ar satisfactorily. With the assumption of a momentum gap law, we have used an RRKM approach to model more successfully our experimental VP data from 6 different initial S1 complex levels. In agreement with the data, it predicts that VP is highly selective among the possible final states. The selectivity has several characteristics: 1) VP does not favor nearby resonant monomer levels, 2) VP does favor small vibrational quantum number changes, 3) the monomer 00 level is a common final state for VP from all initial levels. It also predicts the intramolecular vibrational relaxation (IVR) observed in our experiments.

1H.-K. O, M.-C. Su and C.S. Parmenter (to be published)

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Crossed molecular supersonic beams have been used to study rotationally and vibrationally inelastic scattering from the $7^2$ and the $0^0$ vibrational levels of $^4$Au ($S_1$) glyoxal in collision with $H_2$. Laser excitation was used to select each of the initial vibrational levels with rotational states limited to $J' = 0-10$, $K' = 0$, and dispersed fluorescence was used to monitor quantitatively the final rotational and vibrational $S_1$ glyoxal states. Although many final vibrational levels are energetically accessible and in principle observable, only those reached by $\pm 1$ quantum changes in the lowest frequency mode, the torsion $v_7$, are seen. From the initial level $7^2$, the cross sections for $\Delta v_7 = +1$ and $\Delta v_7 = -1$ are nearly identical, mirroring the UP and DOWN symmetry recently observed in $I_2^*$ + He scattering. The total cross section for pure rotationally inelastic scattering from $0^0$ is about 8 times larger than that for rovibrationally inelastic scattering whereas the two cross sections are nearly equivalent for $7^2$. $\Delta K$ rotational state changes can also be resolved for both rotationally and rovibrationally inelastic scattering from the $0^0$ level. These rotational and rovibrational cross sections obey the same $\Delta E$ exponential scaling law, and where similar $\Delta E$ occurs, they are the same size. In contrast, the $\Delta K$ state-resolved cross sections from $7^2$ are quite different. Some $\Delta v_7 = -1$ cross sections with small $\Delta K$ changes are actually larger than some pure rotational cross sections. These relationships are exactly opposite to the conventional rule of thumb.

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Vibrationally inelastic cross sections have been measured with a crossed beam apparatus at different well-defined collision energies for the $I_2^*$ + He system. By controlling the temperature of the He target beam, we could vary the collision energy from 40 mev to 190 mev. $I_2$ molecules were initially laser pumped to the level $\nu' = 35$ or 15 of the B $Q_u^+$ state. Electronic fluorescence spectroscopy revealed the state-to-state vibrational cross sections. At the higher collision energies, the relative cross sections are very symmetric for $\Delta \nu$ UP versus $\Delta \nu$ DOWN scattering. This symmetry is much reduced when the collision energy more closely approaches the vibrational quantum size. The higher collision energies also create more rotational excitation and it is governed by angular momentum kinematics. Classical trajectory calculations fit the data by assuming a simple repulsive interaction between $I_2^*$ and He.

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MEASUREMENTS OF VIBRATIONAL DEPHASING OF CO ADSORBED ON NaCl(100)

HUGH H. RICHARDSON, HUAN-CHENG CHANG AND GEORGE E. EWING

The infrared spectrum of CO adsorbed on NaCl(100) has been obtained with a Fourier Transform Infrared Spectrometer (1). The apparent band width of the adsorbed CO decreased from 1 cm\(^{-1}\) at 60K to 0.5 cm\(^{-1}\) at 40K. The instrument resolution is 0.5 cm\(^{-1}\) and the CO bandwidth at 40K is limited by the spectrometer resolution. The observed band shape is a convolution of the Instrument Line Shape (ILS) and the true band shape. The true band shape was obtained by deconvoluting the ILS from the observed band shape (2). The temperature dependent change in both the band width and frequency shift is compared with predictions from existing theoretical models for band broadening mechanisms of adsorbed molecules on surfaces.


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HIGH RESOLUTION OPTICAL SPECTRA OF BENZOPHENONE UNDER HIGH PRESSURE

I. Y. Chan, W. M. Chung

Laser excitation and phosphorescence spectra of benzophenone (BP) under high pressure are investigated at 2°K using a diamond anvil cell. BP is doped in a 4,4'-dibromodiphenyl ether (DDE) single crystal. Early high pressure spectral works of BP were performed at room- or LN₂- temperature [1]. Our utilization of LHe has produced highly resolved spectra, separating the intramolecular transitions with their phonon side-band. High pressure does not degrade the known BP/DDE low temperature spectra.

We will report spectral investigation up to 40 kbar. Pressure dependence of the electronic (T₁) origin, C = O stretch and other vibrational frequencies and the Debye-Waller factor of BP/DDE will be presented. These results shed new light on our recent magnetic resonance work on BP under pressure [2]. They also elucidate the modifications of electron-phonon coupling of BP/DDE under compression.


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OPTICALLY DETECTED MAGNETIC RESONANCE OF Mn(IV) HEXAFLUORIDE IN Cs₂GeF₆ AND K₂GeF₆

E. Lifshitz and A. H. Francis

The photoexcitation and luminescence spectra (2E -> 4A₂) of MnF₆²⁻ diluted in Cs₂GeF₆ and K₂GeF₆ host lattices have been recorded at liquid helium temperature. The manganese coordination geometry is O₅ in Cs₂GeF₆ and D₃d in K₂GeF₆. Optically detected magnetic resonance (ODMR) has been employed to determine the g-value of the 2E state in both coordination geometries. The trigonal distortion has a pronounced effect on the g-values and produces a measureable splitting in the optical spectrum, but exerts relatively little effect on the radiative lifetime. In particular, the g-value in the O₅ site (g(2E)=2.0) is as predicted theoretically; however, the value obtained for the D₃d site is unexpectedly large (g(2E)=2.95). The data obtained is compared with theoretical predictions and the results of similar studies of d⁹ ions in a variety of lattices. The differences are shown to arise, in part, from the relative magnitude of the spin-orbit coupling and the trigonal field splitting in the 2E state.

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ANALYSIS OF THE MID-IR ELECTRONIC ABSORPTION SPECTRUM OF Fe$_2$P$_2$S$_6$ AND Co$_2$P$_2$S$_6$

N. NAGASUNDARAM AND A. H. FRANCIS

Single crystal FTIR spectra of Fe$_2$P$_2$S$_6$, Co$_2$P$_2$S$_6$, Cd$_2$P$_2$S$_6$, and Mn$_2$P$_2$S$_6$ were recorded at room temperature. The Fe$_2$P$_2$S$_6$ and Co$_2$P$_2$S$_6$ spectra exhibit bands which can be assigned to electronic transitions between the trigonal field components of the ground electronic state. A point-charge crystal-field model was used to relate the trigonal field splitting to crystal-field parameters ($D_Q$ and $C_P$) and to determine the relative energy of the trigonal field components. The FTIR spectrum of Fe$_2$P$_2$S$_6$ intercalated with pyridine was analyzed in terms of intercalation induced changes in the crystal-field parameters.

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RESTRICTED HARTREE-FOCK WAVEFUNCTIONS AND EXCITATION ENERGIES OF ALKOXY RADICALS

Stella M. Sung and Russell M. Pitzer

Ab initio calculations have been performed that generate the restricted Hartree-Fock wavefunctions and excitation energies for the ground state and lower excited states of the hydroxy (OH$^+$), methoxy (CH$_3$O$^+$), ethoxy (C$_2$H$_5$O$^+$), isopropoxy (C$_3$H$_7$O$^+$), and vinoxy (C$_2$H$_3$O$^+$) radicals. These theoretical results are compared to results obtained from laser-excitation spectra that were recorded in a supersonic free-jet expansion at low temperature for these radicals (Foster, Hsu, Liu, Kung, and Miller).

As anticipated, correlation-energy contributions to the excitation energies are small. The calculations provide assignments of the ground-state symmetry and energy splittings of the ethoxy and isopropoxy radicals. The resulting relative symmetries of the observed transitions are opposite to those obtained from the spectroscopic band assignments for these radicals.

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AN AB INITIO STUDY OF CS AND H ADSORPTION ON BE METAL

M.M. MARINO, M. SAWAMURA, AND W.C. ERMLER

Atomic cesium and hydrogen adsorption on beryllium clusters containing 19 and 33 atoms are studied using restricted Hartree-Fock calculations and ab initio relativistic effective core potentials. The clusters are taken as cylindrical plugs from a Be metal wafer. Be-Cs and Be-H internuclear distances are optimized, while Be-Be internuclear distances are frozen at the bulk metal values. For each system, numerous low-lying electronic states are investigated. The calculations are carried out to determine the effects of Cs and H adsorption on the electronic structure and work function of the systems. The cluster wave functions are Fourier transformed to obtain periodic wave functions and the relation between the finite cylinder and two-dimensionally extended bulk systems is discussed. The calculated ionization potentials for the cesiated systems are in agreement with the experimentally measured work function. Hydrogen is not predicted to adsorb on Be metal, which is consistent with recent experimental findings.1


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

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Ab Initio Calculations on Ag,, Au,, and AgAu Including Polarization Functions and Extended Electron Correlation

R.B. Ross and W.C. Ermler

Multi-configuration self-consistent field and configuration interaction calculations have been performed on Ag,, Au,, and AgAu. Relativistic effective core potentials (REP) and optimized valence basis sets of Slater-type functions, including f-type polarization functions, have been employed. Multi-reference single and double excitation electron correlation studies are reported. The effects of including f-type functions in the basis set and the necessary levels of electron correlation are discussed. Calculated spectroscopic constants are compared to experiment and to previous ab initio all-electron and REP studies.

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Ab Initio Calculations of Polarizabilities Including Relativistic Effects For Elements of Groups IA and IB

J.M. Powers, R.B. Ross and W.C. Ermler

The effects of relativity and the concept of core-valence separation have been examined with respect to polarizabilities for elements of groups IA and IB. The coupled Hartree-Fock method for atomic polarizabilities has been incorporated into an ab initio atomic self-consistent field program. Relativistic effects have been studied via ab initio calculations employing relativistic (REP) and nonrelativistic effective core potentials (NEP). The effects of re-definition of core and valence spaces have been studied by deriving REP's for heavy elements for a set of cases whereby fewer and fewer electrons are "frozen" into the core. In addition, core-valence correlation effects have been examined by calculating atomic polarizabilities via a finite-field formalism and configuration interaction calculations. The magnitudes of relativistic and core-valence correlation effects and the impact of definition of core-valence space are compared. The impact of this work on molecular studies employing effective potentials is discussed.

This work was supported through NSF Grant No. CHE-8712315

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VIBRATIONAL-ROTATIONAL ANALYSIS OF THE HYDROGEN PEROXIDE CATION FROM AB INITIO POTENTIAL ENERGY AND DIPOLE MOMENT SURFACES

Susan Kraft, Hsiuchin C. Hsieh and Walter C. Ermler

Results of ab initio unrestricted Hartree-Fock self-consistent field and Møller-Plesset perturbation theory calculations for the hydrogen peroxide cation are reported. A 6-31G** basis set was employed to compute energies on an extensive grid of nuclear configurations near the planar equilibrium geometry \((R_{OO}=1.32 \text{ Å}, R_{OH}=1.00 \text{ Å}, \angle{HOH}=104^\circ)\). Analytical representations of potential energy and dipole moment surfaces were derived from least squares fits to the grid points and used to calculate spectroscopic constants, dipole moment expectation values and transition moments. A power series expansion to fourth degree in both normal and internal coordinates was used to obtain the spectroscopic constants, expectation values and intensities.

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ULTRAFAST TRANSIENT SOLVATION OF POLAR DYE MOLECULES IN SIMPLE POLAR SOLVENTS

Michael A. Kahlow, Tai Jong Kang, Wlodzimeir Jarzeba, and Paul F. Barbara

Recently we constructed a time resolved fluorescence apparatus with a resolution of less than 300 femtoseconds. We have used this instrument to measure the microscopic solvation dynamics of three simple polar solvents (propylene carbonate, propionitrile, and methanol) by observing the time resolved fluorescence from coumarin 152. The solvation rates are non-singly exponential, with components both shorter and longer than the longitudinal relaxation times \( \tau_l \) of the solvents. Results will be discussed in terms of several recent theoretical models\(^{2,3}\).


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Ab initio CI study of the Magnetic Circular Dichroism Spectrum of Acetone for the $X \rightarrow \tilde{a}^1\text{Bu}$ and $X \rightarrow \tilde{c}^1\text{Bu}$ Electronic Transitions

L. F. Chabalowski, J. O. Jensen, and D. R. Yarkony

A method developed recently for studying spin-orbit (SO) interactions (1) is here applied to calculating MCD spectra. The method can be briefly described as a first-order perturbation technique which involves solving the set of linear equations

$$
\mathbf{H} \mathbf{\psi} = \mathbf{E}\mathbf{\psi},
$$

over Configuration State Functions (CSFs) to obtain the first-order correction $\mathbf{\psi}_1$ to the electronic state $\mathbf{\psi}$. This partially alleviates the impossible task of attempting to calculate explicitly the infinite manifold of perturbing states represented in the local expression for a first-order perturbation:

$$
\mathbf{\psi}_1 = \mathbf{\psi}_0 + \sum_{\text{pert}} \mathbf{\psi}_0 \mathbf{H}^{-1} \mathbf{H}'\mathbf{\psi}_0.
$$

The MCD $B$ term, which acquires its intensity through such perturbations, can be calculated via eq. 1 thus avoiding the need to calculate explicitly the large number of excited states involved in the summation of eq. 2. Results are presented for the new application of the method to the singlet $X \rightarrow \tilde{a}^1\text{Bu}$ and $X \rightarrow \tilde{c}^1\text{Bu}$ transitions in acetone.


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Theoretical Study of the Radiative Lifetime for the Spin-forbidden Transition $X^{1\Sigma_g^+} \rightarrow \tilde{a}^1\text{Bu}^-$ in He$^+$ Using $ab$ $initio$ State Averaged MCSCF CI Methods


The radiative lifetime for the $a^{1\Sigma_g^+}$ state in neutral He$^+$ was calculated including spin-orbit (SO) interactions between the $a^{2\Sigma_g^+}$ and $\tilde{a}^1\text{Bu}^-$ manifold of states, and the repulsive ground state $X^{1\Sigma_g^+}$ and the $X^{1\Pi_g}$ manifold. The SO interactions are treated through first-order perturbation theory wherein the first-order corrections to the wavefunctions are calculated directly by solving a set of linear equations (representing the first-order perturbation expression) involving SO matrix elements between the zeroth-order $(\tilde{a}^{2\Sigma_g^+})$ or $a^{1\Sigma_g^+}$ wavefunctions, and the list of Configuration State Functions generated by a second-order CI for the states of $X^{1\Pi_g}$ or $a^{1\Sigma_g^+}$ symmetries, respectively (1). This partially alleviates the problem of solving explicitly for many eigenstates of the $a^{2\Sigma_g^+}$ or $\tilde{a}^1\text{Bu}^-$ symmetries. The results show a rapidly changing electric transition dipole moment over the bound region of the $a^{2\Sigma_g^+}$, i.e., $r(\text{He-He}) \leq 3.5$ a.u. to 4.0 a.u. A vibrational analysis gives the lifetime of the $v=0$ level of $a^{2\Sigma_g^+}$ to be around 18 s, which is consistent with a recent experimental estimate of 10 s ($v=2$) as a lower bound.


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Address of Longfordsfield III: Lawrence Livermore National Laboratory, P.O. Box 803, Livermore, CA 94550.
RECENT STUDIES IN HIGH-RESOLUTION SPECTROSCOPY OF ATMOSPHERIC GASES

V.E. ZUEV

The paper considers the problems of laser applications and laser equipment developed to investigate the vibration-rotation absorption spectra of atmospheric molecular gases as well as the measurements of their concentration in the field conditions based on researches carried out at the Institute of Atmospheric Optics SB USSR Academy of Sciences.

High resolution laser spectrometers, including intracavity laser spectrometers, laser spectrophotometers, opto-acoustic laser spectrometers, fluorescence laser spectrometer are described. Using these spectrometers, some thousands of new absorption lines, tens of previously unknown H₂O, CO₂, C₂H₂, N₂O, NH₃, CH₄, HBr molecular absorption bands and their isotopes were recorded, assigned and analyzed, various molecular interactions were studied. The quantitative spectroscopic data obtained were widely used for laser gas analysis of the atmosphere, for determining concentrations of different atmospheric gases and, especially, of water vapor and of atmospheric pollutants. A new approach to the development of the differential technique in the trace gas analyzers is discussed.

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DIODE LASER SPECTROSCOPY OF TRIFLUOROHALOMETHANES (CFₓX) IN THE 9-9.5 µm REGION

A. BALDACCI, S. GIORGIANNI, R. VISINONI AND S. GHERSETTI

Diode laser spectra of CFₓX where X = Cl, Br and I, with natural isotopic abundance, have been measured in the 9-9.5 µm region using the SP 5000 Tunable Laser Source Spectrometer (from Spectra Physics) set up in appropriate configuration at the University of Venice.

The frequency range considered mainly comprises the ν₁ fundamental (CF symmetric stretching) and the 2ν₁ overtone; of the latter, only the parallel component (2ν₁) has been observed. The measurements were carried out at low temperature (~ 200 K) in order to simplify the complex structure due to "hot" band congestion.

The rotational fine structure within the P(J) and R(J) manifolds as well as in the Q-branch of the bands mentioned above has been resolved and a least-squares fit of the observed transitions to the energy expression including the quartic centrifugal distortion coefficients was performed. Some lines were found to be rotationally perturbed by 2ν₁ and the different mechanisms involving Δν = Δν = ±2, and Δν = ±2, Δk = ±1 interactions have been considered in the interpretation. Accurate molecular parameters of ν₁ and 2ν₁ bands of the two different isotopic species of CF₃ Cl and CF₃ Br have been determined.

Work on the spectrum of CF₃ I is also in progress; however its fine structure appears so strongly perturbed that the rotational assignments are not quite easy in the scheme of isolated vibro-rotational systems.

Interpretation, details of the spectra, and results obtained will be discussed.

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NEW HIGH-RESOLUTION SPECTRA OF O, IN THE 3-µM REGION

M. A. H. SMITH, V. MALATHY DEVI, C. P. RINSLAND, AND C. T. SOLOMON

We have recorded a series of high-resolution absorption spectra of ozone at room temperature using the McMath Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. The spectra cover a wavenumber range from approximately 1900 cm\(^{-1}\) to 5400 cm\(^{-1}\) at a resolution of 0.01 cm\(^{-1}\). Improvements in the design of our ozone generating system have allowed us to obtain several spectra of nearly pure ozone at high abundances (up to 3800 torr-cm), and lines belonging to at least 16 transitions from the ground state can be observed in these scans. Analysis is in progress to determine line positions, assignments, and intensities.

In the region from 2600 cm\(^{-1}\) to 3600 cm\(^{-1}\), we have used the same experimental apparatus to record a number of absorption spectra of ozone broadened by dry air, by N\(_2\), and by O\(_2\), also at room temperature. These spectra are being analyzed to determine pressure broadening and line shift coefficients.

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LINE POSITIONS AND INTENSITIES OF THE 2v\(_1\), v\(_1\) + v\(_2\), AND 2v\(_3\) BANDS OF \(^{14}\)O,

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

In the present work, we report the results of an analysis of the 2v\(_1\), v\(_1\) + v\(_2\), and 2v\(_3\) bands of \(^{14}\)O, the strongest bands in the 4.8-µm spectral region. The laboratory spectra were recorded at room temperature and 0.005 cm\(^{-1}\) resolution using the Fourier transform spectrometer located in the McMath solar telescope facility on Kitt Peak in Arizona. The ozone samples were prepared from >99.98% pure \(^{14}\)O\(_3\) using the silent electric discharge technique. Initial assignments were obtained from the results of an earlier study, and a first calculation was performed with the aid of a Hamiltonian taking into account the interactions affecting the rovibrational levels. The improved vibrational energies and the rotational and coupling constants derived from this fit were used to calculate extrapolated levels. From these results and subsequent iterations, assignments were obtained up to J=55, K\(_a\)=14 for the 2v\(_3\), J=64, K\(_a\)=17 for the v\(_1\) + v\(_2\), and J=55, K\(_a\)=14 for the 2v\(_1\) bands, significantly extending the set of lines previously assigned.

Experimental rotational energy levels of the three interacting states (002), (101), and (200) were obtained by adding the observed line positions to the known ground-state rotational levels. These upper-state levels were then reproduced using a Hamiltonian which takes into account the Coriolis-type interactions between the rotational levels of (002) and (101) and of (101) and (200), as well as the Darling-Dennison interaction between the levels of (002) and (200). The fit was satisfactory since a standard deviation of 0.00047 cm\(^{-1}\) was achieved, close to the experimental uncertainty.

In addition, 416 relative line intensities were measured from the spectra. The intensities were calibrated with respect to the intensities of lines in the 10-µm region which appear in the same spectra and have been previously determined. Precise transition moment constants for the three bands under study have been deduced. A complete listing of line positions, intensities, and lower state energies has also been generated.


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LINE INTENSITY AND COLLISION-BROADENED LINE WIDTH MEASUREMENTS IN THE ν₁-FUNDAMENTAL OF ¹⁴N₂O AT ATMOSPHERIC TEMPERATURES

S. CHUDAMANI, and P. VARANASI

The need for data on the intensities and air-broadened half-widths of rotational lines in the ν₁-fundamental of ¹⁴N₂O and their temperature dependence at temperatures relevant to the terrestrial atmosphere has prompted us to perform measurements on several lines between 1240 and 1280 cm⁻¹ using a tunable diode laser spectrometer. Line intensities are reported along with N₂-broadened, O₂-broadened and air-broadened line width data at several temperatures between 150 and 296 K.

Supported by the Upper Atmosphere Research Program of the Earth Sciences and Applications Division of NASA under Grant-in-Aid No. NAGW-1238.

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LINEWIDTH NARROWING IN THE INFRARED BAND OF N₂O PERTURBED OF N₂

CAI PEIPEI, SHEN SHANKIONG, YU HAIPING AND I-SHAN CHENG

This preliminary work shows the feasibility of obtaining the phenomenon of collisional narrowing in the infrared vibration-rotation spectrum of N₂O perturbed by N₂.

Using R(16) line of a grating tunable N₂O laser and a White type long cell with variable lengths from 40 to 1000 m, the absorption spectrum of N₂O are obtained. The pressure of N₂O is varied from 10 to 20 Torr. The variation of linewidths is to plot the peak height of absorption as a function of N₂O gas pressure. The peak absorption constant increases with the N₂ gas pressure, reaches a maximum and then decreases. The maximum appears at the N₂ gas pressure of 300 Torr and 250 Torr when N₂O pressures are 10 and 20 Torr, respectively.

The conclusion that a collision partner with equal mass is most effective in changing the velocity through collisions is not exactly obvious in our case, since N₂O and N₂ have quite different masses.

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ABSOLUTE INTENSITIES IN THE \( v_2 \) REGION OF CO\(_2\)

J.W.C. JOHNS

Absolute intensities and pressure broadening parameters have been measured in the region of the \( v_2 \) bending fundamental of CO\(_2\).

The measurements were made with a modified Bomem spectrophotometer and the performance of this instrument as well as the methods used for the data reduction will be briefly discussed.

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STUDIES CONCERNING THE OPTIMUM HAMILTONIAN FOR USE IN LARGE AMPLITUDE, DIRECT NUMERICAL DIAGONALIZATION CALCULATIONS

RICHARD B. WATTSON

It would be desirable to extend the Direct Numerical Diagonalization (DND) calculations\(^1\) to handle the large amplitude vibrations that occur in molecules at very high temperatures approaching dissociation. Many important advances have occurred recently in the formulation of the full rotation-vibration kinetic energy for the quantum mechanical Hamiltonian of a general polyatomic molecule. These new approaches generally utilize curvilinear internal coordinates rather than the rectilinear internal coordinates associated with the traditional form\(^2\) of the kinetic energy. In applying a new technique like DND, there are different requirements on the form of the Hamiltonian than has been usual for perturbation approaches. These formulations are compared with DND calculations in mind, and a valence coordinate Hamiltonian which satisfies the Eckart conditions is derived for comparison. The balance between the range of applicable domain and the minimization of off-diagonal matrix elements will be discussed. Future DND calculations using the most promising Hamiltonians should reveal the optimum approach for the calculation of the large amplitude properties of triatomic molecules.


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CALCULATIONS OF ENERGIES AND INTENSITIES FOR THE ASYMMETRIC SPECIES OF CO₂

R.B. WATTSON, L.S. ROTHMAN, A. NEWBURGH, and R. PAVELLE

The transformation of the potential function expressed in normal coordinates from the principal isotopic species of carbon dioxide to other isotopic species is shown. Required in the intermediary normal to valence coordinate transformation was the use of the Eckart condition as a constraint along with the use of the computer algebra system, MACSYMA. This tool was used in both determining the coordinate transformation and its expansion in Taylor series form. After expansion to seventh order in valence coordinates, the potential function coefficients were calculated to seventh order in normal coordinates via the method presented by Hoy et al.¹

The transformed potential function surfaces were then used to calculate the eigenstate energies for all relevant isotopic species of CO₂ by the direct numerical diagonalization method.² Some kinetic energy terms had to be generalized for the asymmetric species. The dipole moment function was also transformed from the principal isotopic normal coordinate form to the valence coordinate form. This in turn was again transformed to the appropriate form for the various isotopic species including the asymmetric ones; the transition intensities were then calculated. Comparison with measured transitions of the oxygen-18 enriched asymmetric isotope (628), which are forbidden in the principal isotope, gives some indication of the errors inherent in the technique.


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CO₂ SPECTROSCOPIC CONSTANTS DETERMINED BY GLOBAL LEAST-SQUARES FITTING AND DIRECT NUMERICAL DIAGONALIZATION

ROBERT HAWKINS, RICHARD B. WATTSON, and LAURENCE S. ROTHMAN

The ¹²C₁₆O, line positions in the AFGL HITRAN linelist are derived from a database comprising 8,321 measured line positions, assigned to 105 vibration-rotation bands and 63 vibrational levels. Some 285 spectroscopic constants of these levels have been determined simultaneously in a linear least-squares fit, using a Givens rotation algorithm. The resulting constants and calculated line positions are only slightly different from those previously obtained with a level-by-level method; however, the estimated standard deviations are much more realistic, and the amount of work required is reduced.

These spectroscopic constants have been used to fit a new potential function using the Direct Numerical Diagonalization method while employing two successive diagonalizations to obtain ro-vibrational spectroscopic parameters. The parameters obtained for the principal isotope have been determined from ro-vibrational energies evaluated at J = 0 and at J = 30. The results will be shown as O-C plots calculated from the parameters derived from the potential surface and all measured lines of the principal isotope (626) and the carbon-13 enriched isotope (636) (using a transformed potential). Systematic effects will also be discussed.

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SIMPLIFIED EXPRESSION FOR THE TOTAL INTERNAL PARTITION SUM AS A FUNCTION OF TEMPERATURE

ROBERT R. GAMACHE, ROBERT HAWKINS, and LAURENCE S. ROTHMAN

The total internal partition sums have been calculated for the molecules and their isotopic variants on the HITRAN database. The calculations employed nearly complete sets of energy levels for all relevant rotation-vibration states generated from the molecular constants. All degeneracies were accounted for in the calculations. The calculations were performed over a temperature range of 75K to 400K. The accuracies of the resulting partition sums will be shown. For generalized applications, the internal partition sums have been fitted to the expression

$$Q(T) = a + b \cdot T + c \cdot T^2 + d \cdot T^3,$$

where a, b, c and d are constants adjusted by means of a least-squares minimax procedure. The maximum deviation of the fit is on the order of a few tenths of a percent.

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TEMPERATURE DEPENDENCE OF LINE BROADENING OF CO₂ LASER BAND

CAI PEIPSI, SHEN SHANXIAO, XU JIJING, and J-SHAN CHENG

The broadening of CO₂ rotation-vibration lines are investigated in the 280-470 K temperature range. The temperature exponent is showed to be independent of the rotational quantum number for both self and nitrogen broadening.

A single-mode single-line CO₂ laser is used as a source. The sample CO₂ gas is filled in a double-pass cell of 0.6 m base length, constructed of quartz glass with ZnSe window. The pressure shifting of lines is assumed to remain of negligible magnitude so that the emitted frequency coincides with the absorption peak.

An useful computer programme for calculating temperature exponents with ATC theory is designed. The theoretical results are compared with the measured values with reasonable agreement.

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MEASUREMENT OF THE STARK EFFECT IN A FLYGARE-BALLE MICROWAVE SPECTROMETER

T. EMILSSON AND H. S. GUTOWSKY

In the Flygare-Balle Fourier transform spectrometer a microwave pulse is applied to a Fabry-Perot cavity, synchronized with an expanding jet of a gas mixture from a pulsed supersonic nozzle. Measurement of the Stark effect in this type of spectrometer has been hampered by the difficulty of producing an adequately homogeneous electric field without degrading spectrometer performance. The common approach to the production of a homogeneous electric field is to use large, parallel metal plates, spaced as closely as possible. This method works poorly in the present case because the plates disturb both the microwave field and the gas expansion.

We have built a device which generates a good electric field (line broadening <0.5% of the Stark shift) over a volume of \(-5 \times 8 \times 10^4\) cm\(^3\), but does not disturb the gas expansion significantly. It consists of two square Plexiglass frames (13 x 13" o.d., 11 x 11" i.d. and 1" thick), joined at the corners by four aluminum rods 2' long, forming a structure similar to a box kite. Twelve 24 gauge wires are stretched 1" apart along each of the four long faces. At one end, each pair of adjacent wires is connected by a 5 Mohm resistor and the four corner wires to external terminals. The orientation of the electric field is selected by the connections of the terminals to the HV power supply. The microwave field is unaffected by the assembly at frequencies above 10 GHz, tolerable at 9 GHz, but unusable below 8 GHz. Examples of performance will be presented. Modifications to allow operation at lower frequencies are under consideration.

*Work supported by NSF and PRF.


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NOZZLE DESIGN FOR A FLYGARE-BALLE MICROWAVE SPECTROMETER

T. D. KLOTS, T. EMILSSON, AND H. S. GUTOWSKY

We have been experimenting with nozzle design to extend the utility of the Flygare-Balle spectrometer in observing rotational spectra of transient species. The spectrometer traditionally uses a single, pulsed nozzle from which a premixed gas expands into the Fabry-Perot cavity. We have now tried several modifications in which gases from two different sources are mixed in the expansion region, with a much shortened, adjustable contact time. A coaxial source is useful in avoiding unwanted reactions. It consists of a fine inner tube with a continuous (cw) flow of one gas (mixture) and an outer tube generating a pulsed beam of another.

Mixing NH\(_3\) and HX gas ordinarily produces a cloud of solid NH\(_3\)X particles. However, the rotational spectrum of vapor over heated solid NH\(_3\)Cl (450 K) has recently shown it to be a hydrogen bonded NH\(_3\)-HCl dimer.\(^2\) We have observed rotational transitions of the latter at much larger S/N using a coaxial nozzle at ambient temperature with 5% HCl/He in the cw inner tube and 0.3% NH\(_3\)/Ar in the pulsed outer tube. In addition, for the first time, the microwave spectrum of the hydrogen bonded, linear trimer, NH\(_3\)-HCN-HF, has been observed. Preliminary results for B and D are 1067.09 MHz and -0.4 kHz. For it, 5% HF/He was used in the inner tube and 0.3% NH\(_3\), 0.3% HCN/Ar in the outer. Further extensions and applications are in progress.

*Work supported by NSF and PRF.


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CHARGE REARRANGEMENT IN (HCN)_2 AND (HCN)_3

R. S. RUOFF AND H. S. GUTOWSKY

Charge rearrangement during cluster formation may be determined from its effects upon the dipole moments \( \mu \) and the electric field gradients \( \chi_0 \) of the monomeric units, provided that corrections can be made for their vibrational averaging. An isotopic substitution method has enabled us to obtain vibrational amplitudes in the linear dimer and trimer. A dipole moment of 6.552(35) D has been reported for the dimer and we have found 10.6(2) D for the trimer. These lead to induced dipole moments \( \Delta \mu \) of 0.703(3) D for the dimer and 1.75(10) D for the trimer. A similar analysis was made of \( \Delta \chi_0 \).

A mutual polarization model was used to predict the induced dipole moments from the known electrical multipole moments of HCN and its bond polarizabilities. The results are 0.703 D for the dimer and 1.68 D for the trimer. The calculations give ratios of the dipoles induced in the C-N bonds which are essentially identical with the ratios of the experimental \( \Delta \chi_0 \)'s. Equations are derived for calculation of \( \Delta \mu \) of an infinite H-bonded chain and are applicable to HCN. The convergence of multipole expansions for the electric field due to a molecular charge distribution will be discussed. The mutual polarization model works so well on HCN dimer and trimer that any charge transfer between the HCN monomers seems likely to be very small or negligible.

*Work supported by NSF and PRF.


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INDIVIDUAL HYDROGEN-BOND LENGTHS IN HYDROGEN-BONDED TRIMERS

R. S. RUOFF, T. D. KLOTS, C. CHUANG, T. EMILSSON, AND H. S. GUTOWSKY

A linear trimer such as \( Y-(HCN)_2 \) may be viewed as a composite of the two dimers \( Y-HCN \) and \( HCN-HCN \). The trimer formation changes properties of the dimers such as vibrational amplitudes and the center of mass (c.m.) separation \( r \) of adjacent monomers. Accurate values for \( r_1 \) and \( r_2 \) are difficult to obtain from the rotational constants of the trimers because the c.m. of the middle monomer is close to the c.m. of the trimer. However, an isotopic substitution method has given us good results in several cases.

In linear \( (HCN)_3 \), \( r_1 \) and \( r_2 \) are close to equal, 4.389(10) and 4.401(10) A respectively, both about 0.05 Â shorter than the \( r \) for the dimer, 4.448 Â. The overall shrinkage in OC-HCN-CHN is a bit less, 0.083(3) versus 0.106(1) Â, but it is highly asymmetric, 0.071(1) Â for \( r_1 \) and only 0.010(5) Â for \( r_2 \). The figures for \( N_2-HCN-CHN \) are comparable, an overall shrinkage of 0.075(3) Â with 0.065(10) and 0.009(6) Â for \( r_1 \) and \( r_2 \) respectively. The results for these and other hydrogen-bonded trimers will be presented and discussed.

*Work supported by NSF and PRF.


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EMISSION FREQUENCY OF THE 496 \mu m LINE IN $^{13}$CH$_3$F AS A FUNCTION OF PRESSURE AND PUMP OFFSET BY INFRARED-SUBMM DOUBLE RESONANCE TECHNIQUES

R. L. CROWNOVER, D. D. SKATRUD, and F. C. DE LUCIA

The frequency accuracy and reproducibility of OPFIR lasers is important to their application as local oscillators in heterodyne systems and as primary frequency sources in spectroscopy. We have employed an infrared-submm double resonance technique to investigate the gain frequency as a function of both pressure and pump offset. The interpretation of our experiment is greatly simplified by the absence of cavity pulling and other effects associated with an oscillating laser.

The submm probe was obtained from a harmonic multiplier driven by a phase locked klystron; the pump beam was produced by a tunable waveguide CO$_2$ laser. To first approximation the FIR gain peak linearly tracks the IR pump offset; this is consistent with a theory in which the cross section for state changing collisions greatly exceeds the cross section for velocity changing collisions.

We have previously reported pressure broadening parameters for a variety of transitions within the $V_4$ excited vibrational state of this species; the implications of those results to the question of pressure shift will be discussed.

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A COLLISIONAL ENERGY TRANSFER MAP INCLUDING $\Delta K$ PROCESSES IN CH$_3$F

HENRY EVERITT AND FRANK C. DE LUCIA

Time resolved millimeter/submillimeter wave - infrared double resonance techniques were used to study rotational energy transfer in methyl fluoride. A Q-switched CO$_2$ laser pumped molecules into the $J=5$, $K=3$, $V_3=1$ state of $^{13}$CH$_3$F, and the time response of many absorption lines in the $V_3=1$ rotational manifold were monitored. An energy transfer map was obtained which includes state-to-state rates for two processes that change $K$-quantum number in addition to previously measured $\Delta J$ rates and vibrational relaxation rates. The first $\Delta K$ process, a vibrational swapping mechanism, effectively changes $K$ in the $V_3=1$ vibrational state through collisions of nonthermal molecules in $V_3=1$ with thermal molecules in the ground vibrational state. The second is a direct collision induced transition and follows the selection rule $\Delta K=3n$. We have also obtained preliminary results on a similar study of $^{12}$CH$_3$F.

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VERY LOW TEMPERATURE SPECTROSCOPY IN A COLLISIONALLY COOLED CELL:
PRESSURE BROADENING STUDIES BETWEEN 4.2 K AND 1.8 K

D. R. WILLEY, R. L. CROWNOVER, D. N. BITTNER, AND F. C. DE LUCIA

The results of a pressure broadening experiment in the CO-He system in the region between 1.8 - 4.2 K will be described. It was found that the pressure broadening parameters varied from 21.3 MHz/Torr to 40.0 MHz/Torr over this temperature region. Comparison with earlier theoretical calculations showed excellent agreement near 4 K; however, at the lowest observed temperature the theoretical value was about 20% greater than the measurement.

In addition, we have also observed $^{12}$CH$_3$F pressure broadened by He. As expected from its larger dipole moment, very large signals are observed, confirming the expectation of the generality of the collisional cooling technique. Because this species is a symmetric top, effects associated with the $K$ structure can be studied, including rotational cooling. Preliminary observations show a significant variation in the pressure broadening parameter with quantum number at 4 K.

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AN IAM FIT OF THE MICROWAVE SPECTRUM OF DIVINYL ETHER

L. H. COUDERT

Divinyl ether, C$_2$H$_3$O-C$_3$H$_3$, occurs in two conformations, the trans-trans and the cis-trans. The microwave spectrum of this latter conformer has been thoroughly measured by Hirose and coworkers$^{1-2}$, and reflects the effects of a 27 MHz tunneling splitting which appears especially for $b$ and $c$ type transitions. The tunneling motion responsible for the splitting correspond to an antigeared rotation of each vinyl unit about axes coinciding with the respective CO bonds. Because this problem is multidimensional, theory available at the time Hirose and coworkers$^{1-2}$ did their measurements was not adequate to obtain a satisfactory fit. Our goal is to improve this fit using new techniques.

In this work we apply to the cis-trans conformer the IAM-like treatment developed$^3$ for multidimensional tunneling. The use of this method requires first the determination of the various paths connecting the two nonsuperimposable frameworks of the molecule. If this molecule goes through a planar configuration during the tunneling, we have one tunneling path. However, if the intermediate configuration is not planar, two equivalent tunneling paths will occur. The J and K dependence of the splittings in the case of a planar intermediate configuration is quite different from the dependence in the case of a nonplanar intermediate configuration. In our theory this dependence is characterized by three angles, $\phi_d$, $\theta_p$ and $\delta_d$.

Using this IAM formalism the microwave transitions were fit with an RMS deviation of 0.155 MHz and a determination of the value of the angles mentioned above was carried out. Even though one of them turned out to be ill defined, the values obtained show that the cis-trans conformer of divinyl ether displays two tunneling paths. Starting from ab-initio data$^4$ and guessing the equation of the tunneling path(s), a calculation of these angles was also undertaken theoretically.


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Two-dimensional correlation experiments were applied to microwave Fourier transform spectroscopy in order to probe connectivities between rotational transitions. A three-pulse sequence supplied with a phase cycle acting as a double-quantum filter was developed in analogy to NMR experiments. A two-pulse "COSY" sequence was demonstrated to be useful to correlate connectivities within quadrupole hyperfine multiplets.

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The pure rotational spectrum of cyclobutane-1,1-d₂ has been measured between 12-40 GHz with a pulsed microwave Fourier transform spectrometer. The assignment for transitions with J ≤ 40 was confirmed by microwave-microwave double resonance with a continuous pump radiation. All rotational transitions with J > 2 were split into a doublet due to the ring puckering motion. A coupled Hamiltonian for the two lowest states has been used to fit six rotational and five centrifugal distortion constants. The energy difference of 95.19 MHz between these two states has been determined from the rotational constants of cyclobutane-1,1-d₂ and cyclobutane-d₄, and the vibrational transition frequencies of the ring puckering of the parent and the d₄ species.

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Address of Vogelsanger, Meyer and Bauder: Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.
MICROWAVE SPECTRUM, CONFORMATIONAL ANALYSIS, AND BARRIERS TO INTERNAL ROTATION OF CIS-1-FLUORO-2-BUTENE

D. T. DURIG, HOWARD Z. QIU, T. S. LITTLE, AND J. R. DURIG

The microwave spectrum of cis-1-fluoro-2-butene has been recorded in the region 12.0 to 39.0 GHz. A-type R-branches have been observed and assigned for the ground state for the gauche conformer. The determined rotational constants for this conformer were found to have the following values: \( A = 12,681.38 \pm 8.59 \), \( B = 2541.16 \pm 0.05 \), and \( C = 2309.62 \pm 0.04 \) MHz. From the Stark effect the dipole moment components were determined to be \( |\mu_x| = 1.91 \pm 0.02 \), \( |\mu_y| = 1.07 \pm 0.01 \), \( |\mu_z| = 0.31 \pm 0.01 \), and \( |\mu_\| = 2.21 \pm 0.02 \). Barriers to rotation have been determined as well as the conformational stability. These results will be compared to the corresponding quantities obtained from \( \text{ab initio} \) calculations as well as those for trans-1-fluoro-2-butene and methacryloyl fluoride.

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MICROWAVE SPECTRUM, BARRIERS TO INTERNAL ROTATION AND STRUCTURE OF METHYL FLUOROFORMATE

C. L. TOLLEY, T. S. LITTLE AND J. R. DURIG

The microwave spectra of methyl fluoroformate-\( d_3 \), \( CD_3OC(O)F \), and methyl fluoroformate-\( d_2 \), \( CD_2HOC(O)F \), have been recorded from 18.0 to 40.0 GHz. The rotational spectra have been assigned and the rotational constants have been calculated. The determined structural parameters are compared to those for methyl formate and methyl chloroformate. The barrier to internal rotation of the methyl group has been calculated from the A-E splitting observed in the microwave spectrum. This value is compared to values obtained from the far infrared spectrum of methyl fluoroformate in the gaseous state and \( \text{ab initio} \) calculations at the 6-31G* level.

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THE A-X BAND SYSTEM OF C2D2
IR CONSTANTS OF THE TRANSBENDING LEVELS

T R HUET and M HERMAN

The conventional rovibrational analysis of the A-X band system of acetylene, already performed on C2H2 (1-4), is extended to other isotopomers. Results are presented in this first communication, concerning the ν₄(n=0-4) ground levels of C2D₂, involved on the absorption spectra. Improved and new rovibrational constants are provided for 2ν₄ and 3ν₄ respectively. Perturbations encountered on the spectrum, arising because of the proximity of ω₄ and ω₅ in C2D₂, X1Σ⁺, are briefly discussed.

(1) C K Ingold and G W King, J Chem Soc. 2702-2755 (1953)
(4) J C Van Craen, M Herman, R Colin and J K G Watson, J Mol Spectrosc. 111, 185-197 (1985) and 119, 137-143 (1986)

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THE A-X BAND SYSTEM OF C2D2
ROVIBRONIC INFORMATION ON THE A STATE

T R HUET and M HERMAN

The conventional rovibrational analysis of the A-X band system of acetylene, already performed on C2H2 (1-4), is extended to other isotopomers. This second communication concerns the information derived on the A state of C2D₂. Original rovibrational constants are presented and compared to those of C2H2 (1-4).

(1) C K Ingold and G W King, J Chem Soc. 2702-2755 (1953)
(4) J C Van Craen, M Herman, R Colin and J K G Watson, J Mol Spectrosc. 111, 185-197 (1985) and 119, 137-143 (1986)

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HIGH RESOLUTION INVESTIGATION OF THE $^3\text{Au}$ STATE OF GLYOXAL

F VANHORENBEKE, J VANDER AUWERA, M VERVLOET and M HERMAN

The $^3\text{Au}-\text{Ag}$ transition of C$_2$H$_2$O$_2$, observed around 5200 Å, was recorded with the help of a Fourier Transform Spectrometer at Ottawa, with a resolution of 0.020 cm$^{-1}$. Doppler limited and sub-Doppler laser investigations are being undertaken at Brussels in order to allow the analysis of this very dense spectrum. They are based mainly on the Infrared Optical Double Resonance technique, after (1,2) and also on the Inter Modulated Phosphorescence, Laser Induced Phosphorescence and Stark Modulation techniques. Preliminary results will be presented.


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ZEEMAN STUDIES OF MICROWAVE-OPTICAL DOUBLE RESONANCE SIGNALS IN THE $\text{A}_1 - \text{X}_1$ SYSTEM OF THIOFORMALDEHYDE

W. HÜTTLER, J.C. PETERSEN AND D.A. RAMSAY

Zeeman studies have been carried out at fields between 1 and 7 kG on some previously recorded microwave-optical double resonance signals of thioformaldehyde. The microwave transitions originate in the J$_\text{A}_1$ rotational levels of the $^4\text{A}_2$ excited state and terminate in highly excited vibronic levels of the $^4\text{X}_1$ ground state. By observations in parallel ($\Delta M_J = 0$) and perpendicular ($\Delta M_J = \pm 1$) polarizations, rotational g-factors for the two combining levels are determined. The interpretation of the results is facilitated by carrying out the measurements with both parallel and perpendicular polarizations of the microwave and optical fields. The effective g-factors for the highly excited levels of the $^4\text{X}_1$ ground state support the earlier proposition that K$_A$ is not a good quantum number for these levels.

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Address of Petersen: Department of Physics and Astronomy, University of Alabama, Tuscaloosa AL 35486, U.S.A.

Address of Ramsay: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Canada K1A OR6.
THE VIBRONIC SPECTRUM OF SELENOFORMALDEHYDE IN THE NEAR INFRARED

R. H. JUDGE, D. J. CLOUTHIER, D. C. MOULE

The polymers of CH₂Se and CD₂Se were pyrolyzed at 700°C to yield monomeric selenoformaldehyde. Laser excitation spectra of these molecules were recorded. The origin of the weak singlet-singlet $\tilde{A}^1A_2 \leftarrow \tilde{X}^1A_1$ system in CD₂Se was observed at 13631.5 cm⁻¹ while that of CH₂Se has been calculated to be at 13555 cm⁻¹. The much more extensive and intense singlet-triplet $\tilde{A}^3A_2 \leftarrow \tilde{X}^1A_1$ systems of CH₂Se/CD₂Se have origins at 12171.0/12262.7 cm⁻¹. A double minimum potential energy function was used to fit the triplet state $v_4$ inversion levels and was found to be similar to that observed for thioglyoxaldehyde.

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THE INTERNAL ROTATION AND INVERSION MOTIONS OF THIOACEALDEHYDE IN ITS FIRST TRIPLET $\tilde{A}^3\text{A}''$ ELECTRONIC STATE

D. C. MOULE, Y. G. SMEYERS, A. NINO

Thioacetaldehyde, CH₃CHS displays a banded absorption spectrum at 615 nm which is attributed to the $T_1 \leftrightarrow S_0$, $\tilde{A}^3\text{A}'' \leftrightarrow \tilde{X}^1\text{A}'$ electronic transition which arises through $n\rightarrow\pi^*$ excitation.

The spectrum in the $T_0$ region consists of a cluster of bands which was assigned to the activity of the methyl torsional mode $\gamma_{15}$. Substitution of deuterium for the aldehyde hydrogen produces an isotope shift which demonstrates that a strong coupling exists between the aldehyde wagging mode $\gamma_{14}$ and the methyl torsion $\gamma_{15}$.

Ab initio SCF methods were used to generate the potential surface defined by $\theta$(internal rotation) and $\omega$(hydrogen wagging) in both electronic states from which the potential $V(\theta, \omega)$ was derived as a Fourier expansion. The band spectrum of CH₃CHS was synthesized from the energy levels and Franck Condon factors of a two-dimensional torsional-inversion Hamiltonian in which the torsion and inversion motions were treated as $C_3$ and $C_1$ rotations respectively.

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Address of Smeyers and Nino: Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Cientificas, C/ Serrano, 119, 28006 Madrid, SPAIN.
ON THE ASSIGNMENT OF THE EXCITED SINGLET STATES IN THE CO₂ MOLECULE

P. J. Knowles, P. Rosmus and H. J. Werner

High accuracy electronic structure calculations (contracted MRCI wavefunctions with the quality of several 10⁷ uncontracted configurations) for the energies of CO₂ in the lowest states in each of ¹Σ⁺, ¹Π, ¹Δ, and ¹Σ⁻ symmetries, as a function of the symmetric stretching coordinate, will be reported. The positions of the electronically excited states have been determined with an expected accuracy of about 0.05 eV. The geometries and the harmonic force constants for the symmetric stretch modes at the barriers to linearity for the ¹Σ⁺, ¹Δ, and ¹Π states have been calculated. The results show that the electronically excited states ¹Σ⁺ and ¹Δ of linear CO₂ cross in the Franck-Condon region of the absorption spectrum with the ¹Π state. It has been found that the ¹Δ state is separated by a barrier from the lowest dissociation asymptote and has a double minimum potential energy function. Implications for the interpretation of the absorption spectrum and the dynamics of the CO₂ photodissociation will be discussed.

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H.J.Werner: Department of Chemistry, University of Bielefeld, Bielefeld, Germany.

CHEMILUMINESCENCE SPECTRA OF SMALL MOLECULES CONTAINING SULPHUR, SELENIUM, AND TELLURIUM

R. J. GLINSKI

To help identify a novel emission feature extending from 550 nm to 880 nm produced in the gas-phase reaction of F₂ with CS₂, the reaction of F₂ with CSe₂ has been studied. This reaction yields a previously observed emission feature from SeF (A) extending from 500 nm to 870 nm and a banded feature between 350 and 500 nm that resembles fluorescence from Se₂(A) but requires further analysis. An apparently new, broad feature extending from 600 nm to the near IR appears by itself under certain reaction conditions. This broad feature is unresolved at 0.1 nm resolution and is not very useful in understanding the F₂/CS₂ feature.

Reactions of F₂ with CH₃X CH₃, where X = Se, Se₄, Te, and Te₂, are being studied as sources for emission spectra of CH₃Se and CH₃Te. Fruitful chemical trends and analogies are being exploited in effort to identify new spectra of hard-to-study small molecules in chemiluminescence.

Address: Department of Chemistry, Tennessee Technological University, Cookeville, TN 38505.
STEADY STATE PRODUCTION OF THE HNCN IN THE GAS PHASE BY HYDROGEN ABSTRACTION FROM CYANAMIDE

P. E. FLEMING, C. W. MATHEWS, AND M. WINNEWISER

The cyanamidyl radical HNCN was first observed and identified by Herzberg and Warsop in 1963 in the flash photolysis of diazomethane. Spectroscopic studies of this molecule have been limited to flash photolysis conditions. Using hydrogen abstraction, HNCN is produced in the gas phase in steady state concentrations by the mechanism

\[
X + H_2NCN \rightarrow HX + HNCN
\]

The efficiency of the mechanism is monitored by the intensity of the 0 - 0 band of the A - X transition near 3440 Å. The best results are obtained using discharges in CF₄, SF₆ or CCl₂F₂ as hydrogen scavenger sources.


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PICOSECOND ABSORPTION SPECTROSCOPY OF TRANSIENT CONDENSED PHASE RADICALS IN THE SPECTRAL REGION OF 200nm - 300nm.

D. R. Anderson and J. B. Hopkins

A new technique has been developed which makes it possible to obtain picosecond transient absorption spectra in the 200nm - 800nm region of the spectrum.

This method extends the previously useful wavelength range of 800 - 350nm to much deeper ultraviolet wavelengths with an ultimate time resolution of 2ps. In addition, the experimental signal to noise ratio of the transient spectrum has been greatly enhanced by using a 2 KHz regenerative picosecond laser as the excitation source. This novel instrument is applied to study the transient spectroscopy of photogenerated radicals in solution.

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HIGH RESOLUTION LASER SPECTROSCOPY OF AROMATIC IONS AND FREE RADICALS

JAMES M. WILLIAMSON, STEPHEN C. FOSTER, LIAN YU, AND TERRY A. MILLER

High resolution, laser-induced fluorescence spectra of a number of aromatic chemical intermediates that are subject to Jahn-Teller distortion have been recorded. The ions or radicals were prepared by the uv photolysis of precursors seeded in a supersonic free-jet expansion. The hot ions or radicals were cooled in the expansion and probed downstream with an argon-ion pumped cw ring dye laser (1 MHz FWHM linewidth, 100-400 mW output power) seeded into an excimer pumped pulse amplifier (-100 MHz FWHM linewidth, 3-10 mJ/pulse output energy at 30 Hz rep. rate) which is synchronized to the photolysis laser. Sub-doppler LIF spectra were obtained by imaging the total fluorescence through optical slits which viewed a very narrow, central portion of the jet expansion. The experimental arrangement will be detailed and rotationally resolved spectra of C₆F₆⁺, C₆F₅H⁺ and C₆H₆ will be presented.

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Address of Foster: Department of Chemistry, Florida State University, Tallahassee, FL 32306.

ANALYSIS OF ROTATIONALLY RESOLVED SPECTRA OF THE 2A₂ → 2E₁ BAND OF CYCLOPENTADIENYL RADICAL

LIAN YU, STEPHEN C. FOSTER, JAMES M. WILLIAMSON, AND TERRY A. MILLER

Rotationally resolved LIF spectra of the 2A₂ → 2E₁ band (ν₀=29,572.166 cm⁻¹) of cyclopentadienyl radical (C₅H₆) were taken in a supersonic free-jet expansion. An effective Hamiltonian appropriate for C₅H₆ in 2E₁ vibronic state is constructed. A least square fit of the 0₀ band yields molecular constants for both lower and upper states. Intensity distributions of the spectra at different degrees of coldness are reproduced satisfactorily by an intensity simulation based on transition moments, nuclear spin statistics and variable rotational temperatures (0.6 - 10K). Strong (2,2) interactions observed in the vibrationless level of the 2E₁ state may indicate a large Jahn-Teller effect. The spin effects (spin-orbit and spin-rotation interactions) in C₅H₆ are also discussed.

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ROTATIONAL ANALYSIS OF THE A 2A ← X 2E TRANSITION OF CH₃O⁺ AND CH₃S⁻

XIANNING LIU, PRABHAKAR MISRA, STEPHEN C. FOSTER, CRISTINO P. DAMO, T.-Y. LIN, AND TERRY A. MILLER

Rotationally resolved spectra of both CH₃O⁺ and CH₃S⁻ 2A ← 2E transition have been obtained by both cw and pulsed supersonic free jet expansion and LIF techniques. Rotational spectra of the 0₀ and 3⅓ bands of CH₃O⁺ and 0₀ band of CH₃S⁻ are assigned. By joint nonlinear least-square fitting of both microwave and optical spectra, accurate 2E state rotational constants are obtained. In addition, the first accurate rotational constants for the excited A state are determined. A line strength calculation and intensity simulation demonstrate that the rotational spectra obtained with the pulsed jet can be approximately described by a Boltzmann distribution with temperature T = 25 K.

Address of Liu, Misra, Damo, Lin, and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210.
Address of Foster: Department of Chemistry, Florida State University, Tallahassee, FL 32306.
Fast ion beam laser spectroscopy has been used to study the $\tilde{X}^{2}\Sigma^{+} - \tilde{X}^{2}\Pi$ transition of $N_2O^+$ under high resolution. Molecular constants are obtained for several spin-vibronic states, including for the first time levels associated with the $\tilde{X}^{2}\Pi$, v=2 manifold. These data are interpreted in detail in terms of a large - amplitude bending Hamiltonian which allows for the effects of orbital angular momentum, spin - orbit coupling and vibrational anharmonicity.

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LASER SPECTROSCOPY OF ALKALINE EARTH MONOCARBOXYLATES AND MONOFORMAMIDE


The alkaline earth monocarboxylates and monoformamide were synthesised by the reaction of alkaline earth metal vapor with the corresponding carboxylic acids and formamide, respectively, in a Broida type oven. The laser excitation spectra and the resolved fluorescence spectra recorded at low resolution indicate that the carboxylate and formamide anions behave as bidentate ligands when bonding on to the metal ion. Therefore these metal containing free radicals can be represented by the structures $M^{+}O-C-R$ and $M^{+}N-C-R$ (M = Ca, Sr and R = H, CH$_3$). The electronic and vibrational information extracted from the spectra will be presented and discussed.

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THE ROTATIONAL ANALYSIS OF THE $\tilde{B}^2E - \tilde{X}^2A_1$ TRANSITION OF CALCIUM BOROHYDRIDE (CaBH$_4$)

A.M.R.P. BOPEGEDERA, F.S. PIANALTO, P.C. KELLER and P.F. BERNATH

The calcium borohydride molecule was synthesised in the gas phase by the reaction of calcium vapor with diborane ($B_2H_6$). The low resolution analysis performed in our laboratory suggests that CaBH$_4$ molecule is a symmetric top with $C_3v$ symmetry. The $A^2A_1 - A^2A_1$ and $\tilde{B}^2E - \tilde{X}^2A_1$ transitions were observed and some vibrational frequencies were obtained from these low resolution spectra.

A high resolution analysis of the $\tilde{B}^2E - \tilde{X}^2A_1$ transition was undertaken with the view of obtaining a better understanding of the geometry of CaBH$_4$. Two dye lasers were used to record these high resolution spectra: a broad band (1 cm$^{-1}$) dye laser to excite the $3P_{1/2}-1S_0$ atomic line of calcium (at 6573 Å) and a computer controlled Coherent 699-29 ring dye laser to excite the $\tilde{B}^2E - \tilde{X}^2A_1$ electronic transition of CaBH$_4$.

The excitation spectra of the $\tilde{B}^2E_{1/2} - \tilde{X}^2A_1$ and $\tilde{B}^2E_{3/2} - \tilde{X}^2A_1$ spin components were recorded by scanning the frequency of the ring laser over a wide region. Several bandheads separated from each other by a few wave numbers were observed in the excitation spectra of both spin components. The analysis of these band heads however proved to be complicated. To date, four of the band heads (three from the $\tilde{B}^2E_{1/2} - \tilde{X}^2A_1$ component and one from the $\tilde{B}^2E_{3/2} - \tilde{X}^2A_1$ component) have been investigated. The spectra resemble those of a symmetric top molecule. However, our initial attempts to fit the rotational line positions of the individual sub-bands to a $2\Pi-2\Sigma^+$ Hamiltonion were not successful. These initial fits indicate that the electronic states of CaBH$_4$ are strongly perturbed. The origin or the nature of these perturbations, however, have not yet been ascertained. This project is under investigation and the results will be presented at the conference.

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STIMULATED EMISSION POLARIZATION SPECTROSCOPY

D. Frye, H. T. Liou and H. L. Dai

A polarization detection method was demonstrated for Stimulated Emission Spectroscopy (SES) in the study of the vibration-rotation levels of \( \text{X}^1\text{A}_g \) glyoxal. The polarization methods allowed detection of a stimulated emission signal as small as \( 10^{-9} \) of the stimulating laser intensity, while the laser pulses had \( \pm 10\% \) fluctuation in intensity. Analysis of the intensity and the polarization of the stimulating photons unambiguously showed that the observed spectral lines resulted from a stimulated emission process.

The vibrational term value of the \( v_2 = 2 \) CO stretch level was measured to be \( 3473.24(0.2) \) cm\(^{-1}\), and the vibrational constants for the \( v_2 \) mode were determined as \( \omega_2 = 1745.8(5) \) cm\(^{-1}\) and \( \chi_{22} = -4.6(5) \) cm\(^{-1}\). It was observed that the \( K_a = 0 \) rotational levels are perturbed by an \( a \)-axis Coriolis coupling. Only the \( B \) and \( C \) rotational constants are accurately determined as \( 0.1584(8) \) and \( 0.1500(10) \) cm\(^{-1}\). It was observed that the \( K_a : 0 \) rotational levels are perturbed by an \( a \)-axis Coriolis coupling.

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VIBRATION-ROTATION SPECTROSCOPY BY STIMULATED EMISSION PUMPING IN A SUPersonic beam: \( a \)-AXIS CORIOLIS COUPLED \( v_4=1 \) and \( v_8=1 \) LEVELS OF \( \text{X}^1\text{A}_g \text{glyoxal} \)

D. Frye, L. Lapierre, and H. L. Dai

Rotational cooling in a supersonic expansion combined with the rotational-level selection in stimulated emission pumping allowed vibrational levels of medium-size molecules to be studied with single rotational-level resolution and selectivity. We have shown that the vibration-rotation spectra of \( \text{X}^1\text{A}_g \) glyoxal can be obtained at sub-mTorr pressure and 0.04 cm\(^{-1}\) resolution.

As a demonstration, the \( v_4=1 \) C-C stretch and \( v_8=1 \) CH wag levels were studied. The vibrational term values were determined as 1065.78 and 1048.08 cm\(^{-1}\), respectively. The greatly reduced rotational congestion in the spectra makes the assignment straightforward. In addition to the determination of their rotational constants, it was found that the two vibrational levels are strongly coupled to each other through an \( a \)-axis Coriolis coupling.

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SELECTIVE EXCITATION AND SPECTROSCOPY OF HIGH VIBRATIONAL LEVELS OF \( \tilde{a}^1\text{A}_1 \text{CH}_2 \)

BY STIMULATED EMISSION PUMPING

W. Xie, A. Ritter, and H. L. Dai

Using stimulated emission pumping with two laser pulses, we have shown that high vibrational levels of a short-lived radical can be studied, and a large population can be prepared at a single, selected, high vibration-rotation level. The first demonstration was performed on the \( v_2=3 \) level of \( \tilde{a}^1\text{A}_1 \text{CH}_2 \).

The methylene radical was produced by photolysis of the ketene molecule. The pump laser pulse excites the \( b \rightarrow \tilde{a}^1\text{A}_1 \) transition and the dump laser stimulates emission through the \( \tilde{a} \rightarrow b, 2\tilde{a}^1 \) transitions.

In addition to the determination of molecular constants, the double-resonance technique will enable us to determine whether the singlet-triplet coupling that prevails in the \( \tilde{a} \leftrightarrow b \) transitions originates in the \( \tilde{a} \) or \( b \) state. The double minima in the bending potential can also be characterized.

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VAN DER WAALS VIBRATIONAL LEVELS OF THE GLYOXAL($X^1A_g$)-Ar COMPLEX OBSERVED BY STIMULATED EMISSION SPECTROSCOPY

D. Frye, P. Arias and H. L. Dai

Vibrational levels in the van der Waals intermolecular potential of the glyoxal($X^1A_g$)-Ar complex were directly observed by stimulated emission spectroscopy. These van der Waals vibrational levels can be assigned to the fundamental and overtone levels of the Ar-glyoxal stretching and the two bending modes. These van der Waals vibrational levels will allow us to model the intermolecular potential with previously unattainable accuracy.

The stimulated emission spectroscopy may also be used to study all the vibrational levels in the X state with nonvanishing Franck-Condon factors from the electronic excited state with 0.04 cm$^{-1}$ resolution. The width of single rotational lines of three glyoxal vibrational levels were determined to be ~0.2 cm$^{-1}$ for the 4, and 8, levels and <0.04 cm$^{-1}$ for the 5, level. These widths arise from vibrational predissociation of the complex.

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VIBRATIONAL STUDIES OF ELECTRONICALLY EXCITED STATES BY FLUORESCENCE EXCITATION IN A SUPersonic jet

M. Huang, C. M. Cheatham, J. Laane

A Nd:YAG laser is combined with a harmonic generator, pulsed dye laser and wavelength extender to produce a tunable output beam from 217 to 690 nm. The sample is passed through a pulsed valve into a vacuum chamber to form a supersonic jet which intersects the laser. The emitted fluorescence is collected using an ellipsoidal mirror and focused onto a photomultiplier tube. A computer is used to control the stepping of the laser frequency and the data collection from the boxcar which integrates the pulsed fluorescence signal.

In a supersonic jet, the excitation transitions originate almost exclusively from the vibrational ground state, thus simplifying the analysis. The high resolution of the laser allows us to tune through the rovibrational states to determine the vibrational potential energy surface in the electronic excited state. In preliminary work, we have recorded the fluorescence excitation spectrum of iodine and found a vibrational temperature of less than 50 K. Current work is underway on molecules with conformationally significant vibrations in the electronic excited state.

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CURVE FITTING MODEL FOR FOURIER TRANSFORM INFRARED SPECTROSCOPY
H.-H. NAM and G. E. LEROI

While dispersive infrared spectrophotometers are being replaced by more powerful Fourier transform spectrometers, many methods of data manipulation (e.g., derivative, area integration, curve fitting) and their interpretation are being accomplished without proper attention being paid to the attendant differences in data collection. Although it is well understood that the band shapes of FTIR spectra are altered by the use of apodization functions, no quantitative studies of these effects have been reported.

We will discuss the alteration of the Lorentzian line shape when it is convoluted with the widely-used instrumental line shape functions. It will be shown that the experimental band shape depends on the resolution of a spectrum, the half-width and the choice of apodization function. Quantitative criteria for the curve fitting of Fourier transformed infrared spectra will be suggested, based on an analytical formula, and demonstrated by synthetic and real spectra. These guidelines are particularly important when curve fitting is to be used to extract area ratios between overlapped peaks.

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THE INERTIAL DEFECTS OF VIBRATIONALLY EXCITED ORTHO-RHOMBIC MOLECULES AS SOURCE FOR INFORMATION ON HARMONIC FORCE FIELDS: CALCULATIONS ON 1,1 DI-FLUOROETHYLENE
Dinese CHRISTEN and Otto L. STIEFVATER

It is well known that the inertial defect of planar molecules is a (weak) function of the harmonic force field only. For non-planar molecules there is no such relationship, but for ortho-rhombic molecules (planar or non-planar), the harmonic contribution to the inertial tensor of vibrationally excited states are all diagonal, and the first inertial derivatives, \( a_i^* \) (proportional to the anharmonic contributions) only posses diagonal elements different from zero in the totally symmetric states (where all off-diagonal elements are zero) and at most one off diagonal contribution in each non totally symmetric state (where diagonal contributions are zero). Thus for vibrationally excited, non totally symmetric states, the difference between the inertial defect in an excited and the ground state, is purely harmonic. The data from the rotational spectra of 18 different excited states of 1,1 Difluoroethylene will be used in a recalculation of the harmonic force field.

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LOW FREQUENCY VIBRATIONAL SPECTRA AND TWO-DIMENSIONAL VIBRATIONAL POTENTIAL ENERGY SURFACES OF SILACYCLOPENTANE AND 1,3-DISILACYCLOPENTANE

L. F. COLEGROVE, J. C. WELLS, and J. LAANE

The far-infrared spectrum of silacyclopentane-1-d₁, h₂, has been recorded and used along with the infrared and Raman data for the d₀ and d₂ molecules to determine the two-dimensional vibrational potential energy surface in terms of the ring-bending and ring-twisting coordinates. Appropriate kinetic energy expansions were calculated for each vibration and each isotopic species. 1,3-Disilacyclopentane has been synthesized and its far-infrared spectrum has been recorded. The analysis of the data for this molecule and the 1,1,3,3-d₄ species in terms of a two-dimensional surface is underway.

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PSEUDOROTATIONAL POTENTIAL FUNCTIONS AND ENERGY LEVELS FOR SPIRO COMPOUNDS

M. B. KELLY and J. LAANE

Spiro compounds containing two identical joined rings which can undergo ring-puckering vibrations are expected to have two-dimensional potential energy surfaces of the form

\[ V = a(x₁^4 + x₂^4) + b(x₁^2 + x₂^2) + cx₁x₂ \]

where \( x₁ \) and \( x₂ \) represent the ring-puckering of the individual rings and where \( a, b, \) and \( c \) are the potential constants. When the value of the interaction constant \( c \) approaches twice the value of the quartic constant \( a \), the potential function and the energy levels approach those of a free pseudorotor. The calculations are such systems will be discussed.

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INTERNAL ROTATION OF CYCLOPROPYLGERMANE AND CYCLOPROPYLSILANE-d₃

M. B. KELLY, M. DAKKOURI, and J. LAANE

The mid-infrared combination band spectra resulting from the internal rotation of the GeH₃ group of cyclopropylgermane and the SiD₃ group of cyclopropylsilane-d₃ have been recorded in the Ge-H and Si-D stretching regions, respectively. The barrier to internal rotation of 650 cm⁻¹ determined for the deuterated silane agrees well with the value for the undeuterated species and is higher than might be expected based on data for silylalkanes. This reflects an apparent interaction between the cyclopropyl ring and the silicon atom. The barrier of 455 cm⁻¹ determined for the cyclopropylgermane is similar to values previously determined for other organogermes.


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ASYMMETRIC TOP CONTOUR SIMULATION AND VIBRATIONAL SPECTRA OF ISOPROPYL FORMATE

R. S. LEE, J. LA'ANE, and B. J. VAN DER Veken

Isopropyl formate and four isotopically deuterated derivatives have been synthesized. The vapor, liquid, and solid (amorphous and crystalline) infrared (25-10000 cm\(^{-1}\)) and Raman (10-4000 cm\(^{-1}\)) spectra have been recorded and interpreted for all five compounds with attention given to the presence of one or more conformers. Low temperature mid-infrared polarization experiments were used to facilitate assignments of various bonds. Previous investigations have suggested that the dominant conformer has a structure in which the COCH torsional angle is approximately 40°. Using asymmetric top theory, the vapor phase contours for the carbonyl stretch of the d\(_3\) compound and the isolated isopropyl C-H stretch of the d\(_4\) compound were simulated. These contours were compared to experiment in order to determine the identity of the conformers present in the vapor phase.

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APPLICATIONS OF MOLECULAR MECHANICS TO THE CONFORMATIONAL ANALYSIS OF RING MOLECULES

R. S. LEE, C. COOPER, and J. LA'ANE

Molecular mechanics (MM2) methods have been used to predict the structures and to calculate the barriers to planarity and pseudorotation for twenty-three small ring molecules and eight bicyclic molecules. In the case of four- and pseudo-four membered rings (five membered rings with a double bond), molecular mechanics does reasonably well in predicting barriers to planarity. For five-membered rings with pseudorotation, molecular mechanics correctly predicts the preferred equilibrium conformation (C\(_1\), C\(_2\), or planar) and also does reasonably well in predicting the barriers to planarity and pseudorotation. Potential functions and geometries were also calculated for the bicyclo[3.1.0]hexanes and bicyclo[3.2.0]hepta-6-enes as well as for indan and phthalan.

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VIBRATIONAL SPECTROSCOPY AND POTENTIAL ENERGY SURFACES FOR THE OUT-OF-PLANE MOTIONS OF CYCLOHEXENE AND SOME ANALOGUES

J. LA'ANE, V. E. RIVERA-GAINES, and M. M. TECKLENBURG

Cyclohexene, three of its deuterated derivatives, silacyclohex-2-ene, and 5,6-dihydrothiopyran have been synthesized and the far-infrared and Raman spectra have been recorded. A series of bands assigned as the ring-bending (20-180 cm\(^{-1}\)), ring-twisting (230-300 cm\(^{-1}\)), and combinations (80-120 cm\(^{-1}\)) were observed for each molecule. Expressions for calculating the kinetic energy expansions for the bending and twisting vibrations of the six-membered rings were developed. Molecular mechanics calculations were used to make initial estimates for the barriers to conformational interconversion. A two-dimensional analysis for the ring-bending and ring-twisting modes was carried out and the potential energy surface for each molecule was calculated. The twisted (half-chair) conformation was found to be the lowest in energy in each case with a barrier to planarity of approximately 3000 cm\(^{-1}\).

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THE OVERTONE SPECTROSCOPY OF HYDROGEN PEROXIDE ON A MOLECULAR BEAM
C. DOUKETIS AND J.P. REILLY

The 4 - 0 stretching overtone region of $\text{H}_2\text{O}_2$ is investigated via Doppler limited photoacoustic spectroscopy in the bulk gas and also by high resolution (5 MHz) molecular beam spectroscopy. The latter is done using a frequency stabilized ring dye laser that is injected into a high finesse Fabry-Perot cavity that flanks the molecular beam. Vibrational excitation imparted to the beam is detected with a liquid helium cooled bolometer. More than 130 isolated transitions are observed on the molecular beam leading to a full analysis of the overtone transition.

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THE FUNDAMENTAL AND OVERTONE SPECTROSCOPY OF PYRROLE IN THE BULK GAS AND IN A MOLECULAR BEAM
C. DOUKETIS AND J.P. REILLY

The N-H stretching fundamental in the heterocyclic molecule pyrrole ($\text{C}_4\text{H}_4\text{NH}$) is examined at high resolution (1 MHz) on a molecular beam. The molecular beam passes across a laser beam from a single frequency color center laser and the vibrational energy that is imparted is detected with a low temperature bolometer. Fully resolved molecular beam spectra are compared with Doppler limited room temperature results and with theoretical simulations. Applications of this method to large molecule infrared spectroscopy are discussed. In the bulk gas the 4 - 0 overtone is observed but it has not been detected on the molecular beam. Some reasons for this surprising result are proposed.

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TI3. (2:04)

OBSERVATION OF A NEW RO-VIBRONIC BAND OF OOH FREE RADICAL GENERATED FROM $\text{H}_2\text{O}_2$ DECOMPOSITION ON GLASS SURFACES

C. DOUKETIS AND J.P. REILLY

A new ro-vibronic band of OOH free radical near 760 nm has been detected using intracavity photoacoustic spectroscopy. The transition is believed to populate a highly vibrationally excited level in the $^2A'$ electronic manifold. A computer simulation of the rotational structure unambiguously assigns the spectrum. Suggestions are made as to the way in which OOH is formed. It is found that the free radical is completely absent in the presence of oxygen in spite of the fact that a reaction between OOH and $\text{O}_2$ is not known.

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TI4. (2:21)

Velocity Slip in Ultra-cold Molecular Beams

James M. Wilkinson, Clayton F. Giese, and W. Ronald Gentry

Recent experiments$^1$ performed in this laboratory have shown that submillikelvin translational temperatures are accessible in a pure helium expansion. Since the experimental apparatus is somewhat unique an overview of the apparatus will be presented along with the results of an experiment to measure the velocity slip of noble gasses mixed with helium. If the velocity slip goes to zero in the limit of infinitive dilution then a method for testing the Wigner Threshold Laws$^2$ might become available.


$^2$E. P. Wigner, Phys. Rev. 73, 1002 (1948)

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\textbf{A-DOUBLING TRANSITIONS OF METAL OXIDES MEASURED BY MODR: CUO}

T.C. Steimle, W.-L. Chang and D.F. Nachman

The sensitivity of the microwave-optical double resonance (MODR) technique has made it possible to record the spectra of transient chemical compounds in both their ground and excited electronic states. Although the majority of the measured microwave (or rf) transitions involve strong electric dipole allowed transitions between rotational levels, both magnetic dipole allowed and weakly electric dipole allowed A-doubling transitions have been recorded.

A previous limitation in applying the technique to molecules produced in high temperature environments has been designing an effective method of simultaneously introducing the laser and low frequency microwave or rf radiation. This limitation precluded measuring A-doubling transitions in many metal containing compounds.

Here we report on a method for measuring the low frequency transitions by MODR using a tri-plate transmission line for the introduction of the rf radiation. The $X^2\Pi_{1/2}$ (J=1.5) A-doublet transition of gas-phase copper monoxide, CuO, has been recorded. The measured transition frequencies were merged with previous rotational transition measurements\(^1\) and an improved set of spectroscopic parameters were obtained. The results of these experiments will be discussed.

\begin{itemize}
\end{itemize}

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\textbf{ELECTRONIC PROPERTIES OF GAS-PHASE COPPER MONOSULFIDE}

T.C. Steimle, W.-L. Chang and D.F. Nachman

Numerous branch features in the $A^2\Sigma(v=0)-X^2\Pi(v=0,1)$ band systems of gas-phase copper monosulfide, CuS, have been investigated at sub-doppler resolution using the technique of intermodulated fluorescence. A line width of < 50MHz (FWHM) has been achieved and at this resolution the magnetic hyperfine splittings of the optical branch features resulting from the $^6\text{Cu}(I=3/2)$ nuclear spin are observed.

The high resolution spectra has been analyzed using an effective hamiltonian approach and the magnetic hyperfine parameters have been interpreted in terms of possible electronic configurations for the $A^2\Sigma$ and $X^2\Pi$ states. A comparison to the results of the sub-doppler measurements of the analogous states in CuO\(^1\) and the doppler limited results for CuS\(^2\) has been made. Attempts have been made to measure the permanent electric dipole moment of the $X^2\Pi$ state. The results of these experiments will be discussed.

\begin{itemize}
  \item \textsuperscript{1} T.C. Steimle and Y. Azuma, \textit{J. Mol. Spectrosc.} \textbf{118}, 237 (1986).
  \item \textsuperscript{2} F. David, M. Douay and Y. Lefebvre, \textit{J. Mol. Spectrosc.} \textbf{112}, 115 (1985).
\end{itemize}

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\textbf{INFRARED SPECTROSCOPY IN SLIT SUPersonic EXPANSIONS}

C. M. LOVEJOY, A. MCIROY, AND D. J. NESBITT

A 50 cm absorption pathlength, 60 MHz sub-Doppler linewidths, 5 K rotational temperatures, $10^{17}$/cm$^3$ number density, and detection limits of $5 \times 10^7$ molecules/cm$^3$/quantum state for direct absorption: these are the advantages of spectroscopy in a slit supersonic expansion. A system is described which includes a 200-1000 $\mu$s duration, 60 Hz repetition rate pulsed valve with a 4 cm long by 75 $\mu$m wide slit nozzle and multipass optics. Examples are presented from the near-IR (2-4 $\mu$m) spectra of hydrocarbons and van der Waals complexes.

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EXTENDED INFRARED STUDY OF ArHF

C. M. Lovejoy AND D. J. NESBITT

Recent improvements in sensitivity have permitted us to extend previous\(^1,2\) infrared studies of A:HF to encompass all of the low-frequency (\(\leq 75\ \text{cm}^{-1}\)) bending and stretching vibrations of the excited HF(\(v=1\)) potential surface. Accurate vibrational term values, and rotational and centrifugal distortion constants are now known for the ground state (0000), the van der Waals stretch (0001), the HF stretch (1000), and combinations of the HF stretch with the van der Waals stretch (1001), the \(\Sigma\) bend (1200), the \(\Pi\) bend (1110), and the van der Waals stretch overtone (1012), listed in order of increasing energy.


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J-DEPENDENT VIBRATIONAL PREDISSOCIATION IN NeHF

C. M. LOVEJOY AND D. J. NESBITT

The weakly bound complex NeHF is observed for the first time. Infrared absorption spectra are obtained and analyzed for the HF stretching fundamental and for the \(\Pi\) bend combination band. The combination band is approximately an order of magnitude more intense than the fundamental, signalling nearly free internal rotation of the HF subunit within the complex. There are three bending states which correlate with \(j=1\) HF rotation in the free molecule limit; the three states have widely different rotational predissociation rates. Predissociation of the \(\Pi^1\) levels of the perpendicular bend is symmetry forbidden at these vibrational energies, and indeed the \(Q\) branch transitions which access those states exhibit lifetimes of \(\geq 25\ \text{nsec}\), i.e. in excess of the instrument resolution. In contrast, \(J\)-dependent lifetime broadening is observed for the \(P\) and \(R\) branch transitions which access the \(\Pi^0\) levels of the perpendicular bend; predissociation lifetimes range from 2.7 nsec for \(J'=1\) to 0.3 nsec for \(J'=5\). This is discussed in terms of Coriolis mixing of the \(\Pi^0\) levels with the \(\Sigma\) bend, which is not directly observed but which is inferred to have a predissociation lifetime of \(\leq 8\ \text{psec}\). Scattering calculations\(^1\) on a recently obtained \textit{ab initio} potential energy surface\(^2\) predict the observed results nearly quantitatively.

\(^1\)D. C. Clary, S. V. O'Neill, C. M. Lovejoy, and D. J. Nesbitt, to be published.

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THE ROTATIONAL RKR METHOD

DAVID J. NESBITT AND MARK S. CHILD

In the rapidly growing field of high resolution infrared spectroscopy of van der Waals complexes, one often obtains a wealth of rotational information for a single vibrational state. A new RKR based method is described for extracting one dimensional potentials via inversion of high precision data on rotational energy levels alone. This method proves remarkably successful at quantitatively reproducing intermolecular potentials from rotational data for i) weakly bound (e.g. model van der Waals complexes) and ii) strongly bound (e.g. v=0 rotational levels of H2O+ molecules).


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AN INTERMOLECULAR POTENTIAL SURFACE FOR Ar + HF(v=1) FROM HIGH RESOLUTION INFRARED MEASUREMENTS

DAVID J. NESBITT, CHRISTOPHER M. LOVEJOY AND MARK S. CHILD

High resolution infrared data obtained for three vibrational bands in ArHF complexes (the HF fundamental, and combinations with both parallel and perpendicular HF bends) provide detailed rotational data for each of three different bending states of the internal HF(v=1) rotor. We describe a straightforward and accurate extension of the rotational RKR method to invert these data and obtain the potential energy surface for Ar + HF(v=1) as a function of R (Ar-HF internuclear separation) and θ (HF bend angle). The accuracy of this surface is tested by full close coupling calculations, and comparison with experimentally observed rovibrational eigenvalues.


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ABSORPTION INTENSITIES FOR OH X2s (v=1+0)

ABRAHAM SCHIFFMAN, DAVID D. NELSON, AND DAVID J. NESBITT

The OH radical is of keen interest in many processes, including combustion, participation in atmospheric chemistry, and contribution to the infrared night glow. Knowledge of infrared transition moments allows the possibility of determining stratospheric OH concentrations from the strong "Meinel bands" emitted by OH. We have measured integrated line strengths for rotational lines in OH X2s (v=1+0) via infrared laser light absorption. The OH radicals were produced by photolysis of HNO3 with a 193 nm excimer laser; the transient species were probed with a single frequency, continuously tunable, stabilized color center laser. The absorptions were monitored as functions of time to determine peak cross sections, and of frequency to obtain the integrated line strengths.

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VIBRATIONAL MIXING AT THE C-H STRETCH EXCITED LEVEL IN SMALL HYDROCARBONS

A. McILROY AND D. J. NESBITT

C-H stretch infrared spectra of selected hydrocarbons containing from one to six carbons have been recorded in a slit supersonic expansion with a difference frequency laser spectrometer. Rotational temperatures of 5 K and sub-Doppler linewidths of 0.0013 cm⁻¹ were observed for small hydrocarbons such as methane, ethane, and cyclopropane. For larger hydrocarbons, particularly linear chains with low frequency bending and torsion modes, the spectra are qualitatively different as a result of intramolecular coupling of rovibrational levels. Despite the extremely low rotational and vibrational temperatures, excess spectral structure is observed as a function of molecular complexity and state density that varies systematically from isolated perturbations to complete loss of resolvable structure. Analysis of the spectra provides information on the number of strongly mixed vibrational levels as well as estimates of the coupling strengths.

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FOURIER TRANSFORM (INTERFEROMETRIC) NONLINEAR SPECTROSCOPIES

PETER M. FELKER

Results that demonstrate interferometric versions\(^1,2\) of coherent Raman spectroscopy\(^3\) and stimulated emission pumping spectroscopy\(^4\) are presented.

The achievement of high spectral resolution in nonlinear spectroscopies can place stringent demands on laser light sources. When spectral resolution in a nonlinear spectroscopic experiment depends on excitation source bandwidths, one must have the capability of producing narrow bandwidth light with sufficient intensity to drive the nonlinear process of interest. This can lead to significant complexity in performing an experiment. Nonlinear interferometric techniques, analogs to linear interferometric methods such as Fourier transform infrared absorption spectroscopy, obviate the need for narrow bandwidth excitation light in high resolution experiments. Thus, the techniques allow the use of relatively easy-to-use, "broad-band", high power lasers in such experiments.

This talk will encompass the following: (1) an outline of the principles of nonlinear interferometric techniques, (2) a presentation of experimental results on jet-cooled and gaseous samples that show the high resolution capabilities of such techniques, and (3) a discussion of the advantageous features of the interferometric methods.

\(^3\)See, for example, M. D. Levenson, *Introduction to Nonlinear Laser Spectroscopy* (Academic, New York, 1982).

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FTIR Studies of Wood Chemistry

W. B. Banks and H. West

We are using FTIR methods to help distinguish between different types of wood, and to follow chemical changes that occur in the wood polymers. Using diffuse reflectance techniques on solid wood samples, "hard" and "soft" timbers may be distinguished quickly and conveniently. We have also studied reactions of reagents such as alkyl isocyanates which impart a permanently bonded hydrophobic layer onto the wood surface. From our FTIR studies carried out on thin slivers of scots pine, we were able to deduce a reaction profile for the scheme:

\[
\begin{array}{c}
O \\
\mid \\
R-NCO + H-O-Wood \rightarrow R-N-C-O-Wood \\
\mid \\
H
\end{array}
\]

and consequently distinguish between surface and bulk reaction. The formation of an allophanate upon extensive reaction of the isocyanate can also be detected from the spectra. I.R. work on the powdered samples of isolated lignin and holo-cellulose show that the rate and extent of reaction with isocyanate is different for the two components.

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Address of Banks & West: Wood Science Department, University College of North Wales, Bangor, U.K.
BEND-STRETCH INTERACTIONS IN THE CH OVERTONE SPECTRUM OF ACETYLENE
BRIAN C. SMITH AND JOHN S. WINN

High resolution FTIR spectra of C2H2 have been obtained from 1800 to 12,000 cm\(^{-1}\). Over 1600 rovibrational transitions belonging to 30 vibrational bands were assigned and analyzed yielding band origins and rotational constants. Band centers were used to calculate various stretch/stretch and bend/stretch anharmonic coupling constants. Several resonances of the type between \(v_3\) and \((v_2 + v_4 + v_5)\) were analyzed, and an unperturbed value of \(v_3\) was determined. This was combined with other data to obtain \(a_{mn}\), \(x_m\), and \(\lambda\) in the local mode basis. \(X\), \(k\) relations were imposed to yield the normal mode constants for \(v_1\) and \(v_3\). Treatment of Darling-Dennison resonances in the first two overtone manifolds led to reassignments of previously reported spectra and to the discovery of a Fermi resonance involving overtones of \(v_3\) and states containing \(v_1\), \(v_2\), and \(2v_4\). Calculated rotational constants and intensity data confirm the assignments and interactions treated in the vibrational analysis. Treatment of these resonances significantly improves the agreement between calculated and observed transition wavenumbers, providing a coherent picture of acetylene C–H stretch dynamics below 12 000 cm\(^{-1}\).

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ANALYSIS OF WEAKER BANDS OF ACETYLENE IN THE 11 \(\mu\)m REGION
M. HERMAN, T.R. HUET and M. VERVLOET

The absorption spectrum of C2H2 was recorded in the 11 \(\mu\)m region with a Fourier Transform Spectrometer at a resolution of 0.01 cm\(^{-1}\). In addition to the bands already analyzed in the literature(1), a few weaker bands are observed. Preliminary results concerning the rovibrational analysis and intensity studies will be reported.


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SPECTROSCOPIC CONSTANTS OF CO2 DERIVED FROM THE \(v_3\) SPECTRAL REGION
D. CHRIS BENNER, V. MALATHY DEVI, GUY GUELAVHILI AND NARAHARI RAO

Spectroscopic constants for carbon dioxide have been derived from molecular constants obtained from our analysis of over 30 bands of CO2 in the 1500 cm\(^{-1}\) spectral region. The experimental data were obtained with both a high information Fourier transform spectrometer and a tunable diode laser spectrometer system. The tunable diode laser spectra included several scans with a \(^{13}C\)-enriched sample in addition to those obtained with a natural sample. The results obtained will be compared with previously published values.

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Address of Guelachvili: Laboratoire d'Infrarouge, Université de Paris-Sud, Associé a CNRS, Gif-sur-Yvette, France.
Address of Narahari Rao: Department of Physics, Ohio State University, 174 W. 18th Avenue, Columbus, OH 43210.
INFRARED DIODE LASER SPECTROSCOPY OF NaCl

H. UEHARA, K. HORIAI, K. NAKAGAWA, T. KONNO, AND T. FUJIMOTO

A heat-pipe high temperature cell was incorporated into an optical system of a tunable diode laser spectrometer which covered an infrared range of 350-800 cm\(^{-1}\). The heat-pipe cell was made of an alumina tube and was similar in construction to that used by Maki et al.\(^1\) Vibration-rotation spectrum of NaCl was observed in the gas phase under temperatures of 1153-1223 K. The spectral lines in the region of 365-390 cm\(^{-1}\) were measured. The analysis of the \(v=1-0, 2-1, 3-2,\) and \(4-3\) bands of Na\(^{35}\)Cl has yielded accurate values of \(-e, -e\epsilon_x,\) and \(-e\epsilon_y,\) the former two of which are in excellent agreement with those derived in a millimeter-wave molecular-beam study.\(^2\)

Under the high temperature, a small amount of H\(_2\)O which could not be removed from the sample gas reacted with NaCl to have yielded the spectrum of NaOH. Some results of the spectra of NaOH and a related molecule of LiOH will be shown.


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INFRARED SPECTRUM OF THE \(v_3\) BAND OF C\(_2\)H\(_4\) AND ISOTOPIC SPECIES

M.-F. JAGOD, B. D. REHFUSS, M. W. CROFTON, F. SCAPPINI, and T. OKA

We have extended up to \(J=24\) the assignment of the \(v_3\) fundamental vibration-rotation band of C\(_2\)H\(_4\)\(^{13}\) reported last year.\(^1\)\(^2\) Because the upper state is severely perturbed above \(J=10,\) the assignment was completed by \(P-R\) combination-differences and chemical discrimination from other hydrocarbon species. We have also assigned the \(v_3\) band of \(^{13}\)C\(_2\)H\(_4\). These ions were observed using a difference frequency spectrometer and detected by velocity modulation. Both ions were produced in a water-cooled AC glow discharge with a gas mixture of He: H\(_2\): C\(_2\)H\(_2\)/\(^{13}\)C\(_2\)H\(_2\) or in a liquid nitrogen-cooled discharge of He: CH\(_4\)/\(^{13}\)CH\(_4\) (700:20:1) with a total pressure of \(\approx 6\) torr. Our attempt to observe HCCD\(^+\) is in progress.


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Address of Crofton: Lawrence Livermore National Laboratory, Livermore, California 95440.
Address of Scappini: Istituto di Spettroscopia Molecolare del C.N.R., Bologna, Italy.
ASYMMETRIC STRETCHING BAND OF BRIDGED PROTONATED ACETYLENE

M. W. CROFTON, M.-F. JAGOD, B. D. REHFUSS, and T. OKA

The study of the enigmatic infrared spectrum of protonated acetylene \( \text{C}_2\text{H}_2^+ \) which has occupied us for the last three years has come to a plateau and the results are summarized. About 80 \( R \)-branch and \( P \)-branch lines have been assigned. The general asymmetric rotor pattern of a parallel band with intensity alternation for the \( K=1 \) \( K \)-doublets shows that the spectrum is due to \( \text{C}_2\text{H}_2^+ \) with the non-classical bridged structure. The absence of other C-H stretching vibrations also supports this conclusion. Combination differences for the ground state fit well to the asymmetric rotor pattern with the standard deviation of 0.0084 cm\(^{-1}\). The following rotational constants have been obtained:

\[
B = 1.1422(5) \text{ cm}^{-1}, \quad C = 1.0467(4) \text{ cm}^{-1}.
\]

These rotational constants agree well with those predicted from \textit{ab initio} calculations.\(^1\) The anomaly of the spectrum is in high \( J,K \) levels and in the excited state. Attempts have been made to find out whether or not this anomaly is caused by proton tunnelling via the non-classical structure. This tunnelling changes the two proton problem of the rigid model to a three proton problem\(^4\) and thus changes the spin statistical ratio of 3:1 to 4:2. These problems and our study of the \( ^{13}\text{C} \) species will be discussed.


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OBSERVATION OF HOT BANDS OF \( \text{H}_2^+ \) USING AN EXTENDED DIFFERENCE FREQUENCY SPECTROSCOPE

M. G. BAWENDI*, B. D. REHFUSS, and T. OKA

We have extended the range of our difference frequency spectrometer from the previous range of 4200 - 2300 cm\(^{-1}\) to 5400 - 1850 cm\(^{-1}\) by using an angle-tuned LiIO\(_3\) rather than the temperature-tuned LiNbO\(_3\) as the non-linear optical mixing element. Although the infrared conversion efficiency is much lower for LiIO\(_3\) than for LiNbO\(_3\), we have found this extended coverage to be useful in our search for the hot bands of \( \text{H}_2^+ \). We have observed many transitions of \( \text{H}_2^+ \) not assignable to the \( \nu_1 = 0 \) fundamental band using a liquid nitrogen cooled AC discharge with 600 mTorr \( \text{H}_2 \) and 7 Torr He. Many of the lines have been assigned to the \( 2\nu_2, \ell=2 \rightarrow \nu_2, \ell=1 \) band based on the recent calculation of Miller and Tennison\(^2\). We expect most of the remaining lines to belong to the \( 2\nu_2, \ell=0 \rightarrow \nu_2, \ell=1 \) and \( \nu_1 + \nu_2 \rightarrow \nu_1 \) hot bands.

\(^2\) S. Miller and J. Tennison, \textit{J. Mol. Spectrosc.}, 126, 183 (1987), and private communication.

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IS THE DISSOCIATIVE RECOMBINATION OF $H_2^+$ REALLY SLOW? A NEW SPECTROSCOPIC MEASUREMENT OF THE RATE CONSTANT

T. AMANO

The dissociative recombination rate constant of positive ions with electrons have been measured to be of the order of $10^{-6}$ to $10^{-7}$ cm$^3$s$^{-1}$ for most positive molecular ions. These rates are important in model calculations of the interstellar chemical evolution. $H_2^+$ in particular occupies a key role. The dissociative recombination rate constant of $H_2^+$ was measured to be $(2.9\pm0.3)\times10^{-7}$ cm$^3$s$^{-1}$ at 205 K by using the stationary afterglow method. Also the recombination cross sections were measured by using several other techniques such as the inclined beam, the merged beam, and the ion-trap techniques. All the cross sections and the rate constants obtained by the various techniques referred to above are reasonably consistent.

Adams and Smith on the other hand obtained a much smaller value for the rate constant ($\approx 10^{-11}$ cm$^3$s$^{-1}$) by using the flowing afterglow/Langmuir probe (FALP) technique. A theoretical calculation also suggested a small rate constant. Also very recently Hus et al. repeated the merged beam experiments and obtained the smaller cross section by an order of magnitude than the previous values. These authors attributed the faster rate constants previously obtained to vibrationally excited $H_2^+$.

Considering the astrophysical impact of these low values, we have carried out direct measurements of the decay of the infrared absorption signals of $H_2^+$, which can monitor the ion abundance in a particular vibration-rotation state without ambiguity as a function of time. The decay curve was analyzed and found to fit very well to the form expected for a recombination decay. The signal decay is attributed to the dissociative recombination with electrons and the rate constant was determined to be $(1.8\pm1.0)\times10^{-7}$ cm$^3$s$^{-1}$, which disagrees with the recent values.

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A SEARCH FOR THE C-H (BRIDGE) STRETCH VIBRATION-ROTATION BAND OF $C_2H_3^+$

T. AMANO, N. Moazzzen-Ahmadi, and A. R. W. McKellar

Oka and coworkers have detected $C_2H_3^+$ by high-resolution infrared spectroscopy around 3 cm$^{-1}$; their preliminary analysis suggested that the species detected is the non-classical (bridged) form. We are endeavouring to observe the perpendicular C-H (bridge) stretch band ($\nu_2$) of non-classical $C_2H_3^+$ around 5 cm$^{-1}$.

An initial search was made in 2020-2030 cm$^{-1}$ region with diode lasers and a cooled hollow cathode discharge in a mixture of $C_2H_2$ and $H_2$. Several series of lines were detected. Although the assignment is not definitive, the species detected in this search is tentatively identified as $C_2H_3^+$ on the basis of the observed chemistry and the line spacings.

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The tunable FIR-laser sideband system has been used to study the H$_2$O$^+$ ion. Experiments have been done near 30 cm$^{-1}$ using a HCN laser and near 45 cm$^{-1}$ using an optical pumped laser. The tunability is achieved by mixing the radiation of a klystron with that of one of the lasers.

Rotational transitions were observed near 30 cm$^{-1}$, while transitions have been found near 45 cm$^{-1}$ which we have preliminarily assigned to the inversion splittings in H$_2$O$^+$.
Dissociation Of H$_2$ In A Fast Beam: Optical Translational Spectroscopy


An optical probing method has been used successfully to measure the kinetic energy released onto fragments in dissociative charge exchange of H$_2^+$ ions with cesium. By monitoring the laser induced fluorescence of the Balmer beta atomic line (n=2 to n=4), specific molecular fragmentation to the H(1s) + H(2p) or higher dissociation limits was investigated. The spectrum exhibits several peaks and a clear break at 1.9 eV. Predissociation of n=3 Rydberg states is invoked as the dominant contribution.

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Fourier Transform Spectroscopy Analysis Of The 3d-Complex Visible Emission Spectra Of H$_2$

Experimental Results And Theoretical Interpretation

A. Alikacem, M. Larzilliere, J. Tremblay and S.C. Laperriere

An investigation of the triplet 3d-complex of H$_2$, the g (3d) $^3\Sigma_g^+$, 1 (3d) $^3\Pi_g$ and j (3d) $^3\Delta_g$ and the nearby h (3s) $^3\Pi_u^-$ state, has been performed. 3s,3d $\leftrightarrow$ c (2p) $^3\Pi_u^-$ visible emission spectra have been obtained with a low pressure discharge lamp and recorded by Fourier Transform Spectrometer. Transition wavenumbers and rotational energy levels are given for v=0-3 of the four states. The data are represented by an effective Hamiltonian which accounts for the rotational breakdown of the Born-Oppenheimer approximation (L-uncoupling). The eigenvectors obtained from this model provide considerable insight into the nature of the 3d-complex. It has been found necessary to include interactions with the h (3s) $^3\Pi_u^-$ state to describe the complex for lower v values. Molecular constants are also given.

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Also for M. Larzilliere: Laboratoire de Spectrometrie Ionique et Moleculaire, Associe au CNRS, Universite Lyon-1, 69622 Villeurbanne Cedex, FRANCE.
THE NUMBER OF QUASIBOUND LEVELS BEHIND A ROTATIONAL BARRIER

DAVID L. HUESTIS

The number of quasibound or rotationally predissociating levels of diatomic molecules is investigated using a long-range approximation to the difference between the JWKB estimates of the vibrational quantum numbers at the maximum of the rotational barrier and at the dissociation limit. It is found that for a fixed J the expected number of quasibound levels is approximately J/20, essentially independent of the magnitude and form of the potential and independent of the mass of the nuclei. A similar result had been found previously for long range potentials of the form $R^{-6}$, $R^{-8}$, and $R^{-10}$, under more restrictive assumptions. Good agreement is found with accurate calculations of the quasibound levels for the various isotopomers of $H_2$, $H_2^+$, $HeH^+$, $CH^+$, and $HgH$.

This work was supported by the Office of Naval Research.


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A DOUBLE-RESONANCE STUDY OF PREDISSOCIATION OF THE $j^3\pi^g$ STATE OF $H_2$

L. J. LEMBO, D. L. HUESTIS, N. BJERRE, S. R. KEIDING, and H. HELM

A fast-beam photoionization-photodissociation double-resonance technique has been employed to excite transitions from selected rovibrational levels of the metastable $c^3\Pi_u$ state to the rapidly predissociated $j^3\pi^g$ state of $H_2$. Vibrational levels $v' - 7 \cdot 14$ and $v'' - 7 \cdot 12$ were observed (with $N' = 2$, and for $v' = 12$, $N' = 3, 4$ as well). The derived term energies in both states are in good agreement with theory.1,2

Predissociation of the $j^3\pi^g$ state arises from coriolis interaction with the vibrational continuum of the $1^3\Pi_g$ state. The photodissociation resonances are slightly asymmetric, and have widths that decrease with increasing $v'$ from 29 to 10 cm$^{-1}$. Calculated predissociation widths show the same vibrational trend, but are consistently 30% smaller.

Five narrow (1.7 - 4 cm$^{-1}$) photodissociation resonances were also observed. We attribute these to Q(1) and R(1) transitions to the n=4 $2^1\Pi_g$ state.

This work was supported by NSF and AFOSR.


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LASERSPECTROSCOPIC INVESTIGATION OF THE VAN DER WAALS MOLECULE NaKr

I. Kapetanakis, V. Schmatloch, E. Zanger, D. Zimmermann

The absorption spectrum of NaKr due to the transition X I → A n has been investigated in the wavelength region between 16790 and 16950 cm⁻¹ with high resolution by means of laserspectroscopy using a tunable cw dye laser and producing the molecules by supersonic expansion of a mixture of sodium vapor and krypton gas into a vacuum. In order to get an assignment of rotational quantum numbers to the numerous molecular absorption lines, despite of strong overlapping of vibrational bands and despite of the presence of several Kr isotopes, the method of optical-optical double resonance has been applied. In addition, the spectral intensity distribution of the fluorescence light has been investigated, thus allowing an assignment of vibrational quantum numbers.

Up to now, the molecular parameters B, D, H of rotation, A, Ad, Am of fine structure splitting and p, pD of X-type doubling have been determined with high precision for the vibrational states 8 ≤ v' ≤ 14 of the A n-state and 0 ≤ v'' ≤ 2 for the X I -state together with the wavenumbers of the band origins 1. The values of the fine structure splitting constants A, decreasing from A = 939 GHz for v' = 8 to A = 661 GHz for v' = 13, are unexpectedly high in comparison with the 3P-fine structure splitting of the sodium atom of 517 GHz. The X-doubling parameter p decreases with increasing v' and changes sign near v' = 13. The interatomic potential of the A n- and of the X I -state have been deduced from our data and will be compared to the results of recent model potential calculations.

1) Parts of these results have been submitted for publication; E. Zanger, V. Schmatloch, D. Zimmermann. accepted by J. Chem. Phys., to appear in April 88

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ORANGE BANDS OF CaO: OODR SPECTROSCOPY AND ELECTRONIC STRUCTURE MODEL

DAVID P. BALDWIN, AND ROBERT W. FIELD

Although the electronic spectrum of CaO is extremely complex and congested (>10⁴ lines within 700 cm⁻¹ in the Orange Bands), its electronic structure is so simple that it is likely to serve as a zero-order, atomic-ion-in-molecule model for the electronic structure of the transition metal monoxides. With the exception of the nominally Ca⁺⁺O⁻⁻ X's' state, the electronic structure of CaO may be understood as a weakly interacting electron/hole pair, the electron localized on Ca (in Xg, Ax, Σ, Σ⁺, Σ⁻ states borrowed from the corresponding X₂y₂, A₂dr, B₂⁻ states of CaF) and the hole localized on O (2p₁ (σ⁺ or σ⁻) as for NaO). We report here the previously unknown C'v configuration. This completes the characterization of the CaO Orange Bands which consist of transitions between all six Ann-⁻ states and the two X outward (A'₁ TL, A'₁ Ml) lower states. Experimental knowledge of the four lowest ¹Σ states (X'º - Ca⁺⁺O⁻⁻, A¹T, C¹Σ⁺ - Ann⁻, C¹Σ⁻ - Σ⁺⁻) should provide stringent tests of ab initio calculations as well as a model potential curves, energy separations, and intervalence interaction strengths.

A lower level linked OODR scheme has allowed unambiguous J, e/f, and electronic state labelling of the C¹Σ⁻ → A¹T band system in the CaO Orange Bands. This same technique was used to obtain sub-Doppler spectra from which accurate constants for both upper and lower states have been derived. The ¹Σ identity of the upper state in this transition was confirmed by observation of resolved fluorescence spectra in the C¹Σ⁻ → X¹Σ⁺ transition. The preliminary molecular constants for the C¹Σ⁻ state T, B, C, and are 24 635.546, 0.3456, 2.4x10⁻¹, and 549.64 respectively (all in cm⁻¹).


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Dynamics of cw + pulsed optical-optical double resonance excitation of the \( E^2\Sigma^+ - A^2\Pi_1/2 - X^2\Sigma^+ \) transition in CaF

J.E. Murphy, M.C. McCarthy, J.M. Berg and R.W. Field

We present preliminary results of the OODR excitation of the \( E^2\Sigma^+ \) low-lying Rydberg state of CaF using one cw and one pulse-amplified single-mode dye laser. Dynamical information crucial to the study of higher-lying, as yet unobserved Rydberg states in CaF and related molecules will be discussed.

Bernath has obtained and assigned rotationally resolved OODR spectra of the \( E-A-X \) excitation series using two single-mode cw dye lasers. The use of a pulsed laser for the second excitation step is preferred for the study of higher energy states because of the ease with which it can be frequency doubled and because the Rydberg-A transition moments are expected to be quite small. It is important to characterize this excitation scheme using a known transition which can be studied by both pulsed and cw methods. We compare the efficiencies of cw/pulsed with cw/cw fluorescence excitation of \( E-A-X \). The density of molecules in our source and the transition moments for \( E-X \) and \( E-A \) are determined using these data and emission rate measurements.

A first step towards the goal of characterizing the \( n=5-10 \) Rydberg states with double resonance is to obtain quantitative dynamical information on the \( A^2\Pi_1/2 - X^2\Sigma^+ \) initial excitation step. This data is vital for the optimization of molecule source conditions and for determination of the best optical method (pulsed, cw or modulated cw) of exciting the intermediate state. Using an acousto-optically modulated, single-mode cw dye laser with a risetime of \(-10 \text{ ns}\), we observe a transient \( A-X \) fluorescence rate which is twice the steady-state value and which decays to the steady-state value with a lifetime of \(-160 \text{ ns}\). The effects of varying background Ar pressure on both the transient and steady state emission rates were measured.

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HIGH RESOLUTION LASER SPECTROSCOPY OF NIOBium NITRIDE,
THE ORANGE, YELLOW AND NEAR INFRARED BANDS

Y.Azuma, J.A.Barry, G.Huang, J.O.Schroder and A.J.Merer

A hyperfine analysis of the sub-Doppler intermodulated fluorescence spectrum of gaseous niobium nitride (NbN) from 5700 \( \text{Å} \) to 6300 \( \text{Å} \) has been completed. Two triplet systems, the \( 6\delta^{3}\Pi - 0\delta \chi^{4}A \) in the orange region and the \( 6\delta^{3}\Pi - 0\delta \chi^{4}A \) in the yellow region have been studied. Both systems show very impressive hyperfine splittings due to the interaction between the \( I=9/2 \) nuclear spin of Nb and a metal centred unpaired electron.

Severe perturbations occur in the energies of the spin-orbit components. It has been necessary to fit the ground state to a modified form of the case (a) Hamiltonian where the isotropic hyperfine parameters in the matrix elements \( \gamma=\text{diagonal} \) are treated as independent variables. The \( 3\Pi \) state could only be fitted using a case (c) model.

In addition, two new band systems near 8000 \( \text{Å} \), assigned as \( 6\delta^{3}\Pi - 6\delta^{3}\Sigma^+ \) and \( 6\delta^{3}\Pi - 0\delta \Sigma^+ \), have been discovered by state-selected wavelength-resolved fluorescence. Preliminary analyses have been completed. Even though all the triplet states known are in good case (a) coupling, it has been possible to obtain their spin-orbit intervals through the observation of extremely weak spin satellite branches recorded at low resolution by wavelength-resolved fluorescence.

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HIGH RESOLUTION LASER SPECTROSCOPY OF MANGANESE OXIDE, MnO

Y. AZUMA, T. CHANDRAKUMAR AND A. J. MERER

The (0,0) band of $A^4I^+_2 - X^4I^+_2$ system of gaseous manganese oxide (MnO) near 5600 Å has been recorded at sub-Doppler resolution by intermodulated fluorescence. The spectrum shows impressive hyperfine structure due to the interaction between the $I=5/2$ nuclear spin of Mn and a metal-centred unpaired electron. Particularly interesting are the pronounced internal hyperfine perturbations between the middle two electron spin components of the ground state which distort the hyperfine patterns severely.

The upper electronic state is very heavily perturbed and an avoided crossing pattern with another close-lying electronic state has been found. Numerous satellite branches induced by the perturbations, (some of them with unusual selection rules such as $\Delta v=5$), complicate the spectrum massively. However, they are valuable in that they provide direct spin and hyperfine combination-differences within the ground state. The centre of the band is so dense, even at sub-Doppler resolution, that it can only be analysed by a two-dimensional technique, where the patterns of wavelength resolved fluorescence are recorded at intervals of 0.05 cm$^{-1}$, throughout the region.

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FIRST OBSERVATION OF BOUND-CONTINUUM TRANSITIONS IN THE LASER INDUCED $A'^2P^+_2 - X'^2P^+_2$ FLUORESCENCE OF K$_2$

V. Zafiropulos, W. T. Luh, A. M. Lyyra, and W. C. Stwalley

We report an interesting spectrum of K$_2$ excited by a narrow band ring-dye laser. The laser wavelength used (7425.77 Å) coincides with two $A'^2P^+_2 - X'^2P^+_2$ transitions starting from the levels $v'' = 13$, $J'' = 36$ and $v'' = 15$, $J'' = 95$.

The spectrum shows a long series of R-P doublets and a structured continuum with a broad maximum at 1.05 μm. From the analysis we obtain a new value for the ground state dissociation energy of K$_2$.

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Address of W. T. Luh: Dept. of Chemistry, National Kaohsiung Normal University, Kaohsiung 802243, Taiwan, Republic of China
POLARIZATION OF ATOMIC POTASSIUM FLUORESCENCE EXCITED BY LASER PHOTODISSOCIATION OF $K_2$


A tunable dye laser was used to excite $K_2$ from the ground $X^1Σ_u^+$ state into the continuum of the $B^1Σ_u^+$ state. This results in dissociation of the molecule producing an excited $K$ atom which fluoresces.

By monitoring the atomic $D_2$ fluorescence under these molecular beam (collision-free) conditions, we were able to measure the pure bound-free absorption profile. At the same time, the polarization of the atomic fluorescence was measured for different laser excitation frequencies. We believe this to be the first observation of a large variation in the polarization, ranging from $15.1\%$ to $-6.3\% \pm 0.4\%$ as a function of laser excitation wavelength.

The results are explained a) using the theory of Van Brunt and Zare\(^1\), which predicts a maximum polarization of $14.3\%$ (axial recoil) and a minimum of $-7.7\%$ (transverse recoil) and b) the rotating molecule theory\(^2\) where the polarization is a function of the angle of rotation of a half collision.

Classical, semiclassical and quantum-mechanical calculations in the $K_2$ case were also performed and a comparison with the experimental results is given.

\(^2\) J. Vigue, J. A. Beswick and M. Broyer, J. de Physique \textbf{44}, 1225 (1983).

Address of Zafiropulos, X. Zeng, A. M. Lyvra, F. Kleiber, K. Sando and W. C. Stwalley: Iowa Laser Facility, University of Iowa, Iowa City, Iowa 52242-1294

LASENL INDUCED FLUORESCENCE OF $Cs_2$ BY ARGON ION LASER LINES IN THE PRESENCE OF NOBLE BUFFER GASES

J. J. Ha, Chongye Kang, and R. A. Bernheim

The laser induced fluorescence of cesium dimers by the 476.5 nm radiation from an argon ion laser was examined at temperatures above 200°C in the presence of He, Ne, Ar and Kr. Besides the $Cs_2$ fluorescence bands, $Cs - noble$ gas eximer emission is observed in addition to sharp satellite bands on the blue side of the $Cs$ atom $D_2$ fluorescence. These latter bands are due to free-free transitions of the $Cs - X$ systems, where $X = He, Ne, Ar, Kr$. The positions of the satellite bands are in agreement with predictions based upon the theoretical calculations of $Cs - X$ potential curves for the electronic states corresponding to the transition.

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Address of Wang and Bernheim: 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802.
THE ISOTOPIC BEHAVIOUR OF BORN-OPPENHEIMER BREAKDOWN EFFECTS: APPLICATION OF A LEAST-SQUARES PROCEDURE TO THE HCl ISOTOPOMERS

J.A. COXON AND P.G. HAJIGEORGIOU

This work describes the application of a weighted least-squares procedure for the reduction of spectroscopic line positions to effective radial Hamiltonian operators. The method is applied to the $X^1Σ^+$ and $B^1Σ^+$ states of $^3HCl$, $^3DCl$, $^3DCl$, and $^3DCl$.

Extensive spectroscopic data are now available for all four isotopomers; these data have been employed to determine an isotope independent rotationless potential, $U(BO)$, and isotopeinvariant radial functions $U(H)$ and $U(Cl)$ which result in effective potential functions $U(\text{eff})$ for each isotopomer according to Eq. (1).

$$U(\text{eff}) = U(BO) + \frac{U(H)}{M_a} + \frac{U(Cl)}{M_b},$$

where $M_a$ and $M_b$ are the atomic masses of H/D and $^35Cl/37Cl$, respectively. In addition, $J$-dependent non-adiabatic effects are described in terms of a radial function $q(R)$ containing contributions from both atoms, that modifies the conventional rotational Hamiltonian, as in Eq. (2).

$$H(\text{rot}) = \left(\frac{h^2}{2I^2}\right)[1 + q(R)][J(J+1)].$$

The effective rotationless potential of each isotopomer in combination with the appropriate rotational Hamiltonian, yields eigenvalues that reproduce spectroscopic line positions within estimated experimental errors.


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PARITY SELECTED EXCITATION SPECTROSCOPY OF ArCl₂

K. C. Janda, D. D. Evard and J. L. Clime

Parity selected excitation spectra have been recorded of the B-X transition of ArCl₂ with 0.05 cm⁻¹ resolution. The resolution is such that rotational structure is clearly evident, but not cleanly resolved. Since simulated spectra using a rigid-rotor model are able to fit the whole spectrum and the even and odd parity selected spectra, we are confident that the spectrum is correctly assigned. ArCl₂ is found to be a "T" shaped molecule with a 3.7 Å distance between the center of the Ar atom and the center of mass of the Cl₂ molecule. This compares to ArCIF which is a linear molecule with only a 3.3 Å Ar-Cl separation. By measuring the vibrational predissociation threshold, the Ar-Cl₂ bond energy was found to be 178 ± 1 cm⁻¹ in the B state and 188 ± 1 cm⁻¹ in the X state.

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VIBRATION-ROTATION SPECTRUM OF CARBONYL SULFIDE DIMER

R. A. RANDALL, J. M. MILKIE, C. E. JAMES, B. J. HOWARD, AND J. S. MUEINTER

The infrared spectrum of carbonyl sulfide dimer, (OSO),, has been recorded by observing the absorption of iodine laser radiation in a pulsed molecular beam. The observed signal, in the carbonyl stretching region of the infrared spectrum, is from a perpendicular band of a quasi-asymmetric prolate rotor. Energy levels in the ground state with odd K, values are missing, which requires (OSO) to have a center of symmetry. The vibrational origin occurs at 381.760 cm\(^{-1}\), and the rotational constants are \(A'=3075, B'=659, C'=3068\), and \(\epsilon'=894\). MHz. Centrifugal distortion constants, constrained to be equal for both vibrational states, were also obtained in the data analysis. The vibrational origin is shifted to higher frequency by 1.3 cm\(^{-1}\), relative to the isolated monomer transition. The rotational constants and missing levels are consistent with a geometry having parallel monomer axes and opposite monomer orientation. The perpendicular separation of the monomer axes is 3.630 A, and the monomer centers of mass are nearly opposite one another. The horizontal separation of the centers of mass is \(\pm 0.34\) A.

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VIBRATION-ROTATION SPECTRUM OF CARBON DIOXIDE-ACETYLENE

DIANA G. PRICHARD, R. N. NANDI, J. S. MUEINTER, AND B. J. HOWARD

The infrared spectrum of carbon dioxide-acetylene has been recorded in the three micron wavelength region by observing direct absorption of color center laser radiation by a pulsed molecular beam. The spectrum is that of a perpendicular transition in a moderately asymmetric prolate rotor. The vibrational origin is 3281.740 cm\(^{-1}\), and the rotational constants are \(A'=8875, B'=1.65\), \(\epsilon'=894\), \(A'=3068\), \(B'=1.65\), and \(C'=59.\) MHz. The axes of the two monomer molecules are parallel and the complex has C\(_2\) symmetry. The separation of the monomer units is 3.285 \(\AA\). This geometry is readily predicted by considering the quadrupole-quadrupole interaction. Since the monomers have quadrupole moments of opposite sign, this configuration places positive regions of each monomer opposite negative regions of the other. A more detailed model of electrostatic interactions between distributed multipole moments will also be discussed.

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VIBRATION-ROTATION SPECTRUM OF ACETYLENE-NITROGEN

R. N. NANDI, DIANA G. PRICHARD, AND J. S. MUEINTER

The structure of carbon dioxide-acetylene, discussed in the previous paper, was that predicted by the quadrupole-quadrupole interaction. Identical considerations apply to acetylene-nitrogen, and the symmetric parallel geometry was anticipated. However, the observed infrared spectrum is that of a linear molecule. Two hot bands are observed, along with the fundamental transition. Numerous perturbations are also present. The vibrational origin of the fundamental occurs at 383.093 cm\(^{-1}\), with \(B'=1305\) MHz and \(B'=1507\) MHz. These rotational constants give a centers of mass separation for the monomers of 4.822 \(\AA\) and 4.815 \(\AA\), respectively. Low frequency bending vibrations will be discussed in terms of a distributed multipole potential function.

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STRUCTURAL STUDY OF THE H_2O-H_2O-CO_2 TRIMER

K. J. PETERSON, R. D. SUENRAM, AND F. J. LOVAS

The microwave spectrum of the trimeric species H_2O-H_2O-CO_2 has been studied in the 7-18 GHz frequency range using a pulsed-molecular-beam Fabry-Perot Fourier transform microwave spectrometer. Each transition is doubled because of energy level splitting due to coupling of an internal rotation of one of the H_2O subunits with the overall rotation of the complex. Both states can be fit using a centrifugal distortion Hamiltonian. The rotational constants and intertial defects are:

<table>
<thead>
<tr>
<th></th>
<th>Lower State</th>
<th>Upper State</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6161.576(5) MHz</td>
<td>6164.068(7) MHz</td>
</tr>
<tr>
<td>B</td>
<td>2226.156(3) MHz</td>
<td>2226.677(3) MHz</td>
</tr>
<tr>
<td>C</td>
<td>1638.972(2) MHz</td>
<td>1638.839(3) MHz</td>
</tr>
<tr>
<td>η</td>
<td>-0.66197 μA²</td>
<td>-0.57724 μA²</td>
</tr>
</tbody>
</table>

The electric dipole moment has also been measured yielding μ_x=1.57D, μ_y=0.76D and μ_z<0.1D. Several isotopically substituted species have been studied including various 13C, 18O and deuterium substitutions. All except a singly deuterated species exhibit doubled spectra. We conclude that the species has a nearly-planar triangular structure with dimer type structures evident within the trimer complex. The oxygen of one of the H_2O subunits is bonded to the CO_2 carbon with a bond length of 2.8A, within 0.1A of that found in the H_2O-CO_2 dimer. The other H_2O has its oxygen bonded to one of the hydrogens of the first H_2O; the bond distance is 2.0A, within 0.1A of that found in the H_2O-H_2O dimer. This second H_2O is also hydrogen bonded to one of the oxygens in the CO_2 subunit with a bond distance of 2.0A which is what one would expect for a hydrogen bonded H_2O-CO_2 dimer (this species has not been observed). Evidence suggests that this H_2O subunit is involved in the internal rotation.

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Address of Suenram and Lovas: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland 20899.
The microwave spectrum of the trimeric species \( \text{CO}_2-\text{CO}_2-\text{H}_2\text{O} \) has been studied in the 7-18 GHz frequency range using a pulsed-molecular-beam Fabry-Perot Fourier transform microwave spectrometer. Only one set of b-type transitions are observed in contrast to the doubled set observed for \( \text{H}_2\text{O}-\text{H}_2\text{O}-\text{CO}_2 \). Using a centrifugal distortion Hamiltonian, these transitions can only be fit if the symmetric (ee-oo) and antisymmetric (eo-oe) set are analyzed separately. The rotational constants are:

<table>
<thead>
<tr>
<th></th>
<th>symmetric</th>
<th>antisymmetric</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3313.411(1)</td>
<td>3313.419(2)</td>
</tr>
<tr>
<td>B</td>
<td>1470.548(1)</td>
<td>1470.545(1)</td>
</tr>
<tr>
<td>C</td>
<td>1308.851(1)</td>
<td>1308.849(1)</td>
</tr>
</tbody>
</table>

The dipole moment for the complex is \( \mu_b=1.989(2)\text{D} \). These observations imply that the complex has a two-fold axis of symmetry with the \( \text{H}_2\text{O} \) subunit oriented such that its \( \text{C}_2\text{v} \) axis is aligned with the b-axis of the complex. The magnitude of the rotational constants along with information obtained from \(^{13}\text{C} \) substitution suggest that the \( \text{CO}_2 \) subunits lie in a plane perpendicular to the b-axis separated by a distance similar to that observed in the \( \text{CO}_2-\text{CO}_2 \) dimer. It is expected that the oxygen of the \( \text{H}_2\text{O} \) is oriented toward the plane of the two \( \text{CO}_2 \) subunits. The separation of the transitions into two sets suggests that each rotational level is shifted because of an internal motion. The most likely motion is interchange of the hydrogens in the \( \text{H}_2\text{O} \) subunit. The levels are shifted rather than split because of the involvement of the \( \text{CO}_2 \) oxygens which have a spin quantum number of 0.

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HYPERFINE STRUCTURE AND TUNNELING MOTIONS IN HYDRAZINE

L. H. COUDERT and J. T. HOUGEN

For the past two decades, nuclear quadrupole hyperfine structure has been a powerful tool in structural determinations of loosely bound complexes. In the present work, we attempt to determine the limits of existing theory by describing hyperfine structure in a molecule which exhibits significant tunneling splittings because of large amplitude inversion and internal rotation motions, but which still has a well defined equilibrium configuration.

The approach involves setting up a complete quadrupole Hamiltonian for the two nitrogen atoms in hydrazine (\( \text{NH}_2-\text{NH}_2 \)), which is made dependent upon the three large amplitude coordinates necessary to fully describe the various configurations of the molecule, and which contains all five elements of the electric field gradient tensor (i.e., \( q_{aa}, q_{bb}, q_{cc}, q_{ab}, q_{ac}, q_{bc} \)) at one N atom when the molecule is in one of its equilibrium configurations. The mean value of this quadrupole operator is calculated for each tunneling state. One interesting result is that for doubly degenerate E-type levels the hyperfine pattern is expected to be quite different from that for non-degenerate A or B-type levels, because of the influence of the non-diagonal term \( q_{bc} \).

After the theoretical work, measurements of the hyperfine structure of selected transitions are being carried out on the NBS Fourier transform microwave instrument, and a least square fit of all available data will be performed. Transitions involving either non-degenerate or degenerate levels will allow us to determine the two diagonal terms of the electric field gradient tensor, which should be close to those reported for \( \text{N}_2\text{D}_4 \) by Harmony and Baron. Only transitions involving degenerate levels will allow us to determine the non-diagonal term \( q_{bc} \). The quality of the overall hyperfine fit in a molecule like hydrazine, where vibrational averaging should not lead to large differences between various expectation values of the form \( \langle \cos n\theta \rangle \text{fn} \), should be significantly better than the fits obtained for loosely bound complexes, unless our understanding of the tunneling aspects of this problem is seriously flawed.

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QUADRUPOLE HYPERFINE SPLITTING IN THE J = 1 - 0 ROTATIONAL TRANSITION OF CCl₃F

M.D. MARSHALL, H.O. LEUNG, AND R.D. SUENRAM

The hyperfine structure of the J = 1 - 0 transition of CCl₃F has been completely resolved for both K = 0 and K = 1 using a pulsed molecular beam Fabry-Perot cavity microwave spectrometer. Using previously available rotational constants for this molecule it is shown that the hyperfine splitting is qualitatively, but not quantitatively predicted using the classic method of Wolf, et. al. and the effective hyperfine constants, \( e\hat{Q}_{zz} = 29.047 \text{ MHz} \) and \( e\hat{Q}_{xy} = -110.95 \text{ MHz} \). To adequately describe the nuclear quadrupole coupling interaction in this heavy, oblate symmetrical top molecule it is necessary to consider in addition to those matrix elements off-diagonal in the quantum number J those off-diagonal in K. Such matrix elements include not only additional ones arising from the \( e\hat{Q}_{zz} \) term in the hyperfine Hamiltonian, but also those which find their origin in the usually ignored \( e\hat{Q}_{xy} \) term. The ability to measure this additional term will place more stringent limits on the assumption of cylindrical symmetry about the C-Cl bond.


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MICROWAVE SPECTRUM OF THE OZONE-WATER COMPLEX

R. D. SUENRAM, F. J. LOVAS, J. CILLIES, AND C. W. GILLIES

The microwave spectrum of the ozone-water complex has been observed using a pulsed molecular beam microwave spectrometer. The normal species, \( \text{H}_2\text{O} \), and one deuterated species have been assigned. Both a- and g-type transitions have been observed and fit using a centrifugal distortion Hamiltonian. For the \( \text{O}_3\text{H}_2\text{O} \) species the rotational constants are \( A=11960.584(5) \), \( B=4174.036(8) \) and \( C=3265.173(8) \text{ MHz} \). The measured dipole moment components for the complex are \( \mu_a=1.014(2)\text{D} \), \( \mu_b=0.03 \), and \( \mu_c=0.52(3)\text{D} \) which gives \( \mu_T=1.14(1)\text{D} \). From the available data several structural conclusions can be made, but details of the conformation are, at present, somewhat uncertain. The inertial defect \( (A-I_c-I_b-I_a) \) is \(-8.55\text{uA}^2\) which indicates that the complex has a non-planar heavy atom structure. From Ray's asymmetry parameter \( \kappa=(2B-A-C)/(A-C) \) \( (\kappa=-0.8) \) we conclude that the observed conformation must have a sandwich (\( \text{H}_2\text{O} \) and \( \text{O}_3 \) monomer planes parallel) or T-shaped (\( \text{H}_2\text{O} \) and \( \text{O}_3 \) monomer planes perpendicular) as opposed to an elongated structure with water bound to one end of the ozone molecule.

The dipole moment of the complex indicates that the two monomer subunits must be arranged such that substantial cancellation of the monomer dipoles occurs since \( \mu_{\text{water}} = 1.85\text{D} \) and \( \mu_{\text{ozone}} = 0.53\text{D} \). This is also consistent with a sandwich or T-shaped structure. Additional work is in progress involving the second deuterated isotope and \( \text{H}_2\text{O} \). It is hoped that these additional isotopes will allow a more detailed determination of the structure of the complex.

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ELECTRIC DIPOLE MOMENTS OF HCl- AND HCN-HYDROCARBON COMPLEXES

A. WEBER, G.T. FRASER, AND R.D. SUENRAM

Electric dipole moments of several hydrocarbon-HCN and hydrocarbon-HCl complexes have
been measured using a pulsed-nozzle Fourier-transform microwave spectrometer. The dipole
moments (μ) and complexation-induced dipole moments (Δμ) are (in D):

<table>
<thead>
<tr>
<th>Complex</th>
<th>HCl</th>
<th>HCN</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>1.6032(29)</td>
<td>3.4130(42)</td>
<td>2.3681(28)</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1.6167(15)</td>
<td>3.4023(27)</td>
<td>2.264(4)</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.688(10)</td>
<td>2.3839(45)</td>
<td>0.67</td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>1.7405(16)</td>
<td>3.5875(41)</td>
<td>2.5084(28)</td>
</tr>
</tbody>
</table>

The dipole moments for the HF complexes have been measured previously using molecular-
beam electric-resonance spectroscopy. The HCl-benzene result is in good agreement with the
1.6(1) D moment determined by Gandhi et al. using electric deflection techniques. The
induced dipole moments show a number of interesting features. With the same acid binding
partner, the acetylene and ethylene complexes give similar induced moments while the
cyclopropane complexes give the largest induced moments. Except for the benzene complexes,
the induced dipole moments increase as: X-HCN < X-HCl < X-HF and do not follow the dipole
moments of the acid binding partners which are ordered: HCl < HF < HCN.


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Standards, Gaithersburg, Maryland 20899.

DETERMINATION OF THE STRUCTURE OF H2CO CO2

T. A. BLAKE, S. E. NOVICK, R. D. SUENRAM, F. J. LOVAS

The rotational spectrum of the H2CO CO2 van der Waals complex has been measured using a
pulsed beam Fourier transform microwave spectrometer. Each rotational line is split into a "strong" and
"weak" intensity component due to the internal rotation of the formaldehyde moiety about its C2 axis. The
"strong" transitions are assigned to a B symmetry internal rotor state with the rotational constants
A=10,399.1(2) MHz, B=2678.215(1) MHz, and C=2128.340(1) MHz. The "weak", or A state lines were
assigned with the rotational constants A=10,400.5(2) MHz, B=2678.271(1) MHz, and C=2128.312(1)
MHz.

The complex has a planar structure analogous to the "near slipped parallel" structures of
(CO2)2 and CO2 OCS, with the oxygen of H2CO interacting with the carbon of CO2. The structural
parameters and dipole moments of both the A and B states are the same within the stated uncertainties.
The C-O(formaldehyde)-O (carbon dioxide) angle is 102.90(5)°, the O (formaldehyde)-O-C (carbon
dioxide) angle is 102.90(5)°, and the O (formaldehyde)-C (carbon dioxide) distance is 2.980(1) A. The
measured dipole moments are μa=1.661(2) D, and μb=1.671(2) D.

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DETERMINATION OF THE STRUCTURE OF \textit{Ar} H$_2$CO

S.S. NOVICK, R.D. SUENRAM, F.J. LOVAS, and G.T. FRASER

The rotational spectrum of the weakly bound complex \textit{Ar} H$_2$CO has been measured using a pulsed beam Fourier transform microwave spectrometer. The rotational constants of the complex are A=40059.939 MHz, B=2174.588 MHz, and C=2080.318 MHz. The argon atom sits almost directly above the carbon atom of the formaldehyde with an Ar--C distance of 3.66 Å and an Ar--C=O angle of 86°. It is likely that the hydrogen atoms of the formaldehyde execute hindered internal rotation about the C--O axis and thus their positions within the complex are not well specified.

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TUNABLE FAR INFRARED LASER SPECTROSCOPY OF VAN DER WAALS AND HYDROGEN BONDED CLUSTERS FORMED IN A PLANAR SUPERSONIC JET


We have developed a technique in which we use a cw planar supersonic jet expansion and a tunable far infrared (FIR) laser to investigate the low energy vibrations and tunneling motions of weakly bound van der Waals molecules. The planar jet expansion provides a high density of clusters as well as a relatively long pathlength (1.5 inches) for direct absorption spectroscopy. We also observed a factor of 5-10 reduction in the linewidth over a conventional circular nozzle, resulting in an increase in resolution. The tunable far infrared radiation is the product of non-linear mixing in a GaAs Schottky barrier diode of line tunable FIR radiation and tunable (2-75 GHz) microwave radiation. This laser provides much broader tunability and a simplified spectrum over more conventional Stark or Zeeman tuned FIR spectrometers. The first system studied using this technique was the previously studied X bend of \textit{ArHCl}. We greatly extended the existing data set and improved both ground and excited state constants as well as adding higher order centrifugal distortion constants. We have also used this technique to study more complicated dimers, including \textit{ArH}_2O and \textit{HCl}_2.

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TUNABLE FAR INFRARED LASER SPECTROSCOPY OF VAN DER WAALS BONDS: TUNNELING-ROTATIONAL AND VIBRATION-ROTATION SPECTRA OF \textit{Ar}-H$_2$O


The upper component of the ground state perpendicular tunneling-rotation spectrum of the \textit{Ar}-H$_2$O dimer has been observed near 21 cm$^{-1}$ using a cw planar supersonic jet and a tunable far infrared laser system. Analysis of this sub-band suggests an A rotational constant less than 17 cm$^{-1}$ and a tunneling splitting of 2-11 cm$^{-1}$. Observation of one sub-band of the out-of-plane bending vibration, (1,K=0 + G,K=1) near 24 cm$^{-1}$ gives a bending vibration near 40 cm$^{-1}$. The data is used to suggest the structure of the intermolecular potential energy surface.

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A PROGRAM FOR FITTING SPECTRA WITH INTERACTING VIBRATIONS AND SPINS

H. M. PICKETT

A program has been developed for fitting rotation-vibration spectra with interacting vibrations and spins. Currently the program can handle up to 9 vibrational states and up to 4 spins with a variety of general interaction terms. The structure of the input and output of the program will be described along with some organizational details. Selection of algorithms for partitioning the Hamiltonian and calculating the operators required particular care so that the code was general yet testable. One problem which caused considerable trouble was the selection of quantum number assignments for eigenvalues. Since quantum numbers for non-conserved quantities are only approximate, there is always some ambiguity. Nonetheless, a choice has to be made which is consistent with conventional use among spectroscopists. The difficulties with simple eigenvalue or eigenvector assignment approaches will be outlined, along with the approach selected for the program. This latter approach involves assignment to Wang blocks by 'least ambiguous projection', followed by energy ordering within a Wang block. In some cases, higher K states must be forced to have monotonically increasing first-order energy so that energy ordering will be correct.

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PYRROLE·Ar: MICROWAVE SPECTRUM, STRUCTURE, DIPOLE MOMENT, $^{14}$N QUADRUPOLE COUPLING AND BINDING ENERGY

ROBERT K. BOHN, K. W. HILLIG, II, AND ROBERT L. KUCZKOWSKI

The $^{14}$N species has been assigned and the $^{14}$N quadrupole coupling analyzed. The $^{15}$N species has also been assigned and its dipole moment determined. The Ar atom is located 3.56 Å from the pyrrole center of mass and the Ar-center of mass line is tilted 5.8° from the normal to the pyrrole plane toward the N atom. The dipole moment of the complex, 1.7074(11) D, is smaller than that of pyrrole, 1.7675(6) D. From a pseudodiatomic centrifugal distortion analysis, the binding energy is 261(2) cm$^{-1}$.

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THE MICROWAVE SPECTRUM OF $^{13}$C SUBSTITUTED METHYL CYANIDE FOR THE FREQUENCY RANGE 17-95 GHz

J. A. ROBERTS and H. TAM

The microwave spectrum of $^{13}$C substituted methyl cyanide CH$_3$C$^{14}$N was studied for the $v_g = 1, 2$, for both single and double $^{13}$C substitutions, vibrational states in the frequency range of 17 to 95 GHz.

The frequencies of the $I_g J_g 5$ components were measured for each vibration and these frequencies used to produce a constant set which can be used to predict overall frequencies of spectral components in the ground, $v_g = 1, 2$, up to an accuracy of 100 kHz.

Previously obtained experimental data, available from the literature for the naturally occurring isotopes, and our own data for the ground will be presented and compared with the frequencies obtained from a comprehensive equation derived from perturbation techniques.

Some weak interactions which have split the spectrum in the $^{13}$C species will be discussed. Systematic departures for the $K_i = 1, K = \pm 1$ and $K = \mp 1$ spectral components will be discussed.

1. This work supported by Grant B-812 The Robert A. Welch Foundation, Houston, TX. and the Faculty Research Committee of North Texas State University, Denton, TX.
2. Robert A. Welch Foundation Predoctoral Fellow.

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ROTATIONAL SPECTRUM OF 1,3-BUTADIENE-1,1-d$_2$

W. CAMINATI and A. BAUDER

The pure rotational spectrum of s-trans 1,3-butadiene-1,1-d$_2$ has been observed with a pulsed microwave Fourier transform spectrometer between 12-18 GHz. Both $\mu_a$- and $\mu_b$-type transitions with $J$ between 2 and 41 have been assigned. Rotational constants and quartic centrifugal distortion constants have been determined in a least squares fit from the measured transition frequencies. Some transitions of a vibrationally excited state were also observed. The molecule is planar as judged from the inertial defect. The molecular structure from ab initio calculations has been adjusted slightly to the measured rotational constants. During the search for rotational transitions of the s-trans conformer no indication was found for the presence of a second higher energy conformer as in the isoelectronic molecules acrolein and glyoxal. This failure to detect a second conformer was attributed to a small electric dipole moment and a large energy difference to the s-trans conformer.

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Hochschule, CH-8092 Zürich, Switzerland.
TORSIONAL MOTIONS IN METHYLGLYCOLATE

W. CAMINATI, H. HOLLENSTEIN, and R. MEYER

A-E splittings due to the methyl group internal rotation have been measured in several torsionally excited states of the methyl and two skeletal torsions by microwave spectroscopy. The vibrational transitions of the two lowest skeletal torsions have also been measured by Fourier transform far infrared spectroscopy. The obtained data have been used within a two-dimensional flexible model to determine the potential energy surfaces for the three motions.

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MOLECULAR STRUCTURE AND TAUTOMER EQUILIBRIUM OF GASEOUS 1,2,3-TRIAZOLE STUDIED BY MICROWAVE SPECTROSCOPY, ELECTRON DIFFRACTION AND AB INITIO CALCULATIONS

M. BEGTRUP, C. J. NIELSEN, L. NYGAARD, S. SAMDAL, C. E. SJÖGREN AND G. O. SÖRENSEN

Microwave spectra of the parent and the $^{15}$N$_3$ species show the molecule to exist as a mixture of two planar tautomers: a $^{1}$H-form with $C_5$ symmetry and a $^{2}$H-form with $C_{2v}$ symmetry. The dipole moments of the tautomers have been measured as $\mu_{^{1}H} = 4.38$ D and $\mu_{^{2}H} = 0.218$ D in the $^{15}$N$_3$ species. The relative abundance, estimated from rough intensity measurements, is $^{1}$H:$^{2}$H $\sim 1:1000$ at room temperature.

Fully optimized geometries have been calculated for the two tautomeric forms of 1,2,3-triazole at the Hartree-Fock SCF level employing a basis set of double zeta quality. The calculations show the $^{2}$H-form to be the more stable, with $\Delta E_{^{1}H - ^{2}H} = -14.7$ kJ mol$^{-1}$.

Structural refinements of a planar $C_{2v}$ model of the $^{2}$H-tautomer was carried out based on the electron diffraction data in combination with the measured rotational constants (corrected to $A$, $B$, and $C$).

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Address of Nygaard and Sørensen: Chemical Laboratory V, University of Copenhagen, The H. C. Bristed Institute, DK-2100 Copenhagen, Denmark.
Address of Samdal: Oslo College of Engineering, Cort Adelers gate 30, N-0254 Oslo 2, Norway.
STRUCTURAL DETERMINATIONS USING SCALED MOMENTS OF INERTIA

RAJIV J. BERRY AND MARLIN D. HARMONY

Recently published work has shown the usefulness of scaled ground-state moments of inertia for structural determinations.\(^1\),\(^2\) Based on a simplification of Watson's mass-dependence method\(^3\), the procedure has been shown to yield structural parameters for small heavy-atom molecules that are more reliable than \(r_g\) parameters and are very near to \(r_e\) parameters. Procedures for extending the method to molecules containing hydrogen atoms will be described and evaluated for various small polyatomic molecules.\(^4\) Model force-field computations will be presented also to aid in understanding the range of validity of the method and to provide a theoretical framework for the empirical procedures.


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ROTATIONAL SPECTRUM, RING PUCKERING, AND NH INVERSION OF 3-PYRROLINE

J. DOMMEN, W. CAMINATI, R. MEYER, AND A. BAUDER

The microwave spectra of the unsaturated five-membered ring molecule 3-pyrrole \((C_4H_7N)\) and its \(N\)-deuterated species have been reinvestigated between 26.5-40 GHz. The spectra were dominated by \(\mu_\alpha\)-type transitions which showed small splittings due to the intramolecular motion. A few \(\mu_c\)-type transitions with large splittings were located as well. For some of the transitions the \(^{14}N\) quadrupole splittings were resolved. The ring puckering and the NH inversion motion are strongly coupled. From a two-dimensional flexible model treatment of the data, the potential surface was found to have saddle points at puckered ring configurations separated by a maximum at the \(C_2v\)-symmetric configuration of the molecule.

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Address of Dommen, Meyer, and Bauder: Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.
TUNNELING MOTION IN ArH₃ AND ISOTOPOMERS FROM THE ANALYSIS OF THEIR ROTATIONAL SPECTRA

M. BOGEY, H. BOLVIN, C. DEMUYNCK, J.L. DESTOMBES and B.P. VAN EIJCK

The millimeter and submillimeter wave spectra of different H/D isotopomers of ArH₃ were investigated. The ionic clusters were produced inside a negative glow extended by a magnetic field, in Ar/H₂/D₂ mixtures. Most of the observed rotational lines were split by internal motion and spin statistical weights as well as intensity ratios for the components were determined from symmetry considerations. The splittings were interpreted in terms of internal motion of the H₃⁻ triangle. In a first step, the usual rigid top-rigid frame model was used to reproduce the order of magnitude of the splittings. In a second step, a more refined model, which accounts for the flexibility of the top and the frame, led to a better calculation of the observed splittings in ArH⁺ and ArD⁺.

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Address of VAN EIJCK: Department of Structural Chemistry, University of Utrecht Padualaan 8 - 3584 CH UTRECHT The Netherlands.

INFRARED DIODE LASER SPECTRA OF MgH, MgD, CaH AND CaD (X '7' )

B. LEMOINE, C. DEMUYNCK and J.L. DESTOMBES

Rotation-vibration spectra of MgH, CaH and their deuterated forms in the X '7' state have been measured using tunable infrared diode lasers. The hydrides were produced in a D.C. discharge of H₂ or D₂ over heated magnesium or calcium. Transitions from the fundamental bands and from hot bands (ν=2+1 for MgH, and up to ν=4+3 for CaH) were observed. The spectra were analyzed to determine accurate set of molecular parameters, either for each vibrational state or as Dunham coefficients. The mass dependance of the molecular parameters is examined in terms of possible breakdown of the Born-Oppenheimer approximation.

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MICROWAVE SPECTRUM OF THE N₂-H₂O COMPLEX

H. O. LEUNG, M. D. MARSHALL, R. D. SUENRAM, AND F. J. LOVAS

The a-type K=0 microwave spectrum of the N₂-H₂O complex has been observed using a pulsed molecular beam Fabry-Perot cavity microwave spectrometer. Seven isotopic species have been studied in the range of 5-23 GHz. The N₂-H₂O complex exhibits tunneling motions similar to the 1→2 tunneling motion of the H₂O-DOD complex which gives rise to four components for each rotational transition. The molecular constants obtained for ¹⁴N₂-HO⁻⁻ are (in MHz):

<table>
<thead>
<tr>
<th>State</th>
<th>B₁</th>
<th>A₁</th>
<th>A₂</th>
<th>B₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B + C)/₂</td>
<td>2906.362(1)</td>
<td>2906.925(1)</td>
<td>2914.146(1)</td>
<td>2914.252(1)</td>
</tr>
<tr>
<td>D</td>
<td>0.04181(2)</td>
<td>0.04349(2)</td>
<td>0.04263(2)</td>
<td>0.04300(2)</td>
</tr>
<tr>
<td>eQ₆(¹⁴N)</td>
<td>-4.253(2)</td>
<td>-4.227(3)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The structure has a nearly linear N-N-HO geometry with a N-N distance of 2.42(4) Å and an OHN angle of 168° (R(N)-N = 3.37(4) Å). The electric dipole moment along the principal axis was determined for the ¹⁵N₂-HO⁻⁻ species with μₓ = 0.833(3) Debye.


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ROTATIONAL SPECTRA AND STRUCTURES OF THE H₂S-H₂O AND (H₂S)₂ COMPLEXES

F. J. LOVAS, R. D. SUENRAM, AND L. H. COUDERT

A pulsed-beam Fabry-Perot cavity microwave spectrometer has been employed in the measurement of rotational spectra of H₂S-H₂O and (H₂S)₂. The a-type K=0 rotational transitions of both species have been observed in the 6-21 GHz range. The spectrum of H₂S-H₂O is expected to be analogous to that of H₂¹⁸O-H₂O and ¹⁵N₂-H₂O (described in the previous papers) for which two tunneling motions, give rise to four components for each transition. For H₂S-H₂O and its ³⁴S and ¹⁸O isotopic forms, 3 of the 4 components have been resolved. The molecular parameters for H₂S-H₂O are:

<table>
<thead>
<tr>
<th>State</th>
<th>B₁</th>
<th>A₁</th>
<th>A₂</th>
<th>B₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B+C)/₂ (MHz)</td>
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<td>3450.712(1)</td>
<td>3450.777(2)</td>
<td></td>
</tr>
<tr>
<td>D (kHz)</td>
<td>28.71(5)</td>
<td>21.20(4)</td>
<td>24.67(4)</td>
<td></td>
</tr>
<tr>
<td>μ (D)</td>
<td>0.551(3)</td>
<td>0.702(3)</td>
<td>0.697(6)</td>
<td></td>
</tr>
</tbody>
</table>

The energy levels of H₂S dimer and its isotopic forms are expected to be similar to those of water dimer. While hoping to observe a wider range of states than presently known for water dimer, at present only the K = 0 states for the E levels for (H₂S)₂, (H₂³⁴S)₂, and (D₂S)₂, and the similar levels of the mixed isotopic forms have been observed. For (H₂S)₂ the rotational constants are: B (E⁺) = 1749.310(1) MHz and B (E⁺) = 1474.109(1).

The structures of both complexes will be presented based on 9 isotopic species of H₂S-H₂O and 7 species of (H₂S)₂. Comparisons of the hyperfine structure, dipole moments and structural implications will be presented.


Address of Lovas, Suenram, and Coudert: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, MD 20899.
STUDIES OF ISOTOPICALLY ENRICHED WATER DIMER SPECIES

C. D. Suenram, L. H. Coudert, F. J. Lovas, and J. T. Hougen

We have recently reported new measurements on the K=1 states of (H_2O)_2 and K = 0 states of several deuterated species. We have now observed spectra for (HOD)_2, two singly substituted ^17O species, two singly substituted ^18O species and the doubly substituted ^17/18O species.

For (HOD), the unshifted E states of (H_2O)_2 are absent, leaving only A and B states present. The 1-0 and 2-1 K=0 transitions have been observed for these levels. The tunneling frequency corresponding to the HF dimer like motion (exchanging of D atoms in the hydrogen bond) for this species is 2643 MHz.

The nuclear quadrupole coupling constants for the ^17O species have been determined from measurements on the J = 1-0 transitions. The values determined are reported below.

Quadrupole Coupling Constants for ^17O Water Dimer Species (in MHz)

<table>
<thead>
<tr>
<th>Species</th>
<th>H_2O-H^17OH</th>
<th>H^17O-HOH</th>
<th>(H^2^17O^-)^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>State</td>
<td>A_1</td>
<td>A_1</td>
<td>A_2</td>
</tr>
<tr>
<td>eq Q_1</td>
<td>-5.140(16)</td>
<td>-5.171(25)</td>
<td></td>
</tr>
<tr>
<td>eq Q_2</td>
<td>1.942(8)</td>
<td>-1.522(8)</td>
<td>1.954(44)</td>
</tr>
</tbody>
</table>


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VIBRATIONAL SPECTROSCOPY OF SOLID-LIKE CLUSTERS OF HYDROGEN CYANIDE

D. S. Anex and G. E. Ewing

As concentration and stagnation pressure increase in a supersonic expansion of HCN in helium, a diffuse feature appears which has been assigned to a solid-like cluster of HCN. Its central frequency corresponds to that of the low temperature phase of bulk solid HCN and its bandwidth (Δν/2 ≈ 10 cm⁻¹) is substantially broader than other features in the HCN cluster spectrum. The appearance suggests a critical cluster size for its growth and its subsequent disappearance with increasing concentration suggests a phase transition (corresponding to the HCN(II) → HCN(I) phase transition in solid HCN).

The appearance and disappearances of the solid-like feature and its sensitivity on expansion conditions (concentration and pressure) will be discussed with respect to critical cluster size and phase transitions.

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The experimental technique is an extension of vibrational predissociation molecular beam spectroscopy, as previously carried out in our laboratory on neutral clusters, to the problem of solvated ions. The goal of this research is to obtain knowledge of the solvation processes at the microscopic level as well as detailed information concerning the structure of these solvated ions.

The dynamics of the dissociation process will also be discussed.

Address: School of Chemical Sciences, University of Illinois, 505 South Mathews Avenue, Urbana, Illinois 61801.
IR-IR DOUBLE RESONANCE SPECTROSCOPY: A STUDY OF THE TORSIONAL VIBRATIONS OF CYCLIC (HF)$_3$

KIRK D. KOLENBRANDER AND JAMES M. LISY

We report the application of a two-laser IR-IR double resonance spectroscopic technique to the study of both in-plane and out-of-plane torsional vibrations of cyclic (HF)$_3$. Preliminary results of this study were presented at the 1987 OSU Symposium on Molecular Spectroscopy, and the results of a concerted theoretical and experimental investigation which employed this spectroscopic technique have been recently published.¹ Using the double resonance technique, two rovibrational transitions were observed in the 10.6 μ band of the CO$_2$ laser. The transition observed at P(24) (940.5 cm$^{-1}$) has been assigned to the first overtone of the doubly-degenerate in-plane torsional vibration of (HF)$_3$. The second transition, observed at P(8) (954.5 cm$^{-1}$), has been assigned to a combination mode of the singly-degenerate and doubly-degenerate out-of-plane torsional fundamental vibrations. The linewidths which were observed for each of the two transitions show no evidence of homogeneous broadening. These 10-15 MHz FWHM instrument-limited linewidths are three orders of magnitude narrower than those previously observed for the H–F stretching vibration of (HF)$_3$ centered at 3712 cm$^{-1}$. We present several possible explanations for the significant differences in upper state lifetimes which these linewidths reflect.


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THE PHOTODETACHMENT SPECTRA OF NEGATIVE CLUSTER IONS OF WATER


We have recorded the photoelectron spectra of the water negative cluster ions: (H$_2$O)$_n^-$=2,6,7,10-25,30,34,37,40; (D$_2$O)$_n^-$=2,6,7,11-23; Ar(H$_2$O)$_n^-$=2,6,7; and Ar(D$_2$O)$_n^-$=2,6,7, using 2.409 eV photons. The vertical detachment energies of most of these anions were found to increase smoothly with cluster size with their extrema ranging from 0.040 eV for (H$_2$O)$_2^-$ to 1.79 eV for (H$_2$O)$_{40}^-$. The case of the water dimer anion is especially interesting. Its photoelectron spectrum consists of three peaks, two of which are spaced to the low electron kinetic energy side of the largest, origin-containing peak by energies which are characteristic of a water stretch and a water bend. Photodetachment of the deuterated dimer anion confirms this interpretation. This implies that at least one water component within the water dimer anion is structurally distorted.

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Address of Ludewigt, and Haberland: Dept. of Physics, Universitat Freiburg, Freiburg, Germany
THE PHOTODETACHMENT SPECTRA OF HOMOGENEOUS ALKALI METAL CLUSTER ANIONS: \( \text{Na}^-_{n=2}, \text{K}^-_{n=2-5}, \text{Rb}^-_{n=2-4}, \text{and Cs}^-_{n=2,3} \)


The alkali metals are the simplest of metals. We have recorded the photodetachment spectra of \( \text{Na}^-_{n=2}, \text{K}^-_{n=2-5}, \text{Rb}^-_{n=2-4}, \) and \( \text{Cs}^-_{n=2,3} \) using 2.540 eV photons. These highly structured spectra chart both the electron affinities vs. cluster size for these cluster anions studied thus far and the electronic state splittings of their corresponding neutral clusters (at the geometry of their cluster anions) vs. cluster size. The dimer anion spectra have been completely assigned. These provide adiabatic electron affinities, vertical detachment energies, dimer anion dissociation energies, neutral dimer electronic state spacings, and bond lengths for the various excited electronic states of the neutral dimers. Thus far, we have obtained the most complete set of data on potassium cluster anions. Potassium is electronically analogous to copper. A comparison of the electron affinity vs. cluster size trends for potassium clusters with those for copper clusters (measured by Lineberger and by Smalley) of the same size, shows quantitative differences yet strikingly similar qualitative trends.

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PHOTODETACHMENT STUDIES OF HETEROGENEOUS ALKALI METAL DIMER AND TRIMER ANIONS


In our laboratory, we have generated several mixed alkali dimer and trimer anions including: \( \text{NaK}^-, \text{RbCs}^-, \text{Na2K}^-, \), and \( \text{K2Na}^- \). These were formed by injecting relatively low energy electrons directly into an expanding jet of mixed alkali vapors and argon in the presence of a weak magnetic field. We are presently conducting visible photoelectron spectroscopic studies on several of these species in order to determine their electron affinities, their anion dissociation energies, and the electronic energy splittings of their corresponding neutral dimers and trimers.

Address: Dept. of Chemistry, The Johns Hopkins University, Baltimore, MD 21218
PRODUCTION AND PHOTODETACHMENT STUDIES OF Li$_2^-$


Li$_2^-$ is among the simplest and yet most elusive of molecular negative ions. To produce this anion, we have utilized a high temperature seeded nozzle expansion ion source in which a mixture of sodium and lithium is vaporized and expanded with argon as a carrier gas. Directly outside the nozzle a negatively biased filament injects low energy electrons into the expanding jet, inducing the formation of negative ions. Recently, we have used this source to generate mass selected Li$_2^-$ ion currents of 10-50 pamp. We have used a combination of sodium and lithium as a feedstock in the source in order to take advantage of the positive deviations from ideality which occur for lithium vapor in such mixtures. This substantially reduces the necessary operating temperature of the source. Progress in our efforts to record the negative ion photoelectron spectrum of this anion will be discussed.

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THE PHOTODETACHMENT SPECTROSCOPY OF HYDRATED AND DEUTERATED NITRIC OXIDE ANIONS


Hydrated nitric oxide anions may well play an important role in the ion-molecule chemistry of the ionosphere. We have recently recorded the photoelectron (photodetachment) spectra of NO$^-(\text{H}_2\text{O})_{n=1,2}$ and NO$^-(\text{D}_2\text{O})_{n=1,2}$ using 2.540 eV photons. Relative to the photoelectron spectrum of unclustered NO$^-$, these spectra are shifted to lower electron kinetic energies and are heavily broadened. The solvation interaction in hydrated nitric oxide anions will be discussed and compared with other anion-molecule complexes previously studied in our lab including several nitric oxide anion-containing species such as NO$^-(\text{Ar})$, NO$^-(\text{Kr})$, NO$^-(\text{Xe})$, and NO$^-(\text{H}_2\text{O})_{n=1,2}$.

Address: Dept. of Chemistry, The Johns Hopkins University, Baltimore, MD 21218.
THE STRUCTURE AND DYNAMICS OF NeC12

C. R. Bieler, S. R. Hair, J. I. Cline, K. C. Janda

The structure, bond energy, and photodissociation dynamics of the NeC12 van der Waals molecule are studied by a laser pump-probe technique. Analysis of excitation spectra reveals the structure to be nearly tetrahedral. The Cl2 bond length is assumed to be unchanged by formation of the van der Waals bonds. A Ne to Ne distance of 3.13 Å and a Ne to Cl2 distance of 3.25 Å are determined. The dissociation energy is determined to be between 145.6 and 148.6 cm⁻¹. The dissociation product state distributions are modeled by surprisal analysis.

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Address of Cline: JILA, University of Colorado, Boulder, CO 80309-8440.

TUNABLE FAR INFRARED LASER SPECTROSCOPY OF HYDROGEN BONDS: THE K = 0, 1 g ROTATION TUNNELING SPECTRUM OF THE HCI DIMER


The ground state K=0, 1 b-type sub-band of the rotational tunneling spectrum of the symmetric 37Cl35Cl, 35Cl-37Cl and the mixed 35Cl-37Cl hydrogen chloride dimers have been recorded at sub-Doppler resolution in a two-dimensional supersonic jet with a tunable far-infrared laser spectrometer. Quadrupole structure from the chlorine nuclei has been resolved for the first time. From the fitted rotational constants a (HCl), center-of-mass separation of 3.8±(1)Å is derived for the upper tunneling state, while the quadrupole coupling constants yield a vibrationally averaged angular structure of approximately 25 degrees for the hydrogen bonded proton and at least 70-75 degrees for the external. A geared internal rotational tunneling motion has been found for the HF dimer also, but here the splitting is much greater. The ground state tunneling splittings are estimated to lie between 15-20 cm⁻¹.

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Address of Busarow, Cohen, Laughlin, Lee, and Saykally: Department of Chemistry and Lawrence Berkeley Laboratories, University of California, Berkeley, CA 94720.

SUB-DOPPLER DIRECT ABSORPTION IR LASER SPECTROSCOPY IN FACT ION BEAMS


We have recently succeeded in detecting, for the first time, direct absorption of radiation by ions in an ion beam. Direct absorption IR spectroscopy in ion beams offers a number of attractive features: 1) the absolute number density of an ion can be determined from a conventional mass spectrum and a measurement of the total ion current; 2) from the observation of a single line, the charge-to-mass ratio of the absorbing species may be determined; 3) very high resolution, ca. 30 MHz, is attained due to "acceleration cooling"; 4) the method is not limited to systems which exhibit a process secondary to absorption; 5) a variety of ion sources are available which produce clusters, open-shell species, nonclassical ions, and other species of chemical interest; and 6) supersonic sources can produce very cold ions. It has generally been thought that densities in ion beams were prohibitively low for the detection of direct absorption; an apparatus which surmounts this difficulty will be described. Preliminary experiments on HN2⁺ and H3O⁺ will be discussed.

Address of Coe, Owrutsky, Keim, Agman, and Saykally: Department of Chemistry, University of California, Berkeley CA 94720.
RF1. (1:30)

\( \text{C. T. W. HSIEH and S. PADDI REDDY} \)

Collision-induced enhancement absorption spectra of the fundamental band of \( \text{H}_2 \) in \( \text{H}_2 - \text{Ar} \) mixtures were recorded with a 2 m absorption cell for total gas densities up to 500 amagat at room temperature and up to 160 amagat at 201 and 273 K. In the spectra obtained at room temperature, the hexadecapole-induced transition \( \text{U}_1(1) \) corresponding to the rotational selection rule \( \Delta J = \pm 4 \) has been observed. From the analysis\(^1\) of the observed experimental profiles using appropriate line shapes functions and numerical values of the matrix elements of the quadrupole moment of \( \text{H}_2 \), characteristic half-width parameters \( \delta_d \) and \( \delta_q \) of the short-range overlap-induced transitions and \( \delta_q^2 \) and \( \delta_q^4 \) of the quadrupole-induced transitions have been determined. The overlap parameters of the induced dipole moment of \( \text{H}_2 - \text{Ar} \) pairs have also been determined. The absorption coefficient of the \( \text{U}_1(1) \) transition is also estimated.


*Research supported in part by NSERC Grant No. A-2440.

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RF2. (1:46)

\( \text{INFRARED SPECTRUM OF SOLID HYDROGEN: THEORY OF THE INTEGRATED ABSORPTION COEFFICIENTS OF W(AJ=6) TRANSITIONS} \)

\( \text{T.K. BALASUBRAMANIAN, R. D'SOUZA and K. NARAHARI RAO} \)

The present work has been motivated by the efforts\(^1\) to observe \( \text{W(AJ=6)} \) transitions in the induced infrared spectrum of solid \( \text{H}_2 \). Transition with \( \Delta J=6 \) should occur due to the part of the dipole moment induced by the \( 2^{\text{nd}} \) electric multipole moment of \( \text{H}_2 \). Starting with the expressions\(^2,3\) for the dipole moment induced in a molecule by the \( 2^{\text{nd}} \) multipole moment of its neighbour, expressions for the integrated absorption coefficients are derived for the \( \text{W}_{\nu=0}(0), \text{W}_{\nu=0}(1) \) single transitions and the \( \text{W}_{\nu=0}(0)+Q_{\nu=0}(0) \) double transition. On account of the higher order multipolar induction mechanism, these transitions are expected to be extremely weak. Their observation would provide the first experimental value for the \( 2^{\text{nd}} \) moment of \( \text{H}_2 \).

We have also calculated the possible satellite structure around the \( \text{W}_{\nu=0}(0) \) line when the para-\( \text{H}_2 \) crystal contains traces of ortho impurity.

\(^1\)K. Narahari Rao (private communication).

Address of Balasubramanian and L'Souza: Spectroscopy Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay 400 085, India.

Address of Narahari Rao: Department of Physics, Ohio State University, 174 West, 18th Avenue, Columbus, Ohio 43210.
Absolute Po-Vibrational Intensities for the \( \Delta V = 1 \) Vibrational Bands of \( \tilde{X}^2 \Pi \) NH

C. Chackerian Jr., G. Guelachvili, A. Lopez-Pineiro and P. H. Tipping

We determine absolute ro-vibrational line intensities for \( \Delta V = 1 \) \((V'=1-4)\) vibrational bands of the astrophysically important species, NH, independently of any information on its molecular concentration. To this end we measure relative line intensities across \( \Delta V = 1 \) bands. The effect of vibration rotation interaction on the line intensities then allows a direct determination of the derivative of the electric-dipole fundamental band transition moment.\(^1\) The results of these experiments are then compared to theoretical calculations\(^2\) obtained via high quality ab initio calculations of the electric dipole moment function.

\(^2\) C. Chackerian, Jr., C. W. Bauschlicher, S. R. Langhoff, A. Lopez-Pineiro and P. H. Tipping (to be published)

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Address of G. Guelachvili, Laboratoire d’Infrarouge associé au CNRS, Université de Paris-sud, Batiment 350, 91405 Orsay, France
Address of A. Lopez-Pineiro, Departamento de Química Física, Facultad de Ciencias, Universidad de Extremadura, Badajoz, Spain
Address of P. H. Tipping, Department of Physics and Astronomy, University of Alabama Tuscaloosa, Alabama 35487
TWO-TONE FREQUENCY-MODULATION SPECTROSCOPY: MEASUREMENT OF HIGH OVERTONE INTENSITIES OF HBr

C. B. Carlisle, T. F. Gallagher, and R. H. Tipping

The technique of Two-Tone Frequency-Modulation Spectroscopy (TTFMS) using a multimode CW dye laser was employed to study high overtone bands of HBr. Individual vibration-rotational line strengths and positions were measured. On the basis of these measurements, rotationless dipole moment matrix elements and Herman-Wallis coefficients were determined for the 6-0, 7-0, and 8-0 overtone bands. Using the rotationless dipole moment matrix elements obtained previously by other workers for the pure rotational, fundamental, and first four overtone bands, together with the present results and numerical vibration-rotational wavefunctions, we have derived a series expansion for the dipole moment function. This function provides an excellent fit to all existing Herman-Wallis coefficients, and thus represents one of the best known dipole moment functions for any diatomic molecule. The accuracy of the present data also confirms the importance and utility of TTFMS when used for performing ultrasensitive molecular spectroscopic measurements of weak overtone bands.

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HIGH RESOLUTION OBSERVATIONS OF STARS, PLANETS AND THE SUN USING AN FTS/POSTDISPERSER

D. E. JENNINGS AND G. R. WIEDEMANN

Infrared spectroscopy in astronomy at mid-infrared wavelengths often requires resolving powers $\lambda/\Delta\lambda$ as high as $10^3$. Molecular lines in stars, planets and the sun can be very narrow, with widths produced by Doppler broadening due to the temperatures or velocities in the source. Completely resolved line profiles can yield dynamics, composition, temperatures and magnetic fields in atmospheres and circumstellar shells. Spectral resolutions near $0.01 \text{ cm}^{-1}$ are achievable using Fourier transform spectrometers. Until recently, however, such high resolution has been impractical because of detector or background noise.

A postdisperser has been developed at Goddard Space Flight Center to improve the sensitivity of FTS's used for astrogogy. This instrument, a cryogenic grating monochromator, permits $0.01 \text{ cm}^{-1}$ resolution on a variety of sources. By narrowing the spectral bandwidth to $0.6 - 3 \text{ cm}^{-1}$, the background noise is greatly reduced. Examples will be shown of Mg lines in stars, C$_2$H, and HCN in circumstellar shells, CCH detected in Jupiter and Zeeman splitting in sunspots. Observations were performed using the facility FTS's at the McMath and Mayall telescopes at Kitt Peak.


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DETERMINATION OF THE ORTHO-PARA RATIO AND NUCLEAR SPIN TEMPERATURE FROM HIGH
RESOLUTION WATER FLUORESCENCE SPECTRA OF COMETS HALLEY AND WILSON

W.E. BLASS, M.J. MUMMA, H.A. WEAVER, H.P. LARSON, AND S. DRAPATZ

High resolution water fluorescence spectra in the ν3 band has been observed
from comets Halley and Wilson. The observations were made aboard NASA's Kuiper
Airborne Observatory with the University of Arizona high resolution Fourier
transform spectrometer.1

Using a straightforward radiation transfer model of the cometary coma, we
have analyzed the ν3 fluorescence data. A rotationally equilibrated, aperture-
averaged coma is assumed. An effective rotational temperature and ortho-para
ratio for water in the coma are determined.

Results for comets Halley and Wilson will be presented. The implications
of an ortho-para ratio significantly different from 3:1 will be discussed

1 M.J. Mumma, H.A. Weaver, H.P. Larson, D.S. Davis, and M. Williams, Science
232, 1523-1528 (1986).

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REF.

INTERMEDIATE LATTITUDE AND PROTOCOTEL IN THE Z BAND OF 13CH4

MARK A. SMITH, BARTLEY DAVIS, AND CURTIS J. FINKBEINER

A 5-14T L-band, two-temperature system of 13CH4 diluted with air was used
in the 5.5-6.1 mm spectral region using the College Fourier transform spectrome-
ter at the National Solar Observatory on Kitt Peak. A 5% 13CH4-enriched mixture
was diluted to a similar ratio of approximately 1:1000 and mixed in a 5 cm absorption path to reduce the
ratio. The data were measured with pressure approximately 10, 50, 100, and 500 Torr. A
weighted least-square spectral fitting technique was used to determine the halfwidth coefficients
and positions. The derived halfwidth coefficients and pressure shifts will be
presented to values calculated for Zeeman transitions in the J = 3 of 13CH4 as well as to
work in the ν1 band of 13CO2.

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Research Center, Hampton, VA 23681
TUNABLE DIODE LASER MEASUREMENTS OF INTENSITIES AND
COLLISION-BROADENED LINE WIDTHS IN THE $\nu_1$ AND $\nu_6$
FUNDAMENTALS OF $^{12}$CH$_3$D AT LOW TEMPERATURES$^1$

S. CHUDAMANI, and P. VARANASI

For the determination of the D/H ratio in the atmospheres of of the major planets, the
Saturnian satellite Titan and Earth, intensities and half-width data are required at temperatures
between 90 and 288 K on the infrared lines of $^{12}$CH$_3$D broadened by H$_2$, He, N$_2$ and air. Using a
tunable diode laser and the sweep integration technique, we have measured at several temperatures
between 100 and 296 K the intensities and half-widths of several multiplets in the $\nu_1$ and $\nu_6$
fundamentals of $^{12}$CH$_3$D. O$_2$, broadening and Ar broadening have also been considered in addition
to the broadening by the gases already mentioned.

$^1$Supported by the Planetary Atmospheres Branch of the Solar System Exploration
Division of NASA under Grant-in-Aid No. NGR 33-015-139.

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New York, Stony Brook, NY 11794-2300
INTENSITY AND LINE WIDTH MEASUREMENTS IN THE ν₄-FUNDAMENTAL OF ¹³CH₄ AT PLANETARY ATMOSPHERIC TEMPERATURES†

P. VARANASI, and S. CHUDAMANI

Observation of the spectral lines belonging to ¹³CH₄ and comparison of their intensities and collision-broadened half-widths with those of ¹²CH₄ are not only relevant to studies of planetary evolution and exploration but are also of sustained interest to researchers engaged in intensity perturbation and collision-broadening studies of tetrahedral molecules. We present results obtained at several temperatures between 100 and 295 K on P(4), P(5) and P(6) multiplets using a tunable diode laser and H₂, He, Ar, N₂, O₂ and air as broadening gases. The difference in the line widths of the three tetrahedral species of lines and their variation with temperature is also presented.

†Supported by the Planetary Atmospheres Branch of the Solar System Exploration Division of NASA under Grant-in-Aid No. NCR 33-015-139.

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MEASUREMENT OF INTENSITIES AND COLLISION-BROADENED LINE WIDTHS IN THE ν₄-FUNDAMENTAL OF ¹²CH₄ AT LOW TEMPERATURES†

P. VARANASI, and S. CHUDAMANI

In the analysis of the observed ¹²CH₄ spectra of the atmospheres of the major planets, the Saturnian satellite Titan and Earth, intensities and half-width data are required at temperatures between 90 and 288 K on the ν₄ lines broadened by H₂, He, N₂ and air. We have, therefore, measured at several temperatures between 100 and 296 K the intensities and half-widths of P(5), P(6), P(9) and P(10) multiplets located between 1240 and 1280 cm⁻¹ using a tunable diode laser. In addition to the above mentioned broadeners we have also used O₂ and Ar. The temperature dependence and the relative magnitudes of the line widths of the A, E, F species of rotational lines are examined for each of the broadening cases.

†Supported by the Planetary Atmospheres Branch of the Solar System Exploration Division of NASA under Grant-in-Aid No. NGR 33-015-139 and by the Upper Atmosphere Research Program of the Earth Sciences and Applications Division of NASA under Grant-in-Aid No. NAGW-1238.

Address of the authors: Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, NY 11794-2300
PRESSURE SHIFT MEASUREMENTS ON THE INFRARED LINES OF $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, $^{12}\text{CH}_3\text{D}$ AND $^{14}\text{N}_2\text{O}$ AROUND 7.85 $\mu$m USING A TUNABLE DIODE LASER

P. VARANASI and S. CHUDAMANI

Unless very careful and skillful precautions are taken, measurement of collision-induced line shifts using a tunable diode laser can be unreliable on account of the commonly encountered jitter and instability in the laser signal. However, when lines belonging to different molecules appear in the spectral scan as neighbors (reference lines) that do not interfere with the absorption of the observed line, as in the case of the three methanes and $\text{N}_2\text{O}$, accurate line shift measurement is feasible. Using separate absorption cells for the reference and sample gases and placing them in series, we have been able to measure the pressure-induced shifts of the rotational lines of $^{12}\text{CH}_4$, $^{13}\text{CH}_4$, $^{12}\text{CH}_3\text{D}$ and $^{14}\text{N}_2\text{O}$ located between 1265 and 1275 $\text{cm}^{-1}$. The temperature dependence of the shifts is also presented for collisions of the absorbers with $\text{H}_2$, $\text{He}$, $\text{Ar}$, $\text{N}_2$, $\text{O}_2$ and air.

†Supported by the Planetary Atmospheres Branch of the Solar System Exploration Division of NASA under Grant-in-Aid No. NGR 33-015-139 and by the Upper Atmosphere Research Program of the Earth Sciences and Applications Division of NASA under Grant-in-Aid No. NAGW-1238.

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INFRARED BAND STRENGTH MEASUREMENTS OF $\text{CF}_2$ AND $\text{CH}_3$

J. WORMHOUT and K. McCURDY

Infrared tunable diode laser absorption diagnostics of gas phase radical concentrations can yield important information on chemical mechanisms in semiconductor processing systems. Absorption concentration measurements require knowledge of line and band strengths. We have been using fast flow reactor techniques to study the $\text{CF}_2$ radical, of interest in plasma etching systems, and the $\text{CH}_3$ radical, important in metalorganic and diamond chemical vapor deposition systems. $\text{CF}_2$ concentrations are determined by ultraviolet absorption of 248.4 nm radiation from a KrF excimer laser. $\text{CH}_3$ radicals are generated by reaction of $\text{CH}_4$ with $\text{F}$ atoms. They are quantified using the known $\text{CH}_3$ recombination rate constant by observing their concentration decay with residence time for varying initial concentrations. We will present infrared absorption strength measurements for these radicals and compare these results with recently reported measurements.¹ ²


Work supported by AFOSR under Contract F49620-87-C-0052

Address: Center for Chemical and Environmental Physics, Aerodyne Research, 45 Manning Road, Billerica, MA 01821
Theoretical Prediction of Far Wing Infrared Lineshapes

R.C. Brown and J. Wormhoudt

Far wing absorption is important in determining long path atmospheric absorption between strong adsorption bands. Development of a detailed dynamical theory of wing lineshapes for atmospheric molecules is a challenging task. A fully quantum mechanical, time dependent, perturbative theory has been used to evaluate far wing absorption for the 404-515 self-broadened H2O rotational line. The predicted absorption coefficient increases with temperature, in contrast to experimental observations of a strong negative temperature dependence. Replacement of an Anderson-like ad hoc cutoff by a formal resummation of the perturbation series yielded no improvement. We conclude that perturbative methods using multipole expansions are not adequate for this system. Preliminary calculations for an Ar-HCl test case using a non-perturbative technique, the Recursive Residue Generation Method, will be presented.


Work supported by AFSOR under Contract F19628-85-C-0183.

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Theoretical studies of the spectroscopy of first-row molecules

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Abstract

The recent development of ab initio methods such as full configuration-interaction calculations for the calibration of approximate methods of including electron correlation and new methods of contracting large primitive Gaussian basis sets, has substantially increased the accuracy of calculated spectroscopic constants. For example, calculated dissociation energies of both the NH and CN molecules are now more accurate than values deduced from either laboratory or astrophysical sources. The C^5Π_g and A^5Σ^+_g potentials of N_2 have been computed with sufficient accuracy to unambiguously assign the transition between these two states to the previously unidentified Hermann infrared system. The recent advances have also made it possible to compute accurate electronic transition moments from which accurate Einstein coefficients and radiative lifetimes can be derived. For example, the radiative lifetime of the v=0 and v=1 levels of the A^2Σ^- state of OH can now be computed with an uncertainty of only 2%. Other examples of theoretical calculations include the red and violet band systems of CN and the Meinel, first-negative, and second-negative band systems of N_2.

REFLECTION SYMMETRIES OF LINEAR-MOLECULE ROVIBRONIC LEVELS

JAMES K. G. WATSON

Coriolis forces break the infinite-fold axis of symmetry of a linear molecule, but leave a residual plane of symmetry. Thus the rovibrionic (or spin-rovibrionic) wavefunctions can be classified according to their behavior under reflection of the vibronic (or spin-vibronic) variables in this plane. The orientation of the plane depends on the coupling case. In Hund's case (a) or (c) the plane is through the molecular axis normal to the perpendicular component of the angular momentum J, while in Hund's case (b) it is normal to the perpendicular component of N. The former gives an exact symmetry classification equivalent to the e/f classification of Ref. 1, while the latter gives an approximate symmetry classification equivalent to the A', A'' classification proposed in Ref. 2. A simple prescription for the latter notation is given, namely

A' levels have parity (-1)^N.
A'' levels have parity (-1)^N.

This gives a useful characterization even when N is not a perfect quantum number. The classification of case (d) rovibrionic levels in terms of the symmetries of the levels of the core will also be considered briefly.

2. M. H. Alexander et al., to be published.

Address: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.
ON THE ESR OF SMALL CARBON CLUSTERS

D. W. EWING

Electron spin resonance (ESR) signals attributed to the linear \( \text{C}_2 \), \( \text{C}_6 \), \( \text{C}_8 \), and \( \text{C}_{10} \) molecules in their lowest \( ^1 \Sigma \) states, presumably their ground states, have recently been observed in solid neon and argon matrices at 4K. Hyperfine interaction in the \( \text{C}_n \) molecules was small, indicating small on-line bonding with the unpaired spins in p orbitals. The zero field splitting parameters, \( |D| \), were found to be 0.236, 0.363, 0.783, and 0.190 cm\(^{-1}\), respectively, in solid neon.

Ab initio molecular orbital calculations have been performed to help interpret this data. The increase in \(|D|\) through \( \text{C}_8 \) is attributed to a corresponding variation in the spin-orbit coupling with low lying states, principally the \( ^1 \Pi \) states. Cross orbital spin populations and \( \Delta E = X^1 \Sigma - ^1 \Pi \) energy differences were obtained from Hartree-Fock calculations in order to interpret the hfs and \(|D|\) data, respectively. For \( \text{C}_6 \) and \( \text{C}_8 \) electron correlation was included via second (MP2) and third (MP3) order Möller-Plesset perturbation theory.


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Ab Initio Calculations on \( \text{Ag}_2 \), \( \text{Au}_2 \), and \( \text{AgAu} \) Including Polarization Functions and Extended Electron Correlation

R.B. Ross and W.C. Ermler

Multi-configuration self-consistent field and configuration interaction calculations have been performed on \( \text{Ag}_2 \), \( \text{Au}_2 \), and \( \text{AgAu} \). Relativistic effective core potentials (RECP) and optimized valence basis sets of Slater-type functions, including f-type polarization functions, have been employed. Multi-reference single and double excitation electron correlation studies are reported. The effects of including f-type functions in the basis set and the necessary levels of electron correlation are discussed. Calculated spectroscopic constants are compared to experiment and to previous ab initio all-electron and RECP studies.

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VIBRATIONAL-ROTATIONAL ANALYSIS OF THE HYDROGEN PEROXIDE CATION FROM AB INITIO POTENTIAL ENERGY AND DIPOLE MOMENT SURFACES

Susan Kraft, Hsiuchin C. Hsieh and Walter C. Ermler

Results of ab initio unrestricted Hartree-Fock self-consistent field and Möller-Plesset perturbation theory calculations for the hydrogen peroxide cation are reported. A 6-31G** basis set was employed to compute energies on an extensive grid of nuclear configurations near the planar equilibrium geometry \( R_0 = 1.32 \text{ Å}, R_{OH} = 1.00 \text{ Å}, \angle_{HOO} = 104^\circ \). Analytical representations of potential energy and dipole moment surfaces were derived from least squares fits to the grid points and used to calculate spectroscopic constants, dipole moment expectation values and transition moments. A power series expansion to fourth degree in both normal and internal coordinates was used to obtain the spectroscopic constants, expectation values and intensities.

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AN AB INITIO STUDY OF CS AND H ADSORPTION ON BE METAL

M.M. Marino, M. Sawamura, and W.C. Ermler

Atomic cesium and hydrogen adsorption on beryllium clusters containing 19 and 33 atoms are studied using restricted Hartree-Fock calculations and ab initio relativistic effective core potentials. The clusters are taken as cylindrical plugs from a Be metal wafer. Be-Cs and Be-H internuclear distances are optimized, while Be-Be internuclear distances are frozen at the bulk metal values. For each system, numerous low-lying electronic states are investigated. The calculations are carried out to determine the effects of Cs and H adsorption on the electronic structure and work function of the systems. The cluster wave functions are Fourier transformed to obtain periodic wave functions and the relation between the finite cylinder and two-dimensionally extended bulk systems is discussed. The calculated ionization potentials for the cesiated systems are in agreement with the experimentally measured work function. Hydrogen is not predicted to adsorb on Be metal, which is consistent with recent experimental findings.\(^1\)

\(^1\)G.S. Tampa, M. Seidl, W.C. Ermler and W.E. Carr, Surf. Sci. 185 (1987) L453. This work was supported by the Air Force Office of Scientific Research.

Address: Stevens Institute of Technology, Hoboken, New Jersey 07030.
Ab Initio Calculations of Polarizabilities Including Relativistic Effects For Elements of Groups IA and IB

J.M. Powers, R.B. Ross and W.C. Ermler

The effects of relativity and the concept of core-valence separation have been examined with respect to polarizabilities for elements of groups IA and IB. The coupled Hartree-Fock method for atomic polarizabilities has been incorporated into an ab initio atomic self-consistent field program. Relativistic effects have been studied via ab initio calculations employing relativistic (REP) and nonrelativistic effective core potentials (NEP). The effects of re-definition of core and valence spaces have been studied by deriving REP's for heavy elements for a set of cases whereby fewer and fewer electrons are "frozen" into the core. In addition, core-valence correlation effects have been examined by calculating atomic polarizabilities via a finite-field formalism and configuration interaction calculations. The magnitudes of relativistic and core-valence correlation effects and the impact of definition of core-valence space are compared. The impact of this work on molecular studies employing effective potentials is discussed.

This work was supported through NSF Grant No. CHE-8712315

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Charge Stabilization of Excited Electronic States of CN-

C. S. Ewing and J. Tellinghuisen

On excitation with energetic particles or VUV radiation, alkali halide crystals doped with CN- display an ultraviolet spectrum which has been attributed to emission from an excited triplet state of CN- to the 1Σg ground state. This is despite the fact that there are expected to be no bound excited electronic states of CN- in vacuo. Although this metastable (τ ≈ 100 ms) species has previously been labeled 31Π in analogy with CO, there is some evidence it may be 32Σ+ as in N2.

We have computed the energies and spectroscopic properties of excited electronic states of CN- stabilized by counterion lattices, employing an ab initio MCSCF approach. Results will be presented both for the ground 1Σg state and for the low-lying 3Π and 3Σ states. These may be directly compared with experiment. We will also discuss the accuracies of differing countercharge models for simulating the effects of the lattice.

1M. Mendenhall et al., Chem. Phys. Letters (submitted).

An Approximate Ab-Initio Theory of Large Molecular Systems, G.P. Das

An approximate ab-initio method for treating molecular systems is presented. Important simplifications both in the nature of the wavefunction as well as the multicenter integrals makes the approach comparable in cost to some of the existing semi-empirical schemes, while leading to a more consistent and reliable characterization of properties of large systems than the latter. The method is applied to clusters, complexes and polymers.

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Electronic states of Na* and Na+: Calculated PE surfaces and molecular structures

G. H. Jeong, M. Brayer, and P. Labastie

All electronic states of Na* dissociating into 2Na3πv + Na* and some lowest states dissociating into Na3sV + Na3pπ + Na* are calculated in full valence CI using a flexible basis set. D, of the ground state 'A1 with respect to Na(3sV)T + Na* is 1.376 eV. A strong Jahn-Teller effect for the first excited state 'E leads to a linear 'Σ and an acute-angle 'A1 geometries. These states are stable with respect to dissociation into Na(3sV)T + Na*. Other three states are repulsive. Among the molecular states which can be made from Na3sV + Na3pπ + Na*, only the 'A1 state is quite stable (D, = 0.958 eV) with respect to dissociation into Na(3sV)T + Na*. The two Jahn-Teller partner states of 'E are very weakly bound.

The lowest states of Na* are also calculated in full VCI. The ground state (1B1) is stable by 0.290 eV with respect to dissociation into Na(3sV)T + Na3sV. The 1B1 state is only 0.021 eV lower than the 1A1 state and the conic intersection (1F1) lies 0.093 eV higher than the 1B1 state. The dynamic Jahn-Teller character of the lowest states and their bonding nature are discussed.

This work is expected to give precise energetic characteristics and electronic structures for the lowest states of Na* and Na+. The spectroscopic implications of the calculated potential energy curves will be discussed in light of recent experimental observations.

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EMISSION SPECTRUM OF SUPERSONICALLY COOLED BENZYL RADICAL

P. G. CARRICK AND J. I. SELCO

The rotationally cooled gas phase electronic emission spectrum of the benzyl radical was produced with a Corona Excited Supersonic Expansion (CESE). The cooled electronic emission spectrum of the toluene precursor was also observed. Rotational temperatures were estimated to be about 15 K. This is the first observation of emission from aromatic radicals in this source.

Most of the observed bands in both toluene (1B2 → 1A1) and the benzyl radical (2A2 → 2B2) are the result of emission from the lowest vibrational level in the electronic excited state. This suggests extensive vibrational cooling of these relatively large molecules in the CESE source.

Transitions from the second electronic excited state (2B2 → 1B2) in benzyl radical were observed, although greatly reduced in intensity compared to the (2A2 → 2B2) transition and previous gas phase emission spectra.1 The high degree of mixing1 between 2B2 and vibronic states of 1A2 introduces a mechanism that allows collisional electronic quenching to occur during the expansion via removal of vibrational energy.


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FLUORESCENCE SPECTROSCOPY OF PREDISSOCIATED LEVELS OF ELECTRONICALLY EXCITED $\text{S}_2$

Wafaa Fawzy and M. C. Heaven

We have re-examined the laser induced fluorescence spectrum of jet-cooled $\text{S}_2$. In the range of 31,000 to 35,500 cm$^{-1}$ the spectrum shows intense bands of the well-known $B^3\Sigma_u^+ - X^3\Sigma_g^-$ system, and weaker features which belong to the $B^3\Pi_u - X^3\Sigma_g^-$ transition. Predissociation to ground state atoms causes a "breaking off" of the emissions from both bands at energies above 35,570 cm$^{-1}$. However, we have now observed fluorescence from three fragmentary bands which lie at energies above the predissociation limit. One of these features is readily identified as the B-X, 10-0 band. Rotational analysis yields the constants $v_0=35,702.34$, $\lambda=1.3$ and $B_{10}=0.133$ cm$^{-1}$. The two other bands, which have origins at 35,668.54 and 35,723.84 cm$^{-1}$ are not part of the B-X system. The former shows P, Q, and R branches, and rotational perturbations which affect only the Q branch. The higher energy band has only P and R branches. The analyses of these fragmentary structures will be discussed.

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WAVELENGTH - RESOLVED FLUORESCENCE STUDIES OF THE COLLISION DYNAMICS OF $\text{Br}_2$ (B)

M. C. Heaven, E. A. Dorko, G. P. Perram, and L. Hanko

Continuous wave excitation and wavelength-resolved fluorescence techniques have been used to study the self-quenching and energy transfer kinetics of $\text{Br}_2$ (B). A self-quenching rate of 4x10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was observed for the levels with $v>10$, $J>15$, in excellent agreement with the results from pulsed measurements.$^1$ The rate constants for rotational energy transfer (summed over all final states) were found to be around 6x10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. An upper bound of 5x10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ was established for the vibrational energy transfer rate constant. The c.w. measurements are at variance with the energy transfer rate constants obtained from models of the time-resolved fluorescence decay kinetics.$^1$ The reason for these discrepancies will be discussed.

$^1$L. J. van de Burgt and M. C. Heaven, Chem. Phys. 103, 407 (1986)

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ELECTRONIC SPECTROSCOPY OF RARE GAS ISOLATED I₂ AND IBr

M. A. P. MACLER and M. C. HEAVEN

The electronic spectroscopy of I₂ and IBr, isolated in solid rare gas matrices has been studied using time and wavelength resolved fluorescence techniques.

Argon isolated I₂, excited at a wavelength of 193 nm, showed a broad feature at about 380 nm, that has a very short life-time (= 20 ns). This transition has been tentatively assigned as the D' (3P₁) - A' (3P₂) system.

Ar, Kr and Xe isolated IBr, excited at a wavelength of 532 nm, exhibited both A' (3P₁) - X' (3Σ) and A (3P₂) - X (3Σ) systems. The lifetimes of these transitions decrease with increasing atomic number of the host.

Spectral and temporal analyses will be discussed.

Work supported by AFOSR under grant 85-0210

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ON THE HARMONIC FORCE FIELD OF n-BUTANE

W. F. MURPHY

Ab initio quadratic vibrational force fields have been calculated for the trans and gauche conformers of n-butane, at the Hartree-Fock level with a 6-31G* basis set. Gas phase Raman trace scattering and infrared absorption spectra have been recorded for several isotopically substituted species. The assignment of the observed spectra is complicated because of the presence of the two conformers and, in the case of partially deuterated species, more than one isomer for each conformer, differing in the positions of the H and D atoms. The ab initio force fields must be scaled appropriately to reproduce the frequency assignments for the observed spectra. The current status of this work will be presented.

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ON THE LIMITS OF THE CONCEPT OF TRANSFERABILITY OF VIBRATIONAL PARAMETERS

WILLIS B. PERSON AND K. KUBULAT

Ab initio molecular orbital calculations have been carried out to predict the infrared spectra (frequencies and intensities) of a number of chemically related molecules. These include two different ethanethiol conformers, diethylsulfide, and their chlorinated derivatives, a number of fluorinated and alkylated derivatives of HPO and H$_2$POH, and several cytosine tautomers and methylated and fluorinated derivatives. Hence, we may examine the values calculated for force constants and dipole moment derivatives for chemically similar bonds (C=O, C=S, C=Cl, P=H, P=O, C=N, etc.) in these chemically different, but related, molecules to determine the limits that may be expected for the concept of transferability of these parameters. Selected examples from these systems will be presented and discussed.

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THE THEORY OF VIBRATIONAL CIRCULAR DICHROISM: ALTERNATIVE REPRESENTATIONS OF ATOMIC POLAR AND AXIAL TENSORS

P.J. Stephens, K.J. Jalkanen, R.D. Amos, N.C. Handy, P. Lazzeretti and R. Zanasi

Prediction of vibrational rotational strengths and vibrational circular dichroism (VCD) spectra requires the calculation of atomic polar tensors, $P_{ij}$, and atomic axial tensors, $M_{ij}$ [1,2]. Ab initio calculations of $P_{ij}$ and $M_{ij}$ tensors and, thence, of vibrational rotational strengths using coupled Hartree-Fock (CHF) perturbation theory have recently been reported [3-8]. In some cases [4,7,8], comparisons to experimental VCD spectra have been possible.

We discuss here the implementation at the ab initio level of alternative formalisms for $P_{ij}$ and $M_{ij}$ tensors. We report a previously unnoted representation of $P_{ij}$ tensors, involving the electronic momentum operator, and its implementation using CHF perturbation theory. Alternative representations of both $P_{ij}$ and $M_{ij}$ tensors in terms of nuclear electromagnetic shielding tensors, $\chi_{ij}$ and $\gamma_{ij}$ [9,10] are discussed. $\chi_{ij}$ exists in length, momentum and force representations; $\gamma_{ij}$ exists in angular momentum and torque representations. The calculation of $\chi_{ij}$ and $\gamma_{ij}$ have been implemented by means of the random phase approximation (RPA) [9]. Calculations on simple molecules are presented in order to exhibit the relative accuracies of the various formalisms now available for the calculations of $P_{ij}$ and $M_{ij}$ tensors. The implications for the ab initio calculation of VCD spectra are discussed.


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MEASUREMENT OF VIBRATIONAL CIRCULAR DICHROISM SPECTRA USING DISPERSIVE INSTRUMENTATION

F. Devlin and P.J. Stephens

We report improved dispersive instrumentation for the measurement of vibrational circular dichroism (VCD) spectra. The lower frequency limit is currently ~ 650 cm$^{-1}$ [1]. Measurements at ~ 5 cm$^{-1}$ resolution are practicable over the entire spectral range. Performance is documented using 3-methylcyclohexane and $\alpha$-pinene. New VCD spectra of several molecules will also be reported.


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VIBRATIONAL CIRCULAR DICHROISM OF β-LACTONES

K.J. Jalkanen, F. Devlin, P.J. Stephens, T. Polonski, R.D. Amos and N.C. Handy

The vibrational absorption and circular dichroism spectra of 3-methyl-2-oxetanone and 4-methyl-2-oxetanone have been measured. Scaled quantum-mechanical (SQM) force fields for these molecules have been obtained. Predictions of the absorption spectra and VCD spectra, using $\mathbf{P}_\alpha$ and $\mathbf{M}_\alpha$ tensors calculated ab initio at the SCF level, are compared to the experimental spectra.

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VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF MOLECULES CONTAINING SECOND-ROW ELEMENTS

R. Bursi and P.J. Stephens

The accuracy of ab initio predictions of vibrational circular dichroism (VCD) spectra of molecules containing H, C, N, O and F is becoming increasingly well-defined. However, no studies have been reported so far on molecules containing second-row atoms. We present calculations on several molecules containing second-row atoms. Scaled quantum-mechanical (SQM) force fields have been obtained for the molecules studied. Predictions are compared with existing experimental data.

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VIBRATIONAL SPECTRA OF TETRAFLUOROOXIRANE-16O AND 18O

NORMAN C. CRAIG, DIANE GESTY, AND ALLEN G. KASTELLE

The Raman spectrum of tetrafluorooxirane-16O (tetrafluoroethylene oxide-16: TFEO-16) has been obtained at -80°C. From this spectrum and a previous infrared study we have developed a complete assignment of the vibrational fundamentals. These fundamentals in cm$^{-1}$ are: (al) 1610, 1161, 792, 502, 320; (a2) 1240, 516, 234; (b1) 1128, 776, 696, 528, (b2) 1282, 558, 186. The newly available Raman spectrum led to revisions in the assignments for $v_7$, $v_{10}$, $v_{11}$, and $v_{12}$ and the replacement of estimates for $v_5$ and $v_8$. The assignments for $v_5$, $v_9$, and $v_{12}$ are supported by values of 306(17), 226(17), and 182(23) cm$^{-1}$, respectively, derived from vibrational satellites in the microwave spectrum.

From the infrared and Raman spectra of TFEO-18 the fundamentals in cm$^{-1}$ are: (a1) 1607, 1136, 789, 494, 321; (ag) 1240, 516, 234; (b1) 1127, 777, 679, 516; (b2) 1282, 539, 185. Because $v_1$ shifts very little with 18O substitution, this mode is not "ring breathing" but is CC stretching presumably raised in frequency by mixing with CF stretching and bond strengthening due to the fluorine substituents. Other modes that depend significantly on 18O substitution are $v_2$ (sym CO stretching), $v_{11}$ and $v_{12}$ (asym CO stretching), and $v_{14}$ (COC flapping).


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VIBRATIONAL SPECTRA OF 1-CHLOROCYCLOBUTENE

NORMAN C. CRAIG AND STEVEN S. BORICK

The gas-phase infrared spectrum and the liquid-phase Raman spectrum have been recorded for 1-chlorocyclobutene, which is a newly prepared substance. Much evidence in the literature on cyclobutenes indicates that the cyclobutene ring is essentially planar. The vibrational spectra for 1-chlorocyclobutene are consistent with a planar ring structure and Cs symmetry. The axis of least moment of inertia, a', is essentially parallel to the CCl bond. In the gas-phase infrared spectrum modes of a' symmetry have hybrid type-A/B band shapes, and modes of a'' symmetry have type-C band shapes. As a consequence of structural variety and some symmetry in this molecule, an essentially complete assignment of vibrational fundamentals is possible. The fundamentals in cm⁻¹ are: (a') 3090, 2947, 2940, 1594, 1452, 1434, 1250 (average of Fermi resonance doublet), 1192, 1164, 1120, 980, 969, 943, 299; (a'') 2980, 2966, 1070, 1016, 854, 751, (751), 395, 211. Of particular interest is the ring puckering frequency of 211 cm⁻¹ which compares with 325 cm⁻¹ in cyclobutene, 2 132 cm⁻¹ in 1-fluorocyclobutene, 2 132 cm⁻¹ in 3,3,4,4-tetrafluorocyclobutene, 3 and 98 cm⁻¹ in perfluorocyclobutene. 3


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INTEGRATED INTENSITIES OF CO$_2$ AND SF$_6$ VIBRATIONAL BANDS FROM 1800 TO 5000 cm$^{-1}$ AS A FUNCTION OF DENSITY AND TEMPERATURE

Michael F. Thomas and Milton J. Linevsky

The integrated intensities of selected vibrational bands of CO$_2$ and SF$_6$ are measured as a function of density at various temperatures using a BOMEM DA3.02 FTIR. Densities from 4x10$^{-5}$ to 2x10$^{-3}$ mole/cc and temperatures from 295K to 470K are examined. The spectral region covered is from 1800 cm$^{-1}$ to 5000 cm$^{-1}$.

Both allowed bands and collision-induced bands of CO$_2$ are measured. The integrated intensity for the allowed bands is linear in density and independent of temperature. The forbidden bands are due to collision-induced absorption and the integrated intensity is parabolic in density, again showing no observable temperature dependence.

Vibrational spectra of SF$_6$ are also examined. All the observed bands are infrared allowed. However, the integrated intensities of selected bands are quadratic in density, with the linear term dominating. The significance of the density squared term is currently not understood.

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STUDY OF ZEOLITE FRAMEWORK STRUCTURE AND ITS FORCE FIELD

BY VIBRATIONAL SPECTRA

HU JIEHAN AND NI JIANYI

Infrared spectroscopy has been widely used to study zeolites and vibrational bands have been empirically assigned. We have chosen T-O$_2$ (T=Si, Al) as a basic model of the D5R unit in ZSM-5 zeolite, and calculated it by four kinds of previous force fields, but none seems satisfactory.

This is because these previous force fields come from studies of silicates. So we have combined Badger's force field with Batsarov's. The results are in good agreement with the observed frequencies.

We have also used the normal coordinates to study the TO$_4$ tetrahedron and its variation with Si/Al ratio in X Y zeolites. We get the relationship between the bond length and Si/Al as well as frequencies. By adjusting stretching, bending and interaction constants we obtain a linear relationship between the T-O stretching constant and Si/Al ratio:

$$ FR = 2.595 \times \text{N4E} + 5.587 $$

The changes of the bending constant are very small.
FOURIER TRANSFORM INFRARED SPECTROSCOPY OF NITRIC OXIDE IN ELECTRIC AND MICROWAVE DISCHARGES

K.T.-. McNesby and R.A. Fifer

A multiple path length flow cell has been modified so that infrared Fourier transform absorption spectra are obtained of gases in which an electric discharge is occurring. Also, a microwave discharge flow cell has been constructed such that infrared Fourier transform absorption spectra may be obtained of gases undergoing excitation by the microwave radiation.

The work involved nitric oxide as the gas in which each type of discharge occurs. NO is the only diatomic molecule which shows a Q branch in the fundamental absorption spectrum in the infrared.1 The nitrosyl ion (NO+) is isoelectronic with CO, which does not possess a Q branch in the fundamental absorption spectrum. The effects of pressure and intensity of discharge on observed species in the discharge are discussed. Calculation of fundamental infrared absorption frequencies for the nitrosyl ion are compared with those observed experimentally.


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FOURIER TRANSFORM DETECTION OF THE \( \nu_3 \) FUNDAMENTAL OF THE \( \text{N}_3 \) RADICAL

C. W. BRAZIER, P. F. BERNATH, J. B. BURKHOLDER, AND C. J. HOWARD

We have observed the \( \nu_3 \) asymmetric stretching fundamental of the azide radical. \( \text{N}_3 \) was produced in a long pathlength absorption cell by the reaction of \( \text{HN}_3 \) with \( \text{Cl} \) atoms. The use of multipass mirrors gave an effective pathlength of about 100 m and absorption of up to 10% was seen for the strongest lines. The spectrum was recorded in 8 hours of averaging using a BOMEM Fourier transform spectrometer at a resolution of 0.004 cm\(^{-1}\). The vibrational frequency was found to be unusually low at 1645 cm\(^{-1}\), and lambda doubling was observed in both the \( ^2\Pi_{3/2} \) and \( ^2\Pi_{1/2} \) spin components.

The observed transitions and molecular constants will be presented.

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DIODE LASER SPECTROSCOPY OF ALKALI HALIDES

C. R. BRAZIER, M. DOUAY, AND P. F. BERNATH

The first overtone transitions of the alkali halides LiBr and NaF have been observed in absorption using a diode laser spectrometer near 10 μm. Both species were produced in the gas phase in a heat pipe oven at temperatures from 800 °C for LiBr to 1000 °C for NaF. Numerous hot bands were observed (up to 9–7) due to the high temperature and the increase in the transition strength of the overtones with increasing ν.

Molecular constants and RKR curves for the X1Σ+ states of LiBr and NaF will be presented.

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Progress on NH3:
More rotational assignments, a Hamiltonian for band origins, and modeling of N-H stretch intramolecular dynamics

Stephen L. Coy
and Kevin K. Lehmann

Our continuing application of microwave-detected microwave optical double resonance to rotational assignment of NH3: vibrational overtones and combination bands from 6000 cm−1 to 18000 cm−1 has lead to the assignment of several new bands. These include ν2 + ν3 − ν1 at about 6850 cm−1, and 3ν1 and 3ν2 both near 16100 cm−1. The Hamiltonian used to fit band origins in the N-H stretch overtone regions includes Darling-Dennison or local mode coupling which mixes ν1 and ν3, and the Fermi resonance between 2ν2, and the N-H stretches in an essentially phenomenological way but also uses x-k relations to reduce the number of independent parameters. With the assumption that all overtone intensity derives from the local mode state, this Hamiltonian leads directly to a time-dependent picture of delocalization of the initial local-mode state that would be created by a sub-picosecond light pulse. The five quanta region is shown to be local mode in character, but lower regions rapidly delocalize into normal mode components.

Address of Coy: Harvard Chemistry Department, 12 Oxford Street, Cambridge, MA 02138.
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INVESTIGATION OF HOT BAND TRANSITIONS OF NH3 IN THE 10 μm REGION

R. D'CUNHA, K. SINGH AND V. B. KARTHA

Intensity measurements and N2 pressure broadening studies have been carried out on several vibration rotation transitions in the a2Σ+ → X2Σ+ hot band of 14NH3, using a tunable diode laser system. The intensity data have been used to obtain precise values for the transition dipole moment of the hot band. Intensity measurements made by the direct and equivalent width methods will be compared. Results of optogalvanic studies in low pressure D.C. discharges through ammonia, using a line tunable CO2 laser will be presented and the role of hot bands in the interpretation of these signals will be discussed.

Address of D'Cunha, Singh and Kartha: Spectroscopy Division, Khanna Atomic Research Centre, Modular Laboratories, Trombay, Bombay 400 085, India.
Numerous transitions have been identified and assigned in the $\tilde{a}2v_4 \rightarrow \tilde{a}2$ hot band of $^{14}$NH$_3$ and $^{15}$NH$_3$, from the long-path Fourier transform spectra recorded with a White-type multiple reflection cell at the Kitt Peak National Observatory. Intensity perturbations in this band arising from the strong Coriolis resonance of the $s2v_4$ levels with the corresponding $v_2$ levels will be briefly discussed.

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Address of Guelachvili: Laboratoire d'Infrarouge, Associe au CNRS, Bat. 350, Universite Paris XI, 91405 ORSAY-Cedex, France.
HIGH RESOLUTION SUPERSONIC BEAM INFRARED SPECTRA OF ACETYLENE TETRAMER

Gary S. Bryant, R.O. Watts, and D.F. Eggers

Acetylene-helium mixtures were expanded to provide supersonic beams that were collimated with skimmers. Spectra were obtained with a color center laser scanned under computer control; absorption was detected by changes in beam energy deposition on a helium-cooled bolometer. A number of different bands have been found in the CH stretching region that can be associated with various acetylene clusters. Those due to dimers and trimers have already been reported.1,2

Two bands appear centered at 3261.3 and 3262.2 cm⁻¹; these are assigned as perpendicular and parallel fundamentals, respectively, of a symmetric top molecule and arising from the monomer v₁ mode coupled in different ways in the cluster. The structure in the perpendicular band has been assigned and fit as an oblate symmetric top. The rotational constants, combined with relative intensities of the parallel and perpendicular bands, lead to a suggested structure that has the molecules displaced from a symmetrical square planar arrangement. The molecular centers of mass are displaced above and below a reference plane, and molecular axes are also tilted with respect to the plane.


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THE STRUCTURE AND TUNNELING MOTION OF ACETYLENE DIMER STUDIED BY FREE-JET INFRARED ABSORPTION SPECTROSCOPY IN THE 14 µm REGION

Yasuhiro Ohshima, Yoshiyasu Matsumoto, Michio Takami, and Kozo Kuchitsu

Several infrared bands of C₂H₂ dimer have been recorded in the monomer v₅ band region by pulsed free-jet direct absorption spectroscopy with a frequency tunable diode laser. More than 100 transitions, located on the ~9 cm⁻¹ higher-frequency side of the monomer band origin, have been assigned to the a-type q₀₁, q₀₂, q₀₃, q₀₄, and q₀₅ transitions of a prolate asymmetric top. Each transition splits into three tunneling components, and the splitting between the lowest and highest components is 0.02-0.03 cm⁻¹. The distance between the centers of mass of the monomer subunits is determined to be 4.4 Å from the B and C constants. This distance is too large for a slipped parallel geometry of C₂h symmetry but is consistent with a hydrogen-bonded T-shaped geometry of C₂v symmetry where the bonded H and the adjacent C atoms are close to the van der Waals contact. The tunneling splittings and the intensity alternation due to the nuclear spin statistics are well accounted for in terms of the simultaneous internal rotation of two monomer subunits among four equivalent equilibrium T-shaped configurations.

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Address of Matsumoto and Takami: RIKEN, The Institute of Physical and Chemical Research, Wako, Saitama 351-01, Japan.
INFRARED DIODE LASER SPECTROSCOPY OF THE BF3 VAN DER WAALS COMPLEXES WITH RARE GASES

YOSHIIYASU MATSUMOTO, YASUHIRO OHSHIMA, MICHIKO TAKAMI, AND KOZO KUCHITSU

The high resolution infrared absorption spectra of van der Waals(vdW) complexes of BF3 with rare gases have been measured near the BF3 monomer ν4 band (ν4 = 1453.98 cm⁻¹). The vdW complexes of BF3 with Ne, Ar, and Kr were effectively formed in a supersonic free jet and the spectra were recorded by observing direct absorption of a tunable diode laser. The absorption lines of complexes were in the forest of the monomer band, however, the spectrum taken with the sample seeded in He helped to identify these lines out of monomer lines. The observed linewidths were in the range of 70 - 120 MHz mostly contributed by the instrumental and Doppler widths. Thus the lifetime of the vibrationally excited state is much longer than 10⁻⁹ sec.

A preliminary analysis of the observed spectra has been done by using a symmetric top rigid rotor Hamiltonian. The complex bands are all red shifted from the monomer band by -566, -1767, and -2571 cm⁻¹ for the complexes with Ne, Ar, and Kr, respectively. These shifts in the band origins show a good correlation with the polarizability of the rare gases.

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Address of Ohshima and Kuchitsu: Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, JAPAN

FAR-INFRARED SPECTRA OF HCI - RARE GAS VAN DER WAALS MOLECULES

A.R.W. MCKELLAR AND J.W.C. JOHNS

We have recorded spectra of the van der Waals molecules HCl-Ar and HCl-Xe in the far-infrared (20-120 cm⁻¹) using a Bomem spectrometer and a 20 m absorption path at low temperatures. This work extends to considerably higher resolution the earlier studies of Boom and van der Elsken on the same systems.

Spectra of HCl-Ar show numerous partially resolved features in the 20-40 cm⁻¹ region, and it is interesting to speculate exactly how these relate to the now extensively studied bands of this species as observed at very low temperatures in supersonic expansions by other workers. HCl-Xe shows especially strong and detailed spectra in the 40-60 cm⁻¹ region, where it almost appears that we resolve individual rotational lines. However, it is not clear whether the present spectra can be properly understood without significant assistance from theory or from other experiments.


Address of McKellar and Johns: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.
Spectra of $^3$P$_2$ - rare gas van der Waals molecules are being studied using long absorption paths (113-160 m) at low temperatures and a Bomem DA3.32 spectrometer. Among the interesting results are:

1. Low spectra of H$_2$-Ne, obtained at about 25 K, are much cleaner and better resolved than previously available results.
2. Spectra of O$_2$-Ar accompanying the $Q_1(1)$ transition are observed for the first time.
3. The first observed manifestation of the excited van der Waals stretching state (n=1) in this class of molecules is noted in the $Q_1(0)$ region of H$_2$-Ar.
4. Excellent spectra of H$_2$-Ar and H$_2$-Kr in the $S_1(0)$ (350 cm$^{-1}$) and $S_1(1)$ (590 cm$^{-1}$) regions have been obtained.

Detailed analysis of these results will result in improved 3-dimensional potential energy surfaces for the hydrogen-rare gas systems. Some new results on the H$_2$-O$_2$ and H$_2$-Kr molecules will also be presented.

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INFRARED SPECTRA OF HYDROGEN DIMERS

A.R.W. McKellar

(H$_2$)$_2$ was one of the first van der Waals molecules to be studied spectroscopically. However, since the pioneering work of Watanabe and Welsh$^1$ in 1964, there have been only 2 further experiments: a detailed study of the fundamental infrared spectrum,$^2$ and a study of the $^3P_2$ hyperfine spectrum,$^3$, which corresponds to the fundamental hydrogen stretching band, and an extension to the far-infrared (15-30 cm$^{-1}$) region, which corresponds to the H$_2$ pure rotational transitions. The experiments are performed with long absorption paths (113-160 m) of H$_2$ or O$_2$ at low temperatures (77 or <29 K) and moderate pressures (20-500 torr), using a Bomem interferometric spectrometer.

Spectra of (H$_2$)$_2$, in the far-infrared at 77 K now provide$^8$ experimental verification of the assignment of hydrogen dimers in Voyager spacecraft spectra of Jupiter and Saturn. Precise high resolution spectra of (H$_2$)$_2$ and (D$_2$)$_2$ in the fundamental band regions show details not previously detected. Most interesting is (D$_2$)$_2$ in the $S_1(0)$ region (3160 cm$^{-1}$), where almost 3 distinct rotational lines are resolved.


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FA14. (11:31)

FAR-INFRARED SPECTRUM OF THE HCl DIMER


The two high frequency modes of the HCl dimer have been partially analyzed by Ohashi and Pine.1 In an effort to identify and analyze the remaining 4 low frequency modes, we have recorded the spectra of HCl samples at low temperature (~140 K) with a long pathlength (20 m) in the 20-200 cm⁻¹ far-infrared region. The spectra were obtained with a Bomem DA3.002 spectrometer at a resolution of ~0.003 cm⁻¹ which was chosen to match approximately the expected dimer pressure broadening for the sample pressures used (5-8 torr).

In addition to the very strong pure rotational lines of the HCl monomer, rather weak but very extensive and congested spectral features were observed over almost the entire region studied; most if not all of these features are probably due to (HCl)₂. So far, we have tentatively assigned a band with an origin near 150 cm⁻¹ that appears to be the torsional fundamental of the dimer. It is analogous to the HF dimer band recently reported by von Puttkamer and Quack.2 We plan to record the spectrum of an enriched sample of HCl, and anticipate that this will simplify and strengthen the spectrum sufficiently that further analysis will be possible in the near future.


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FA15. (11:47)

CALCULATION OF THE TUNNELLING SPLITTING IN SEVERAL ROTATIONAL STATES FOR (HF)₂

Tucker Carrington and Philip R. Bunker

Kofranek, Lischka and Karpfen have done extensive ab initio calculations on (HF)₂.1 Their ab initio points have been fitted to an analytic form. Using this potential energy function tunneling splittings have been calculated by using a reaction path model. The reaction path, the steepest descent path in mass-weighted Cartesian coordinates, has been found. If (HF)₂ is approximated as a symmetric top (γ=0.998 for (HF)₂), it is particularly easy to calculate rotational-vibrational energy levels if the reaction coordinate is used as the large amplitude motion coordinate, because the effective moment of inertia tensor takes a very simple form.


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FA16. (12:03)

The 5 μm INFRARED SPECTRUM OF NH₃ COLLISION-BROKEN BY H₂

C. CHAPADOS AND G. BIRNBAUM

Measurements on mixtures of ammonia and hydrogen in the 5 μm region are reported. These measurements are made in a window region of ammonia in order to understand the behavior of the trough with increasing pressure of hydrogen. Using a 975 cm White cell, a series of measurements were performed on pure hydrogen, on pure ammonia and on the mixtures of the two in the pressure range from 35 to 120 psi at 36°c. The density dependance of these results and their significance will be discussed.

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THE MICROWAVE SPECTRUM OF DIFLUOROMETHANIMINE, CF$_2$=NH

P. GRONER, H. NANAIE, J. R. DURIG AND D. D. DESMARTEAU

During our investigation of CF$_2$=NCl and CF$_2$=NBr, we noticed that these compounds decompose in the Stark cell. The microwave spectrum of a common decomposition product has now been assigned. The assignment was difficult because the predominant b-type spectrum has only five R transitions between 12.4 and 40 GHz. With the correct assignment, three weak a-type R-transitions and many a-type Q-transitions could be identified. Utilizing the rotational constants $A = 11464.042(7)$, $B = 11151.888(7)$ and $C = 5643.146(7)$ MHz, the decomposition product has been identified as CF$_2$=NH. Centrifugal distortion and nuclear quadrupole coupling constants have also been obtained.

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MICROWAVE SPECTRUM AND STRUCTURE OF DIMETHYLAMINODIFLUOROPHOSPHINE

R. J. HARLAN, P. GRONER AND J. R. DURIG

The microwave spectra of dimethylaminodifluorophosphine-$_d_0$, (CH$_3$)$_2$NPF, and dimethylaminodifluorophosphine-$_d_3$, have been recorded from 26.5 to 39.0 GHz. The rotational spectra of five vibrational satellites in the $d_0$ compound and the ground states in the two $d_3$ compounds have been assigned and the rotational constants calculated. The determined structural parameters show that the molecule has a semiplanar configuration in which the phosphorus, nitrogen, and two carbons lie on the symmetry plane of the molecule. Additionally, analyses of the relative intensities of the series of excited states give a vibrational frequency of $35 \pm 10$ cm$^{-1}$ which is the NC$_2$ out-of-plane wag.

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MILLIMETER AND SUBMILLIMETER SPECTROSCOPY OF SMALL INTERNAL ROTORS

S. L. SHOSTAK, T. ANDERSON, R. L. CROWNover, E. C. SUTTON, E. HERBST, and F. C. DE LUCIA

Small internal rotor molecules possess a complex rotational spectrum due to the interaction of rotational and torsional degrees of freedom and to the existence of low-lying torsional excited states. At the Duke Microwave Laboratory, we have in recent years studied the rotational spectra of a variety of these species at frequencies up to 1 THz. We have also made corresponding advances in the analysis of the rotational spectra of small internal rotors, chiefly by extending the classical PAM and IAM techniques.

In the last year, we have started work on the spectrum of dimethyl ether and a novel method of analysis in which van Vleck perturbation theory is used only when appropriate. We have also continued work on the spectrum of HNO$_3$ $v_9$ and of methanol and its isomers. For HNO$_3$ $v_9$, we have extended our experimental studies of the torsional splittings to include states in which the symmetric top approximation to the splittings is invalid. We have analyzed all existing laboratory data for $^{12}$CH$_3$OH up to $J = 22$ on a supercomputer and have measured and assigned a large number of excited torsional state transitions in $^{13}$CH$_3$OH. In this talk, some of our recent progress will be discussed.

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PRESSURE BROADENING OF MILLIMETER WAVE TRANSITIONS OF HNO$_3$, NO$_2$, CF$_2$Cl$_2$, HDO, AND HOOH BY NITROGEN AND OXYGEN

T. M. GOYETTE, W. L. EBENSTEIN, S. L. SHOSTAK, F. C. DE LUCIA, and P. HELMINGER

Pressure broadening coefficients for nitric acid (HNO$_3$), nitrogen dioxide (NO$_2$), freon-12 (CF$_2$Cl$_2$), partially deuterated water (HDO), and hydrogen peroxide (HOOH) interacting with O$_2$ and N$_2$ have been measured. The data were recorded using a broadband mm wave spectrometer with pressures in the range of 0.1-1 torr. The sixteen nitric acid transitions represent a good selection of strong lines in the rotational spectrum from 230-460 GHz and make possible a systematic comparison with earlier theoretical calculations. Comparison shows larger pressure broadening coefficients than predicted by theory, in addition to a larger state to state variation. Two transitions from each of NO$_2$, CF$_2$Cl$_2$, HDO, and HOOH near 230 GHz were studied. Comparison among the results for all five molecules shows the expected qualitative relationship between broadening parameters, molecule sizes, and dipole moments.

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THE MICROWAVE SPECTRUM OF DIFLUOROMETHANIMINE, F.CNH

K. MOELLER, M. WINEWISSER, G. PAWELKE and H. BORGER

The rotational spectrum of difluoromethanimine, F.CNH, has been observed for the first time. In the region from 16 to 40 GHz 99 strong b-type transitions belonging to the branches \( b_{R_i} \) and \( b_{Q_i} \), and 4 weak a-type transitions belonging to the \( a_{Q_0} \) branch have been assigned. Most of the observed rotational lines show the effects of the nuclear quadrupole interaction due to the \(^{14}\)N nucleus. All assigned 103 transitions could be fitted to Watson's Hamiltonian with A-reduction in the \( I' \)-axis representation. The preliminary spectroscopic constants are: \( A = 11464.021 \) MHz, \( B = 11151.888 \) MHz, \( C = 5643.143 \) MHz, \( A, = 5.25 \) kHz, \( \delta, = 0.184 \) kHz, \( \Delta, = 9.555 \) kHz, \( \delta, = 2.175 \) kHz, and \( \Delta, = 5.087 \) kHz. These results confirm the assumption that F.CNH is a planar oblate asymmetric rotor molecule having \( C_2v \) symmetry with asymmetry parameters \( \kappa = 0.8927 \) and \( \beta = -0.02756 \), respectively. Further measurements in the millimeter wave region and the analysis of the nuclear quadrupole hyperfine structure of the individual rotational lines for F.CNH will be reported at the meeting.

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MICROWAVE SPECTRUM OF \(^{13}\)CD\(_3\)OH

I. MUKHOPADHYAY, K.V.L.N. SASTRY, AND R.M. LEES

In addition to contributing to the fundamental understanding of torsion-vibration interactions in methanol and its isotopic species, a spectroscopic study of \(^{13}\)CD\(_3\)OH is currently of interest in supporting identifications of optically-pumped far-infrared laser lines in this species, particularly the strong and efficient 127 \( \mu \)m FIR line reported not long ago.

In this work, the microwave absorption spectrum of \(^{13}\)CD\(_3\)OH has been investigated, and the a-type R-branch transitions have been measured for \( J=1 \) to \( J=2 \) for the lowest three torsional states. The asymmetry splittings were observed for the \( K=1 \) A transitions. In addition, frequencies have been measured for a substantial number of b-type transitions, including the \( K=0 \) E, \( K=2 \) E, and \( K=3 \) A Q branches. The frequencies are being fitted to a semi-empirical torsion-rotation model, and the a-type and b-type parameters will be reported.\(^{1}\)


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THE SUBMILLIMETER-WAVE SPECTRUM OF THE $^{12}$CH$_3$O AND THE $^{13}$CH$_3$O RADICALS

TAKAMASA MOMOSE, YASUHIKO ENDO, EIZI HIROTA, AND TADAMASA SHIDA

The pure rotational spectrum of the isotopically substituted methoxy radical $^{13}$CH$_3$O was observed in the millimeter and the submillimeter wave regions. The $^{12}$CH$_3$O radical was also studied in the same wavelength regions and the molecular parameters of the previous work were reexamined.

It was found necessary to add a few higher order terms for the centrifugal distortions of the rotation and the spin rotation interactions in order to analyze the spectrum in the submillimeter-wave region.

With reference to the rotational constants of CD$_3$O, the $r_0$ structure was determined. Parameters of the structure are $r$(CO)·1.3926A, $r$(CH)·1.1178A, and $<$HCO·113.8°.

The hyperfine coupling constants of the carbon nucleus were determined for the first time. The Fermi interaction constant was found to be -43.6MHz. The negative value is compared favorably with the result of ab-initio calculations.

It is emphasized that we have improved the accuracy of the molecular parameters by observing the submillimeter-wave spectrum of relatively low $J$ values alone, without having recourse to the information from the far-infrared LMR experiment as was done in our previous work.


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Address of Hirota: Institute for Molecular Science, Okazaki 444, Japan.
MILLIMETER WAVE ABSORPTION AND FAR INFRARED LASER MAGNETIC RESONANCE SPECTROSCOPY OF F02*
M. BOGEY, C. DEMUYCK, J. L. DESTOMBES, P. B. DAVIES AND T. J. SEARS

We have recorded many absorptions due to the F02 radical at frequencies between 130 and 270 GHz. The spectra are all weak, however we have assigned them to fine and hyperfine split components of a-dipole transitions between levels with 6<N<15 and 0<K<7. Analysis proved difficult because, in this species, the fine and hyperfine splittings are of the same order of magnitude for many levels. The millimeter wave data were fit together with a set of combination differences extracted from the infrared spectrum of the radical in order to determine the molecular parameters. The main uncertainty remaining lies in the K-dependent rotational parameters since no b dipole transitions have yet been assigned. We hope that predictions based on the current parameters will allow their detection by FIR LMR and progress will be reported at this meeting.

* Research performed in part under contract DE-AC02-76CH00014 with the U.S. Department of Energy.

THE DETERMINATION OF THE COMPLETE CHLORINE NUCLEAR QUADRUPOLE COUPLING TENSOR IN CHLOROTRIFLUOROETHYLENE
W. LEWIS-BEVAN, M. C. L. GERRY, E. BITTNER, K. W. HILLIG II, AND R. L. KUCZKOWSKI

Two different rotational assignments have been reported for C2F3Cl. The spectrum has been reexamined using a PTFW spectrometer. 255 components from 51 transitions were measured to a precision of a few KHz. The quadrupole coupling constants were evaluated by least squares fits using the exact quadrupole Hamiltonian. The fitting program simultaneously determined the rotational and centrifugal distortion constants. The calculated rms deviation of the fit was comparable to the measurement errors. It is noteworthy that the extensive and precise data set leads to a determination of $I_{ab}$ even when transitions likely to be perturbed by near degeneracies are left out of the fit. The results will be compared with the previous report.

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Address of Bittner, Hillig, and Kuczkowski: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.
THE MICROWAVE SPECTRUM OF KR.PF₃
K. H. HILLIG II, M. S. LABARGE, R. BITTNER, R. BORN, R. C. TAYLOR, AND
P. L. KUCZKOWSKI

The rotational spectrum of the weak complex between krypton and phosphorus trifluoride has been observed using a Fourier transform microwave spectrometer with a pulsed supersonic nozzle molecular beam source. The complex is an asymmetric top. The distance rₑₑ between the krypton atom and the center of mass of the PF₃ molecule is 4.072 Å and the angle between the rₑₑ vector and the C₁ axis of the PF₃ is 68.25°. The P₁ centrifugal distortion constants, the dipole moment and the ⁴¹Kr quadrupole coupling constants have also been determined. The results will be compared to those of Ar.PF₃.

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CONFORMATIONAL STUDY OF 1,2-AMINO ALCOHOLS BY VIBRATIONAL CIRCULAR DICHLROISM

N. RAGUNATHAN, L. A. NAFIE AND T. B. FREEDMAN

Vibrational circular dichroism spectra of (S)-(+-)1-amino-2-propanol and (S)-(+-)2-amino-1-propanol in tetrachloroethylene solvent have been obtained in the OH- and NH-stretching regions. In dilute solution, absorption bands corresponding to free OH and NH and to both OH--N and NH--O hydrogen-bonded species are observed. No VCD intensity is observed for the "free" OH or NH stretches. Negative VCD bands for v(NH<sub>2</sub>)<sup>s</sup<y<br>and v(NH<sub>2</sub>)<sup>y</sup>l are observed for NH--O conformations in both compounds. Only (S)-(+-)1-amino-2-propanol exhibits an intense negative OH-stretching VCD band for the OH--N species; no VCD corresponding to v(OH) is observed for (S)-(+-)2-amino-1-propanol. An interpretation of the VCD spectra based on the ring current mechanism will be presented that identifies the most abundant solution conformations in these amino alcohols.

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CIRCULAR DICHLROISM IN THE FAR INFRARED AND MILLIMETER WAVELENGTH RANGE: NEW TECHNIQUES

P. L. POLAVARAPU

The measurement of circular dichroism in the long wave length range is of special interest. Such measurements would permit the low frequency vibrations to be investigated as probes of molecular stereochemistry. Also the recent theoretical predictions that the circular dichroism is supported by the molecular rotational transitions of chiral molecules can be verified. In the last three years we have been investigating the feasibility of such measurements and identified two different procedures. In this presentation (1) A Martin-puplett interferometer operating in step-integrate mode and incorporated with path difference modulation will be shown to give circular dichroism as Cosine Fourier transform; (2) Tilt tunable waveplates (TTW) in combination with a rotating polarizer will serve as the sources for modulating circular polarization states. Hence dispersive monochromator coupled to TTW can be used to measure circular dichroism in the long wave length range. Necessary theoretical expressions for the above mentioned procedures are developed and will be presented. Preliminary measurements in the 50-1 cm<sup>-1</sup> region have also been carried out, in collaboration with Dr. J. R. Birch, at the National Physical Laboratory in December of 1987.

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ON THE CIRCULAR DICHLROISM MEASUREMENTS IN THE 800-600 cm<sup>-1</sup> RANGE

P. L. POLAVARAPU

Circular dichroism measurements in the 800-600 cm<sup>-1</sup> range were shown to be feasible about five years ago. Some of these earlier results were 'misinterpreted' recently. These differences will be clarified and new results will be presented.


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NEW DEVELOPMENTS IN RAMAN OPTICAL ACTIVITY

P. L. Polavarapu

Raman optical activity (ROA) is conventionally measured by modulating the incident laser polarization between right and left circular polarization states and measuring the difference in the scattered Raman intensities with a dispersive spectrograph. In this presentation a new procedure for measuring ROA using a Fourier transform technique based on Martin-Puplett interferometer will be explained. Two experimental quantities, namely the Stokes parameters $S_1$ and $S_3$ can be simultaneously measured.

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AB INITIO VIBRATIONAL PROPERTIES OF LARGE OPTICALLY ACTIVE MOLECULES: GLUCOSE ET AL.

P. K. Bose AND P. L. Polavarapu

The availability of supercomputers and sophisticated ab initio programs now permit detailed and reliable estimates of vibrational properties of large size molecules. In particular our efforts are concentrated on the ab initio vibrational normal coordinates and Raman optical activity (ROA). We will present the details of ab initio ROA calculations and a summary of other calculations we have carried out to date. $\alpha$-D-glucose represents the largest system ever attempted for ab initio vibrational properties.

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RAMAN OPTICAL ACTIVITY SPECTROMETER

M. Vavra AND T. Keiderling

A Raman optical activity ROA spectrometer has been constructed from a commercially available optical multichannel analyzer (OMA) and off the shelf optical and electro-optical components. A software driven interface for controlling the electrooptic modulator from the OMA computer is described. Acquisition, real time display, and storage of data are controlled by application programs written in the vendor supplied language. Data for depolarized ROA of $\alpha$-Pinene and $R +$ Limonene will be presented.

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VIBRATIONAL CIRCULAR DICHROISM OF S-2,2'-DIMETHYL-6,6'-DIAMINOBIPHENYL

C. N. Su, M.-C. Tissot, T. A. Keiderling

We have measured the VCD spectra of the title compound in the near and mid-ir and have compared the results to predictions of the coupled oscillator model. A consistent interpretation was found for the sym NH stretch, $C_6$ ring deformation and CN stretch modes with the expected 60 degree tilt of the phenyl rings.

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VIBRATIONAL ANALYSIS AND VCD OF TRANS-1,2-DICYANOCYCLOPROpane

Adel A. EI-Azhary and Timothy A. Keiderling

FT-IR and Raman spectra were measured for trans-1,2-dicyanocyclopropane and its trans-1,2-d2 isotope. Force fields from 6-31G* and 4-31G calculations were scaled and optimized in a conventional manner. The resulted force fields were used to perform FPC and LMO calculations on the above two isotopes. FTIR-VCD were measured in the mid-IR region; dispersive VCD was measured previously in the CH and CN stretch regions. Comparison was made between the experimental and calculated results. The results show that these two methods of calculation failed to reproduce the experimental results. A priori results by Jalkanen et al. showed a better agreement.


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VIBRATIONAL CIRCULAR DICHIROISM OF 1,3-DIDEUTERIOALLENE, CALCULATIONAL RESULTS

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We have developed a refined force field for allene starting from an ab initio quantum mechanical calculated force field and using vibrational data from five isotopomers. VCD calculations were done at the coupled oscillator, FPC, LMO, APT and a priori levels. The latter used three different basis sets and two gauge formulations. In terms of dipole strengths, the higher level calculations did better with the LMO being off for the C=C=C and the FPC being generally poor. In the absence of experimental VCD, the calculations were all compared to triple zeta level results with the a priori calculation in the distributed origin gauge. In detail, the models showed extensive disagreement, even for the CH stretches. However, the gross patterns were qualitatively present in all the calculations with the restrictions that only large VCD be considered and that only the net VCD over close lying bands be evaluated. While there is no doubt that the FPC is quantitatively inadequate for both dipolar and rotational strength analysis, these results imply that there may be a qualitative use for these simpler models if the proper restrictions are taken into account.

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COLLECTION OF ROA SPECTRA USING LINEAR INCIDENT POLARIZATION

K. M. Spencer, T. B. Freedman, and L. A. Nafie

The symmetry involved in a Raman optical activity (ROA) experiment allows reversal of the traditional experimental geometry. An ROA spectrum can be obtained by focusing linearly polarized incident radiation on the sample and collecting the Raman scattered left and right circularly polarized light, rather than comparing the Raman scattering intensities for left and right circularly polarized incident radiation.

A simple apparatus has been built at Syracuse University which allows collection of Raman scattered circularly polarized light by means of a zero order quarter wave plate, a linear polarizer, a spectrograph and a multichannel detector. Preliminary results for the depolarized ROA of (+)- and (-)-pinene will be presented. Advantages of this ROA apparatus, which include stability, throughput, and reproducibility, will be discussed. Problems encountered with this system and efforts to overcome them will also be addressed.

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VIBRATIONAL CIRCULAR DICHRISM STUDIES OF EPHEDRINE AND RELATED MOLECULES

T. B. FREEDMAN, N.-S. LEE, AND L. A. NAFIE

Vibrational circular dichroism spectra of (1R,2S)-ephedrine, (1R,2S)-norephedrine, (1R,2R)-pseudoephedrine and (1R,2R)-norpseudoephedrine in the CH-stretching region will be presented. The most abundant conformations of these pharmacologically active molecules in CDCl₃ and in D₂O solution at high and low pH can be deduced from the sign and magnitude of the methine stretching VCD bands for chiral centers 1 and 2. The interpretation is based on application of Rule 1 of the ring current mechanism, due to current in OH--N or NH--O intramolecularly hydrogen-bonded rings. The VCD spectrum of norephedrine is consistent with only one of the two gauche conformations indistinguishable by NMR. The trans conformer is preferred in norpseudoephedrine.

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VIBRATIONAL CIRCULAR DICHRISM OF SMALL PEPTIDES AND PEPTIDE MODELS IN SOLUTIONS: EXPERIMENTAL DATA AND CALCULATIONS

S. M. ROBERTS, O. LEE and M. DIEM

We have observed VCD in the amide I, II and III region of peptides in aqueous solution (1250 - 1750 cm⁻¹), and for certain amino acids down to 900 cm⁻¹ in heavy water. VCD of peptide models was obtained from solutions in aqueous as well as organic media. Strong coupling of amide I vibrations was observed even in very small peptides in solution. This coupling is interpreted in terms of a stable solution conformer. The coupled oscillator formalism is used to deduce the angles between the interacting transitions.

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VIBRATIONAL CIRCULAR DICHROISM OF OLIGO-NUCLEOTIDES: EXPERIMENTAL DATA AND CALCULATIONS

M. OLOTTA and M. DIEM

We have observed VCD in the base carbonyl stretching region (1550 - 1750 cm⁻¹) of model oligo-nucleotides in buffered aqueous solution. Our experimental results agree well with those reported by Keiderling [1]. We have initiated a detailed study of the VCD as a function of the nucleotide chain length, salt concentration and temperature. Methods to reproduce the observed VCD data via an extended "Coupled Oscillator" will be presented.


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