Forty-Third

symposium on

MOLECULAR SPECTROSCOPY

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THE OHIO STATE UNIVERSITY

June 13-17, 1988

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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

ACCOMMODATIONS. The schedule for dormitory accommodations is listed in Drackett Tower on Curl Drive.

BANQUET. This will take place at the Center for Tomorrow on Thursday June ... 1985 at 7:00 p.m. preceded by a reception starting at 6:00 p.m. Nobel Laureate Kenneth Wilson from Cornell University will speak on "A PHYSICIST LOOKS AT ELECTRONIC STRUCTURE".

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

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

REGISTRATION: The Registration Desk will be located in Room 1008, Physics Laboratory. It will be kept open between 8:00 a.m.—Noon and 1:00—4:30 p.m., Monday through Friday. The registration fee is $55.00 per participant and $50.00 if paid by June 1. The special rate of $20.00 per Graduate Student will be reduced to $18.00 if paid by June 1. Please send the completed registration form along with your check by June 1.

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

THE OHIO STATE UNIVERSITY

1. Taylor Tower

2. Independence Hall

3. Post Office

4. Physics Laboratory
   (Smith Lab)

5. Evans Laboratory

6. Drackett Tower
   (Check-In)

7. Electronics Laboratory

8. Faculty Club

REPORT DOCUMENTATION PAGE

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K. Narahari Rao

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FIELD	GROUP	SUB-GROUP	

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

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.

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Professor E. BRIGHT WILSON

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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.

MONDAY, JUNE 13, 1988 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman Before Intermission: WAFAA FAWZY, Department of Chemistry, Emory
University, Atlanta, Georgia.

Chairman After Intermission: L. HALONEN, Department of Physical Chemistry,
University of Helsinki, Helsinki, Finland.

ME1. OPTICAL DESIGN OF EFFICIENT ABSORPTION SAMPLING SYSTEMS FOR FTIR SPECTROMETERS...10 min.(1:30)

WM. 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.

ME.4. 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 CH_2Cl_2 AND CD_2Cl_2 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.(3:15)

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   CANCELLED
Giessen, Heinrich-Buff-Ring 58, D-6300 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)

Vl. G. TYUTEREV, Institute of Atmospheric Optics SB USSR Academy of
Sciences, 1, 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 J569, 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)

WAFAA FAWZY, Department of Chemistry, Emory University, Atlanta,
Georgia, 30322; and JON T. HOUGEN, Molecular Spectroscopy Division,
National Bureau of Standards, Gaithersburg, Maryland, 20899.

ME12. RENNER-TELLER ROVIBRONIC SPECTRUM OF THE HCS RADICAL AND THE
ROVIBRATIONAL SPECTRUM OF HCS⁻..10 min.(4:51)

P. ROSMUS, N. C. HANDY, University Chemical Laboratory, University of
Cambridge, United Kingdom; J. SENEKOWITSCH, S. CARTER, Department of
Chemistry, University of Frankfurt, Frankfurt, Germany; and
H.-J. WERNER, Department of Chemistry, University of Bielefeld,
Bielefeld, Germany.

ME13. BOUND ROVIBRATIONAL STATES OF HeN_2^+..10 min.(5:02)

S. MILLER, J. TENNYSON, Department of Physics, University College,
London, United Kingdom; B. FOLLMEG, Department of Chemistry, University
of Frankfurt, Frankfurt, Germany, P. ROSMUS, University Chemical
Laboratory, University of Cambridge, Cambridge, United Kingdom; and
H.-J. WERNER, Department of Chemistry, University of Bielefeld,
Bielefeld, Germany.

IMPORTANT--PLEASE ACT   THANK YOU

RAO

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 dis-
cussion 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 13, 1988 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman Before Intermission: COLAN LINTON, 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)

B. SIMARD, S. A. MITCHELL, and P. A. HACKETT, Laser Chemistry Group,
Division of Chemistry, National Research Council of Canada, Ottawa,
Ontario, Canada, K1A 0R6.

MF2. NEW INFRARED ELECTRONIC SPECTRA OF C_2 AND SiC...................................15 min.(1:41)

M. DOUAY, LSM, Universite des Sciences et Techniques de Lille,
59655 Villeneuve d'Ascq, France; R. A. NIETMANN, C. R. BRAZIER,
L. C. O'BRIEN, P. F. BERNATH, 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. RODGERS 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. KRISHNAMACHARI, 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.(2:28)

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 Laboratoires, 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, Vanadisvägen 9, S-113 46 Stockholm,
Sweden; and S. O'CONNOR, Department of Physics, University College
Dublin, 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 $B^3\Sigma_u^-$ STATE OF MOLECULAR OXYGEN.............................15 min.(3:27)

R. S. FRIEDMAN and A. DALGARNO, Harvard-Smithsonian Center for Astro-
physics, 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.

GUO BUJIN and C. LINTON, Department of Physics, University of
New Brunswick, P.O. Box 4400, Fredericton, New Brunswick, Canada,
E3B 5A3.

C. LINTON and D. N. HEUFF, Department of Physics, University of
New Brunswick, P.O. Box 4400, Fredericton, New Brunswick, Canada,
E3B 5A3.

B. McFEETERS, L. HANKO, G. P. PERRAM, and E. A. DORKO, AFWL/ARBI,
Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico,
87117-6008.

M. C. VAN HEMERT, Department of Chemistry, Gorlaeus Laboratories,
Leiden University, Postbus 9502, 2300RA Leiden, The Netherlands;
and S. D. PEYERIMHOFF, Lehrstuhl fuer Theoretische Chemie,
Universitaet Bonn, Wegelerstrasse 12, D 5300 Bonn 1, Federal
Republic of Germany.

THE FOLLOWING PAPER WAS INADVERTENTLY OMITTED FROM THE PRELIMINARY PROGRAM

S. PADDI REDDY and C.V.V. PRASAD, Department of Physics,
Memorial University of Newfoundland, St. John's, Newfoundland,
Canada, A1B 3X7.

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.

Chairman: ??? ? SANDS, Department of Chemistry, San Jose State University,
San Jose, California ?????.

MG1. THE "RED" AND ? ... ?: CYANOGEN-LIKE EMISSION IN A SUPERSONIC JET..............15 min.(1:30)

S. ? OBRIEN, ?. ? MANURY, and ?. ?. RIVERS, Department of Chemistry,
Virginia Commonwealth University, Richmond, Virginia, 23284-2006.

MG2. PHOTO-ASSISTED FRAGMENTATION SPECTROSCOPY BY NEUTRALIZATION-REIONIZATION
MASS SPECTROMETRY..15 min.(1:46)

SUSAN E. STIMSON and GREGORY L. GELLENE, Department of Chemistry,
University of Notre Dame, Notre Dame, Indiana, 46556.

MG3. EXCITATION AND DISPERSED FLUORESCENCE SPECTRA OF THE ETHOXY FREE RADICAL..........15 min.(2:02)

STEPHEN C. FOSTER, Department of Chemistry, Florida State University,
Tallahassee, Florida, 32306; PRABHAKAR MISRA, L.-Y. LIN, CELESTINO P. DANG,
CHRISTOPHER ?. CASTER, and TERRY A. MILLER, Laser Spectroscopy Facility,
Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

MG4. LASER EXCITATION AND DISPERSED FLUORESCENCE SPECTRA OF METHOXY PRODUCED BY
PHOTODISSOCIATION IN A PULSED SUPERSONIC JET EXPANSION...........................15 min.(2:18)

STEPHEN C. FOSTER, Department of Chemistry, Florida State University,
Tallahassee, Florida, 32306; PRABHAKAR MISRA, L.-Y. LIN, CELESTINO P. DANG,
CHRISTOPHER ?. CASTER, and TERRY A. MILLER.

MG5. LASER DISPERSED EMISSION AND C_2H_3 $^2B_2$, X~He, NeOR Ar I IN A SUPERSONIC JET.....15 min.(2:34)

L.-Y. LIN, TERRY A. MILLER, Laser Spectroscopy Facility, Department of
Chemistry, The Ohio State University, Columbus, Ohio, 43210; RICHARD A.
KENNEDY, Department of Chemistry, The University of Birmingham,
P.O. Box 363, Birmingham, B15 2TT, United Kingdom; and DAVID A. DOLSON,
Department of Chemistry, Murray State University, Murray, Kentucky, 42071.

MG6. PHOTOPHYSICS OF AZULENE FROM S_1 MANIFOLD................................10 min.(2:50)

SHOBIE K. SULKALNI and JONATHAN E. KENNY, Department of Chemistry, Tufts
University, Medford, Massachusetts, 02155.

MG7. RESONANCE RAMAN INTERFERENCE IN LINEAR POLYENES.........................15 min.(3:02)

L. SZLAINECH and G. E. LEROI, Department of Chemistry, Michigan State
University, East Lansing, Michigan, 48824.

Intermission

MG8. CHARACTERIZATION OF EXCITED ELECTRONIC STATES OF LIGAND-BRIDGED Ru(II)
BIMETALLIC COMPLEXES BY RESONANCE RAMAN SPECTROSCOPY........................15 min.(3:30)

C. FERRO, P. J. WAGNER, and G. E. LEROI, Department of Chemistry, Michigan
State University, East Lansing, Michigan, 48824.

MG9. FLUORESCENCE EXCITATION SPECTROSCOPY OF p-$C_6H_4Cl_2$ AND p-$C_6D_4Cl_2$ IN A SUPERSONIC
FREE JET EXPANSION...15 min.(3:46)

W. D. SANDS and R. MOORE, Department of Chemistry, Virginia Commonwealth
University, Richmond, Virginia, 23284.

MG10. ULTRA HIGH-RESOLUTION ELECTRONIC SPECTROSCOPY IN MOLECULAR BEAMS.
THE $S_1 \leftarrow S_0$ TRANSITION OF 1-FLUORONAPHTHALENE........................15 min.(4:02)

D. F. PLUSQUELLIC, W. A. MAJEWSKI, and D. W. PRATT, Department of
Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

MG11. CONFORMATIONAL CHANGE ON ELECTRONIC EXCITATION. THE LOWEST EXCITED TRIPLET
AND SINGLET STATES OF ACETOPHENONE AND 2-METHYLPYRAZINE.....................15 min.(4:18)

L. L. LOMER, S. YAMAUCHI, and D. W. PRATT, Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

MG12. ROTATIONALLY RESOLVED PHOSPHORESCENCE EXCITATION SPECTRUM OF p-BENZOQUINONE
IN A SUPERSONIC JET. ORBITAL SYMMETRY OF THE LOWEST TRIPLET STATE..............15 min.(4:34)

L. E. JOHNSON, S. YAMAUCHI, and D. W. PRATT, Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

MG13. HIGH RESOLUTION ABSORPTION SPECTRUM OF THE MOLECULAR EIGENSTATES OF PYRAZINE.....15 min.(4:50)

W. M. VAN HERPEN, P.A.M. UIJT DE HAAG, and W. LEO MEERTS, Fysisch
Laboratorium, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

MG14. INTERSYSTEM CROSSING IN NAPHTHALENE AT ROTATIONAL RESOLUTION......................15 min.(5:06)

P.A.M. UIJT DE HAAG and W. LEO MEERTS, Fysisch Laboratorium,
Toernooiveld, 6525 ED Nijmegen, The Netherlands.

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

NOVEMBER 2-7, 1988

International Conference on
Raman Spectroscopy and Raman
Centenary Celebration

Calcutta, India

JUNE 19-23, 1989

7th International Conference
on Fourier Transform Spectroscopy

George Mason University
Fairfax, Virginia

FOR MORE INFORMATION CONTACT:

Dr. Dusan Papousek
Czechoslovak Academy of Sciences
Dolejsova ul 3
182 23 Praha 8
Czechoslovakia

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

Dr. Robert F. Cozzens
George Mason Institute
George Mason University
Fairfax, VA. 22030-4444

Presiding/Session Chairman: JOHN S. WINN, Department of Chemistry, Dartmouth
College, Hanover, New Hampshire.

Incoming Chairman/Presiding: LESTER ANDREWS, Department of Chemistry, University
of Virginia, Charlottesville, Virginia.

MH1. INFRARED SPECTRUM AND STRUCTURE OF THE $AlCH_4$ MOLECULE IN SOLID ARGON.............15 min (1:30)

LAURENT MANCERON, Laboratoire de Spectrochimie Moléculaire,
CNRS, LA0508, Université Pierre et Marie Curie, 4 Place Jussieu,
75005 Paris, France; and LESTER ANDREWS, Department of Chemistry,
University of Virginia, Charlottesville, Virginia, 22901.

MH2. MATRIX REACTIONS OF OXYGEN ATOMS WITH P_4. INFRARED SPECTRA OF P_4O,
P_4, P, AND PO...15 min.(1:46)

LESTER ANDREWS and ROBERT WITHNALL, Department of Chemistry,
University of Virginia, Charlottesville, Virginia, 22901.

MH3. INFRARED SPECTROSCOPY AND PHOTOCHEMISTRY ON SALT FILMS.....................15 min.(2:02)

J. BERG and G. E. EWING, Department of Chemistry, Indiana University,
Bloomington, Indiana, 47405.

MH4. "ISOELECTRONIC" TRANSITION-METAL DIATOMIC MOLECULES:
ScNi, ScPt, YNi, YPd...10 min.(2:15)

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

MH5. S = 4 AND S = 5 SPIN STATES OF THE "ANTIFERROMAGNETIC" Mn_2 MOLECULE.............10 min.(2:29)

M. CHEESEMAN, R. J. VAN ZEE, and W. WELTNER, JR., Department of
Chemistry, University of Florida, Gainesville, Florida, 32611.

MH6. ESR OF TRANSITION METAL DIATOMIC IONS: Mn_2^+...............................10 min.(2:40)

R. J. VAN ZEE, M. CHEESEMAN, and W. WELTNER, JR., Department of
Chemistry, University of Florida, Gainesville, Florida, 32611.

Intermission

MH7. FTIR ISOTOPIC STUDY OF THE C_3H RADICAL IN AN ARGON MATRIX AT 9 K.................15 min.(3:05)

JIUNWOEI HUANG and W.R.M. GRAHAM, Department of Physics, Texas Christian
University, Fort Worth, Texas, 76129.

MH8. HIGH RESOLUTION, HIGH DILUTION SPECTRA OF OCS IN Ar, N_2, AND Xe................15 min.(3:21)

VALERIE I. LANG, Jet Propulsion Laboratories, 183-301, 4800 Oak Grove
Drive, Pasadena, California, 91109; and JOHN S. WINN, Department of
Chemistry, Dartmouth College, Hanover, New Hampshire, 03755.

MH9. SPATIALLY-RESOLVED MATRIX ISOLATION ACTION SPECTRA OF $Cr(CO)_6$....................15 min.(3:37)

VALERIE I. LANG, Jet Propulsion Laboratories, 183-301, 4800 Oak Grove
Drive, Pasadena, California, 91109; and JOHN S. WINN, Department of
Chemistry, Dartmouth College, Hanover, New Hampshire, 03755.

MH10. THE EFFECT OF HYDROGEN BONDING ON THE VIBRATIONAL SPECTRUM OF t-HOCO
TRAPPED IN SOLID Ar AND CO...15 min.(3:53)

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

MH11. INFRARED SPECTRA OF H_2O AND D_2O ON SODIUM CHLORIDE FILMS........................10 min.(4:09)

J. REYNOLDS, K. PENSAK, C. A. BAUMANN, Department of Chemistry,
University of Scranton, Scranton, Pennsylvania, 18510; and B. STONE,
Department of Chemistry, San Jose State University, San Jose,
California, 95192.

MH12. SPECTRA AND ISOTHERMS OF NITROSOTRIFLUOROMETHANE (CF_3NO) ON SODIUM
CHLORIDE FILMS..15 min.(4:20)

J. REYNOLDS, K. MILLER, K. PENSAK, and C. A. BAUMANN, Department of
Chemistry, University of Scranton, Scranton, Pennsylvania, 18510.

MH13. INFRARED SPECTROSCOPY OF CO ON NaCl(100)....................................15 min.(4:36)

H.-C. CHANG, G. E. EWING, Department of Chemistry, Indiana University,
Bloomington, Indiana, 47405; and H. H. RICHARDSON, Department of
Chemistry, Ohio University, Athens, Ohio, 45701.

MH14. ELECTROSTATIC MODELING OF HCN ADSORBED ON NaCl(100)..............................15 min.(4:52)

D. S. ANEX, Department of Chemistry, Indiana University, Bloomington,
Indiana, 47405.

MH15. TBA WILL BE PRESENTED HERE (BRUCE S. AULT)........................ ....10 min.(5:08)

MH16. TBA WILL BE PRESENTED HERE (BRUCE S. AULT)....................................10 min.(5:19)

44TH MOLECULAR SPECTROSCOPY SYMPOSIUM
JUNE 12-16, 1989

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, 1988 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairman Before Intermission: G. 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..............................INVITED PAPER............................30 min.(8:30)

  A. F. KRUPNOV and E. N. KARYAKIN, Applied Physics Institute, USSR
  Academy of Sciences, Gorky, USSR 603600.

TA2. OPTOTHERMAL-INFRARED AND PULSED-NOZZLE FOURIER-TRANSFORM MICROWAVE
SPECTROSCOPY OF RARE GAS-CO_2 COMPLEXES..15 min.(9:03)

  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 CO_2 DIMER AND TRIMER AND RARE GAS-CO_2
COMPLEXES...15 min.(9:19)

  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.(9:35)

  A. S. PINE and G. T. FRASER, Molecular Spectroscopy Division,
  National Bureau of Standards, Gaithersburg, Maryland, 20899.

TA5. OPTOTHERMAL SPECTROSCOPY OF HF COMPLEXES WITH CO_2, OCS, AND NO...................15 min.(9:51)

  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. LAFFERTY, 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 NO_2 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
  British Columbia, Vancouver, British Columbia, Canada, V6T 2A6.

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 $(H_2O)_2$ K=1 TRANSITIONS OF E SYMMETRY AND DISCUSSION OF
NUCLEAR HYPERFINE SPLITTINGS...15 min.(11:07)

  A. HU and T. R. DYKE, Department of Chemistry, University of Oregon,
  Eugene, Oregon, 97403.

TA10. ROTATIONAL SPECTRA OF CARBOXYLIC ACID DIMERS...................................15 min.(11:23)

  W. KRESA and A. BAUDER, Laboratorium für Physikalische Chemie,
  Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.

TA11. Z2 WILL BE PRESENTED HERE (D. DAYTON)...10 min.(11:39)

TA12. Z3 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. EGGERS, Department of Chemistry, University of Washington, Seattle, Washington.

TB1. ANALYSIS OF THE ν_6 BAND IN CH_2DF, AND ASSIGNMENT OF SOME SMMW LASER LINES..15 min.(8:30)

> D. F. EGGERS, Department of Chemistry BG-10, University of Washington, Seattle, Washington, 98195; W. LEWIS-BEVAN, M.C.L. GERRY, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, VT6 1Y6; M. S. TOBIN, and T. W. DALEY, U.S. Army Electronics, Research and Development Command, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, Maryland, 20783.

TB2. THE INFRARED SPECTRUM OF AMINODIFLUOROBORANE, NH_2BF_2: PARTIAL ASSIGNMENT OF THE FUNDAMENTALS AND ANALYSIS OF THE 2^1_0 BAND NEAR 1608 CM^{-1}...................15 min.(8:46)

> W. LEWIS-BEVAN, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois, 62901; H. M. JEMSON, Sci-Med New Zealand Limited, 60-66 France Street, South Newton, 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, V6T 1Y6.

TB3. HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CH_2F_2: THE ν_8 BAND AT 1435 CM^{-1}........15 min.(9:02)

> R. D'CUNHA, P. K. WAHI, V. 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)

> YUKARI MATSUO, 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 ν_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 SIDEBANDS................................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 G. MAGERL, Institut für Nachrichtentechnik, Technische Universität Wien, Gusshausstr. 25, A-1040 Wien, Austria.

TB8. COLOR CENTER LASER SPECTROSCOPY OF C_2H AND $^{13}C_2H$................................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 F. SCAPPINI, Istituto Di Spettroscopia 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. MAKI, WM. B. OLSON, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899; R. ESCRIBANO, Instituto de Estructura de la Materia, Serrano 119 - 28006 Madrid, Spain; A. GOLDMAN, Department of Physics, University of Denver, Denver, Colorado, 80208; J. BURKHOLDER, and C. H. HOWARD, NOAA Aeronomy Laboratory, 325 Broadway, Boulder, Colorado, 80303.

TB11. A FORBIDDEN BAND IN THE FAR INFRARED SPECTRUM OF $H^{13}CNO$..........................15 min.(11:20)

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

TB12. THE LOWEST SKELETAL BENDING MODE OF N_2O_5 IN THE GAS PHASE......................10 min.(11:36)

F. DELUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706; M. WINNEWISSER, B. P. WINNEWISSER, Physikalisch-Chemisches Institut, Justus Liebig Universität, D6300 Giessen, West Germany; and G. PAWELKE, FB 9, Anorganische Chemie, Gesamthochscule Wuppertal, D5600 Wuppertal 1, West Germany.

TB13. HIGH RESOLUTION INVESTIGATION OF CH_3CHO IN THE INFRARED..........................10 min.(11:47)

I. KLEINER, M. GODEFROID, 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; M. D. 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 0R6.

TB14. 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.

TUESDAY, JUNE 14, 1988 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chairman: DAVID CATLETT, Samford University, Birmingham, Alabama, 35229.

TC1. PHOTOFRAGMENTATION OF JET-COOLED ACETIC ACID.....................................15 min.(8:30)

S. S. HUNNICUTT, L. D. WAITS, and J. A. GUEST, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

TC2. PHOTOFRAGMENTATION OF KETENE AT THE SINGLET THRESHOLD............................15 min.(8:47)

I-CHIA CHEN, WILLIAM H. GREEN, JR., and C. BRADLEY MOORE, Department of Chemistry, University of California- Berkeley, Berkeley, California, 94720.

TC3. PICOSECOND RAMAN INVESTIGATIONS OF THE VIBRATIONAL ENERGY DEPENDENCE OF INTER-LIGAND ELECTRON TRANSFER IN TRANSITION METAL COMPLEXES......................15 min.(9:04)

L. K. ORMAN and J. B. HOPKINS, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70803.

TC4. INVESTIGATION OF THE RESPONSE OF THE NO/NO_2, N_2O_4 SYSTEM TO AN INTENSE OPTICAL PERTURBATION...10 min.(9:21)

M. VAN ROOZENDAEL, Y. DE WILDE, 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; and P. MILLER, Department of Physics, Lowell University, Lowell, Massachusetts, 01854.

TC5. HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF THE SINGLET MOLECULAR OXYGEN-IODINE REACTION AND POPULATIONS OF THE B 0^+ AND A 1u STATES THROUGH NON LINEAR INVERSION OF EMISSION SPECTRA.................................15 min.(9:33)

D. CERNY, R. BACIS, Laboratoire de Spectrométrie Ionique et Moléculaire, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France; and J. VERGES, Laboratoire Aimé Cotton, CNRS II, 91405 Orsay, France.

TC6. LASER EXCITED SPECTRA OF THE SINGLET MOLECULAR OXYGEN-IODINE REACTION AND POPULATIONS OF INTERMEDIATE STATES...15 min.(9:50)

P. CROZET, R. BACIS, A. BOUVIER, A. J. BOUVIER, and S. CHURASSY, Laboratoire de Spectrométrie Ionique et Moléculaire, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France.

TC7. J-REORIENTATION IN THE H_2CO $\tilde{A}$ $^1A_2 4^1$ $1_{0,1}$ ROTATIONAL LEVEL.....................15 min.(10:07)

S. HALLE, S. L. COY, R. J. SILBEY, R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; and J. L. KINSEY, Wiess School of Natural Sciences, Rice University, Houston, Texas, 77251.

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. BUSSERY, Laboratoire de Spectrométrie Ionique et Moléculaire, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne, France; and J. VERGES, Laboratoire Aimé Cotton, CNRS II, 91405 Orsay, France.

Intermission

TC9. INTERMEDIATE CASE LEVEL STRUCTURE IN INFRARED SPECTRA; EVIDENCE FOR BOTH ANHARMONIC AND CORIOLIS 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 DAVID S. PERRY, Department of Chemistry, University of Akron, Akron, Ohio, 44325.

TC10. A MODIFIED RRKM APPROACH TO THE VIBRATIONAL PREDISSOCIATION DYNAMICS OF THE S_1 p-DIFLUOROBENZENE-Ar VAN DER WAALS COMPLEX...........................15 min.(11:02)

HYE-KEUN O, MENG-CHIH SU, and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

TC11. OBSERVATIONS OF ROTATIONALLY AND VIBRATIONALLY INELASTIC SCATTERING FROM AN EXCITED STATE POLYATOMIC; S_1 GLYOXAL....................................15 min.(11:19)

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

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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.

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 Cs_2GeF_6 AND K_2GeF_6...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 $Fe_2P_2S_6$ AND $Co_2P_2S_6$...15 min.(9:34)

N. NAGASUNDARAM and A. H. FRANCIS, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

TD'1. T 14 WILL BE PRESENTED HERE (STELLA M. SUNG)...................................15 min.(10:00)

TD'2. T 15 WILL BE PRESENTED HERE (M. SAWAMURA)....................................15 min.(10:16)

TD'3. T 16 WILL BE PRESENTED HERE (R. B. ROSS).......................................15 min.(10:32)

TD'4. T 17 WILL BE PRESENTED HERE (J. M. POWERS)....................................15 min.(10:48)

TD'5. T 18 WILL BE PRESENTED HERE (SUSAN KRAFT).....................................15 min.(11:04)

TD'6. T 19 WILL BE PRESENTED HERE (M. LARSSON)......................................10 min.(11:15)

TD'7. T 23 WILL BE PRESENTED HERE (MICHAEL A. KAHLOW)..............................10 min.(11:26)

TD'8. T 24 WILL BE PRESENTED HERE (C. F. CHABALOWSKI)..............................10 min.(11:37)

TD'9. T 25 WILL BE PRESENTED HERE (CARY F. CHABALOWSKI)...........................10 min.(11:48)

TUESDAY, JUNE 14, 1988 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman Before Intermission: LAURENCE S. ROTHMAN, Optics Division, Air Force
Geophysics Laboratory, Hanscom AFB, Massachusetts.

Chairman After Intermission: D. CHRIS BENNER, Department of Physics, College
of William and Mary, Williamsburg, Virginia.

TE1. RECENT STUDIES IN HIGH-RESOLUTION SPECTROSCOPY OF ATMOSPHERIC GASES
....Invited Paper..... ....30 min.(1:30)

V. E. ZUEV, Institute of Atmospheric Optics SB USSR Academy of
Sciences, 1. Akademicheskii Avenue. Tomsk, 634055, USSR.

TE2. DIODE LASER SPECTROSCOPY OF HALOMETHANES............Specially Requested..........15 min.(2:05)

SERGIO GHERSETTI, A. BALDACCI, S. GIORGIANNI, and R. VISINONI.
Dipartimento di Chimica Fisica, Universitá di Venezia, D.D. 2137,
30123 Venezia, Italy.

TE3. NEW HIGH-RESOLUTION SPECTRA OF O_3 IN THE 3-μm REGION...........................15 min.(2:22)

M.A.H.SMITH, C. P. RINSLAND, Atmospheric Sciences Division,
Mail Stop 401A, NASA Langley Research Center, Hampton, Virginia,
23665-5225; V. MALATHY DEVI, Department of Physics, College of
William and Mary, Williamsburg, Virginia, 23185; and
C. T. SOLOMON, Fabrication Division, Mail Stop 390, NASA Langley
Research Center, Hampton, Virginia, 23665-5225.

TE4. LINE POSITIONS AND INTENSITIES OF THE $2\nu_3$, $\nu_1 + \nu_3$, AND $2\nu_1$ BANDS OF $^{16}O_2$........ 5 min.(2:39)

C. P. RINSLAND, M.A.H. SMITH, Atmospheric Sciences Division, NASA
Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225;
J.-M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et
Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris,
France; and V. MALATHY DEVI, Department of Physics, College of
William and Mary, Williamsburg, Virginia, 23185.

TE5. LINE INTENSITY AND COLLISION-BROADENED LINE WIDTH MEASUREMENTS IN THE ν_1
FUNDAMENTAL OF $^{14}N_2O$ AT ATMOSPHERIC TEMPERATURES..............................15 min.(2:46)

S. CHUDAMANI and P. VARANASI, Laboratory for Planetary Atmospheres
Research, State University of New York, Stony Brook, New York,
11794-2300.

TE6. LINEWIDTH NARROWING IN THE INFRARED BAND OF N_2O PERTURBED BY N_2..................10 min.(3:03)

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

Intermission

TE7. ABSOLUTE INTENSITIES IN THE ν_2 REGION OF CO_2.....................................15 min.(3:30)

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

TE8. STUDIES CONCERNING THE OPTIMUM HAMILTONIAN FOR USE IN LARGE
AMPLITUDE, DIRECT NUMERICAL DIAGONALIZATION CALCULATIONS........................15 min.(3:47)

RICHARD B. WATTSON. Visidyne, Inc., 10 Corporate Place, S. Bedford St.
Burlington, Massachusetts, 01803.

TE9. CALCULATIONS OF ENERGIES AND INTENSITIES FOR THE ASYMMETRIC SPECIES OF CO_2.......15 min.(4:04)

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.

TE10. CO_2 SPECTROSCOPIC CONSTANTS DETERMINED BY GLOBAL LEAST-SQUARES
FITTING AND DIRECT NUMERICAL DIAGONALIZATION..................................15 min.(4:21)

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.

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

CAI PEIFEI, SHEN 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. DEMUYNCK, 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)

> R. S. RUOFF, T. D. KLOTS, C. CHUANG, T. EMILSSON, and H. S. GUTOWSKY, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.

TF5. EMISSION FREQUENCY OF THE 496 um LINE IN $^{12}CH_3F$ AS A FUNCTION OF PRESSURE AND PUMP OFFSET BY INFRARED-SUBMM 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.

Intermission

TF6. A COLLISIONAL ENERGY TRANSFER MAP INCLUDING ΔK PROCESSES IN CH_3F.................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 IAM 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. VOGELSANGER, 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-d_2.....................15 min.(4:13)

> B. VOGELSANGER, 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.

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 $\tilde{A}$-$\tilde{X}$ BAND SYSTEM OF C_2D_2: 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 $\tilde{A}$-$\tilde{X}$ BAND SYSTEM OF C_2D_2: ROVIBRONIC INFORMATION ON THE $\tilde{A}$ 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 $\tilde{a}^3A_u$ 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. ZEEMAN STUDIES OF MICROWAVE-OPTICAL DOUBLE RESONANCE SIGNALS IN THE $\tilde{A}$ $^1A_2$-$\tilde{X}$ $^1A_1$ SYSTEM OF THIOFORMALDEHYDE...15 min.(2:03)

W. HÜTTNER, 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 INTERNAL ROTATION AND INVERSION MOTIONS OF THIOACETALDEHYDE IN ITS FIRST TRIPLET $\tilde{a}^3A''$ 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 Cientificas, c/Serrano, 119, 28006 Madrid, Spain.

TG7. ON THE ASSIGNMENT OF THE EXCITED SINGLET STATES IN THE CO_2 MOLECULE..............10 min.(2:41)

P. J. KNOWLES, P. ROSMUS, University Chemical Laboratory, University of Cambridge, Cambridge, United Kingdom; and H. J. WERNER, Department of Chemistry, University of Bielefeld, Bielefeld, Germany.

TG8. CHEMILUMINESCENCE SPECTRA OF SMALL MOLECULES CONTAINING SULFUR, SELENIUM, AND TELLURIUM...15 min.(2:52)

R. J. GLINSKI, Department of Chemistry, Tennessee Technological University, Cookeville, Tennessee, 38505.

Intermission

TG9. STEADY STATE PRODUCTION OF THE HNCN 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-Universitat 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.

TUESDAY, JUNE 14, 1988 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chairman before Intermission: HE HEHAN, Dalian Institute of Chemical
Physics, Dalian, Liaoning, People's
Republic of China.

Chairman After Intermission: HAI-LUNG DAI, Department of Chemistry,
University of Pennsylvania, Philadelphia,
Pennsylvania.

TH1. STIMULATED EMISSION POLARIZATION SPECTROSCOPY.................................15 min.(1:30)

D. FRYE, H. L. LIOU, and H. L. DAI, Department of Chemistry,
University of Pennsylvania, Philadelphia, Pennsylvania, 19104-6323.

TH2. VIBRATION-ROTATION SPECTROSCOPY BY STIMULATED EMISSION PUMPING IN A SUPERSONIC
BEAM: a-AXIS CORIOLIS COUPLED $v_4=1$ AND $v_8=1$ LEVELS OF $\tilde{X}^1A_g$ GLYOXAL..............15 min.(1:47)

D. FRYE, L. LAPIERRE, and H. L. DAI, Department of Chemistry,
University of Pennsylvania, Philadelphia, Pennsylvania, 19104-6323.

TH3. SELECTIVE EXCITATION AND SPECTROSCOPY OF HIGH VIBRATIONAL LEVELS OF $\tilde{a}^1A_1$ CH$_2$
BY STIMULATED EMISSION PUMPING..15 min.(2:04)

W. XIE, A. RITTER, and H. L. DAI, Department of Chemistry,
University of Pennsylvania, Philadelphia, Pennsylvania, 19104-6323.

TH4. VAN DER WAALS VIBRATIONAL LEVELS OF THE GLYOXAL($\tilde{X}^1A_g$)·Ar COMPLEX OBSERVED BY
STIMULATED EMISSION SPECTROSCOPY...15 min.(2:21)

D. FRYE, P. ARIAS, and H. L. DAI, Department of Chemistry,
University of Pennsylvania, Philadelphia, Pennsylvania, 19104-6323.

TH5. VIBRATIONAL STUDIES OF ELECTRONICALLY EXCITED STATES BY FLUORESCENCE
EXCITATION IN A SUPERSONIC JET..15 min.(2:38)

M. HUANG, C. M. CHEATHAM, and J. LAANE, Department of Chemistry,
Texas A&M University, College Station, Texas, 77843.

Intermission

TH6. CURVE FITTING MODEL FOR FOURIER TRANSFORM INFRARED SPECTROSCOPY................15 min.(3:05)

H.-H. NAM and G. E. LEROI, Department of Chemistry, Michigan State
University, East Lansing, Michigan, 48824.

TH7. THE INERTIAL DEFECTS OF VIBRATIONALLY EXCITED ORTHO-RHOMBIC MOLECULES AS
SOURCE FOR INFORMATION ON HARMONIC FORCE FIELDS: CALCULATIONS ON 1,1
DIFLUOROETHYLENE..15 min.(3:22)

DINES CHRISTEN, Institut für Physikalische & Theoretische Chemie,
Universität Tübingen, D-7400 Tübingen, B.R.D.; and OTTO L. STIEFVATER,
Adran Cemeg, University College North Wales, Bangor, Wales.

TH8. LOW FREQUENCY VIBRATIONAL SPECTRA AND TWO-DIMENSIONAL VIBRATIONAL POTENTIAL
ENERGY SURFACES SILACYCLOPENTANE AND 1,3-DISILACYCLOPENTANE........................10 min.(3:39)

L. E. COLEGROVE, J. C. WELLS, and J. LAANE, Department of Chemistry,
Texas A&M University, College Station, Texas, 77843.

TH9. PSEUDOROTATIONAL POTENTIAL FUNCTIONS AND ENERGY LEVELS FOR SPIRO COMPOUNDS.......15 min.(3:51)

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

TH10. INTERNAL ROTATION OF CYCLOPROPYLGERMANE AND CYCLOPROPYLSILANE-d$_3$.................15 min.(4:08)

M. B. KELLY, J. LAANE, Department of Chemistry, Texas A&M
University, College Station, Texas, 77843; and M. DAKKOURI,
Department of Chemistry, Universität Ulm, Ulm, West Germany.

TH11. ASYMMETRIC TOP CONTOUR SIMULATION AND VIBRATIONAL SPECTRA OF ISOPROPYL FORMATE...15 min.(4:25)

R. S. LEE, J. LAANE, Department of Chemistry, Texas A&M University,
College Station, Texas, 77840; and B. J. VAN DER VEKEN, Laboratorium
Anorganische Scheikunde, Universiteit Antwerpen, Rijksuniversitair
Centrum Antwerpen, Groenenborgerlaan 171, 2020 Antwerp.

TH12. APPLICATIONS OF MOLECULAR MECHANICS TO THE CONFORMATIONAL ANALYSIS OF
RING MOLECULES..15 min.(4:42)

R. S. LEE, C. COOPER, and J. LAANE, Department of Chemistry, Texas
A&M University, College Station, Texas, 77843.

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J. LAANE, M. M. TECKLENBURG, Department of Chemistry, Texas A&M
University, College Station, Texas, 77843; and V. E. RIVERA-GAINES,
Bristol-Meyers USBNG, Evansville, Indiana 47721.

TUESDAY, JUNE 14, 1988 -- 1:30 P.M.

Room 2027, Robinson Laboratory

Chairman Before Intermission: D. J. NESBITT, Joint Institute for Laboratory
                                Astrophysics, National Bureau of Standards
                                and University of Colorado, Boulder, Colorado.

Chairman After Intermission: T. C. STEIMLE, Department of Chemistry,
                                Arizona State University, Tempe, Arizona.

TI1. 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.

TI2. THE FUNDAMENTAL AND OVERTONE SPECTROSCOPY OF PYRROLE IN 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.

TI3. OBSERVATION OF A NEW RO-VIBRONIC BAND OF OOH FREE RADICAL GENERATED
      FROM H_2O_2 DECOMPOSITION ON GLASS SURFACES...............................15 min.(2:04)

        C. DOUKETIS and J. P. REILLY, Department of Chemistry,
        Indiana University, Bloomington, Indiana, 47405.

TI4. VELOCITY SLIP IN ULTRA-COLD MOLECULAR BEAMS...................................15 min.(2:21)

        JAMES M. WILKINSON, CLAYTON F. GIESE, and W. RONALD GENTRY,
        Chemical Dynamics Laboratory, University of Minnesota,
        207 Pleasant Street, S.E., Minneapolis, Minnesota, 55455.

TI5. A-DOUBLING TRANSITIONS OF METAL OXIDES MEASURED BY MODR: CaO.................15 min.(2:38)

        T. C. STEIMLE, W.-L. CHANG, and D. F. NACHMAN,
        Chemistry Department, Arizona State University, Tempe,
        Arizona, 85287.

TI6. ELECTRONIC PROPERTIES OF GAS-PHASE COPPER MONOSULFIDE.........................10 min.(2:50)

        T. C. STEIMLE, W.-L. CHANG, and D. F. NACHMAN,
        Chemistry Department, Arizona State University, Tempe,
        Arizona, 85287.

intermission

TI7. 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.

TI8. 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.

TI9. 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.

TI10. THE ROTATIONAL RKR METHOD..15 min.(4:06)

        DAVID J. NESBITT and MARK S. CHILD, Joint Institute for
        Laboratory Astrophysics, National Bureau of Standards and
        University of Colorado, Boulder, Colorado, 80309-0440.

TI11. AN INTERMOLECULAR POTENTIAL SURFACE FOR Ar + HF(v=1) FROM HIGH
      RESOLUTION INFRARED MEASUREMENTS...15 min.(4:23)

        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.

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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.

        JAMES K. G. WATSON, Herzberg Institute of
        Astrophysics, National Research Council of
        Canada, Ottawa, Ontario, Canada, K1A OR6.

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.

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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 Astro-
       phys'cs, 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 WINNEWISSER, 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. SCHROTTER, Sektion Physik, Ludwig-Maximilians-Universitat
Munchen, Munchen, 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)

N. L. OWEN, Department of Chemistry, Brigham Young University, Provo,
Utah, 84602; W. B. BANKS, and H. WEST, Department of Wood Science,
University College of North Wales, Bangor, United Kingdom.

RA4. BEND 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 um REGION...................... 5 min.(9:46)

M. HERMAN, T. R. HUET, Laboratoire de Chimie Physique Moléculaire -
CP.160, Université Libre de 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.

RA6. SPECTROSCOPIC CONSTANTS OF CS_2 DERIVED FROM THE ν_3 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. HORIAI, K. NAKAGAWA, T. KONNO, Department of Chemistry,
Josai University, Keyakidai, Sakado, Saitama 350-02, Japan; and
T. FUJIMOTO, Research Institute for Catalysis, Hokkaido University,
Kita-Ku, Sapporo 060, Japan.

Intermission

RA8. INFRARED SPECTRUM OF THE ν_3 BAND OF $C_2H_2^+$ 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.

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RA9. ASYMMETRIC STRETCHING BAND OF BRIDGED PROTONATED ACETYLENE......................15 min.(10:46)

M. W. CROFTON, Lawrence Livermore National Laboratory, Livermore,
California, 95440; M.-F. JAGOD, B. D.REHFUSS, and T. OKA, Department
of Chemistry and Department of Astronomy and Astrophysics, University
of Chicago, Chicago, Illinois, 60637.

RA10. OBSERVATION OF HOT BANDS OF H_3^+ USING AN EXTENDED DIFFERENCE FREQUENCY
SPECTROMETER...15 min.(11:02)

M. G. BAWENDI, B. D. REHFUSS, and T. OKA, Department of Chemistry and
Department of Astronomy and Astrophysics, University of Chicago, Chicago,
Illinois, 60637.

RA11. IS THE DISSOCIATIVE RECOMBINATION OF H_3^+ REALLY SLOW?
A NEW SPECTROSCOPIC MEASUREMENT OF THE RATE CONSTANT..........................15 min.(11:18)

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

RA12. A SEARCH FOR THE C-H (BRIDGE) STRETCH VIBRATION-ROTATION BAND OF $C_2H_3^+$...........10 min.(11:34)

T. AMANO, N. MOAZZEN-AHMADI, and A.R.W. McKELLAR, Herzberg Institute
of Astrophysics, National Research Council of Canada, Ottawa, Ontario,
Canada, K1A 0R6.

RA13.. FIR LASER SIDEBAND SPECTROSCOPY OF H_3O^+......................................15 min.(11:45)

P. VERHOEVE, 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.

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RB12. LASER INDUCED FLUORESCENCE OF Cs_2 BY ARGON ION LASER LINES IN THE PRESENCE
OF NOBLE BUFFER GASES...10 min.(11:19)

J. J. HO, 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..................15 min.(11:30)

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

RB14. PARITY SELECTED EXCITATION SPECTROSCOPY OF $ArCl_2$................................15 min.(11:46)

K. C. JANDA, D. D. EVARD, and J. I. CLINE, Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

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.(9:18)

> 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 $H_2O-H_2O-CO_2$ 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 $CO_2-CO_2-H_2O$...............................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 Spectrosocpy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RC8. QUADRUPOLE HYPERFINE SPLITTING IN THE J=1+ 0 ROTATIONAL TRANSITION OF CCl_3F......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 HC1- 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 H_2CO CO_2.................................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 H_2CO....................................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 Labaoratory

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, ^{14}N QUADRUPOLE
COUPLING AND BINDING ENERGY...15 min.(8:42)

ROBERT K. BOHN, 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 ^{13}C 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-d$_2$....................................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. HOLLENSTEIN, and R. MEYER, Laboratorium für Physikalische Chemie
Eidgenössische Technische Hochschule, CH-8092 Zürich, Switzerland.

RD6. MOLECULAR STRUCTURE AND TAUTOMER EQUILIBRIUM OF GASEOUS 1,2,3-TRIAZOLE
STUDIED BY MICROWAVE SPECTROSCOPY, ELECTRON DIFFRACTION AND AB INITIO
CALCULATIONS...15 min.(9:35)

M. BEGTRUP, Department of Organic Chemistry, Technical University
of Denmark, DK-2800 Lyngby, Denmark; C. J. NIELSEN, C. E. SJØGREN,
Department of Chemistry, University of Oslo, P. O. Box 1033, Blindern,
N-0315 Oslo 3, Norway; L. NYGAARD, G. O. SØRENSEN, Chemical Laboratory
V, 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 ArH$_3^+$ AND ISOTOPOMERS FROM THE ANALYSIS OF THEIR
ROTATIONAL SPECTRA....................Late Paper.............................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. VAN EIJCK, Department of Structural Chemistry, University
of Utrecht Padulaan i -3584 CH Utrecht, The Netherlands.

RD10. INFRARED DIODE LASER SPECTRA OF MgD, CaH AND CaD (X $^2\Sigma^+$).......Late Paper........10 min.(10:56)

B. LEMOINE, 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 1153, Physics Laboratory

Chairman: MARK D. MARSHALL, Department of Chemistry, Amherst College, Amherst, Massachusetts.

RE1. MICROWAVE SPECTRUM OF THE N_2-H_2O COMPLEX...................................15 min.(1:30)

      H. O. LEUNG, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138; M. D. MARSHALL, Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002; R. D. SUENRAM, and F. J. LOVAS, Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RE2. ROTATIONAL SPECTRA AND STRUCTURES OF THE H_2S-H_2O AND $(H_2S)_2$ COMPLEXES...........15 min.(1:46)

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

RE3. STUDIES OF ISOTOPICALLY ENRICHED WATER DIMER SPECIES............................15 min.(2:02)

      R. D. SUENRAM, L. H. COUDERT, F. J. LOVAS, and J. T. HOUGEN, Molecular Spectrosocpy Division, National Bureau of Standards, Gaithersburg, Maryland, 20899.

RE4. VIBRATIONAL SPECTROSCOPY OF SOLID-LIKE CLUSTERS OF HYDROGEN CYANIDE..............15 min.(2:18)

      D. S. ANEX and G. E. EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

RE5. VIBRATIONAL PREDISSOCIATION STUDIES OF $Cs^+(MeOH)_n$ AND $Cs^+(EtOH)_n$
SOLVATED ION CLUSTERS...15 min.(2:34)

      WEN-LONG LIU and JAMES M. LISY, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801.

RE6. SOLVATION OF ALKALI IONS WITH NON-POLAR SOLVENTS...............................15 min.(2:50)

      JEFFREY A. DRAVES and JAMES M. LISY, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801.

RE7. IR-IR DOUBLE RESONANCE SPECTROSCOPY : A STUDY OF THE TORSIONAL VIBRATIONS
OF CYCLIC $(HF)_3$..15 min.(3:06)

      KIRK D. KOLENBRANDER and JAMES M. LISY, School of Chemical Sciences, University of Illinois, Urbana, Illinois, 61801.

Intermission

RE8. THE PHOTODETACHMENT SPECTRA OF NEGATIVE CLUSTER IONS OF WATER....................15 min.(3:35)

      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, Universitat Freiburg, Freiburg, Germany.

RE9. THE PHOTODETACHMENT SPECTRA OF HOMOGENEOUS ALKALI METAL CLUSTER ANIONS:
$Na^-_{n=2-5}$, $K^-_{n=2-8}$, $Rb^-_{n=2-4}$, AND $Cs^-_{n=2,3}$.................................15 min.(3:51)
      K. M. McHUGH, J. G. EATON, H. W. SARKAS, L. H. KIDDER, G. H. LEE, J. T. SNODGRASS, M. R. MANAA, and K. H. BOWEN, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218.

RE10. PHOTODETACHMENT STUDIES OF HETEROGENEOUS ALKALI METAL DIMER AND TRIMER ANIONS....15 min.(4:07)

      D. PATEL-MISRA, J. G. EATON, H. W. SARKAS, G. H. LEE, S. T. ARNOLD, and K. H. BOWEN, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218.

RE11. PRODUCTION AND PHOTODETACHMENT STUDIES OF Li_2^-.................................15 min.(4:23)

      H. W. SARKAS, S. T. ARNOLD, K. M. McHUGH, D. PATEL-MISRA, J. G. EATON, G. H. LEE, and K.H. BOWEN, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218.

RE12. THE PHOTODETACHMENT SPECTROSCOPY OF HYDRATED AND DEUTERATED NITRIC OXIDE ANIONS..15 min.(4:39)

      S. T. ARNOLD, J. G. EATON, G. H. LEE, D. PATEL-MISRA, and K. H. BOWEN, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218.

RE13. THE STRUCTURE AND DYNAMICS OF Ne_2Cl_2...15 min.(4:55)

      C. R. BIELER, S. R. HAIR, K. C. JANDA, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; and J. L. CLINE, JILA, University of Colorado, Boulder, Colorado, 80309-8440.

RE14. Z5 WILL BE PRESENTED HERE (G. A. BLAKE)..10 min.(5:11)

RE15. Z8 WILL BE PRESENTED HERE (J. V. COE)...10 min.(5:22)

THURSDAY, JUNE 16, 1988 -- 1:30 P.M.

Room 1009, Physics Laboratory

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

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

RF1. $U(\Delta J = +4)$ TRANSITIONS AND OVERLAP PARAMETERS FOR H_2-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 $W(\Delta J=6)$ 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. NARAHARI RAO, Department of Physics, The
   Ohio State University, Columbus, Ohio, 43210.

RF3. ABSOLUTE RO-VIBRATIONAL INTENSITIES FOR THE $\Delta v = 1$ VIBRATIONAL BANDS OF $^3\Sigma^-$ NH....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, Departmento
   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)

   D. E. JENNINGS and G. R. WIEDEMANN, Planetary Systems Branch, Code 693,
   Laboratory for Extraterrestrial Physics, NASA/Goddard Space Flight
   Center, Greenbelt, Maryland, 20771.

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 ν_2 BAND OF $^{13}CH_4$..............10 min.(2:50)

   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 ν_3 BAND SPECTRAL REGION OF $^{12}CH_4$...............................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 ν_3 AND ν_6 FUNDAMENTALS OF $^{12}CH_3D$ AT LOW TEMPERATURES..........15 min.(3:31)

   S. CHUDAMANI and P. VARANASI, Laboratory for Planetary Atmospheres
   Research, State University of New York, Stony Brook, New York,
   11794-2300.

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

RG1. THEORETICAL STUDIES OF THE SPECTROSCOPY OF FIRST-ROW MOLECULES...Invited Paper...30 min.(1:30)

C. W. BAUSCHLICHER, S. R. LANGHOFF, H. PARTRIDGE, and P. R. TAYLOR, NASA Ames Research Center, Moffett Field, California, 94035.

RG2. REFLECTION SYMMETRIES OF LINEAR-MOLECULE ROVIBRONIC LEVELS......................15 min.(2:03)

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

RG3. ON THE ESR OF SMALL CARBON CLUSTERS......................................10 min.(2:19)

D. W. EWING, Department of Chemistry, John Carroll University, Cleveland, Ohio, 44118.

RG4. AB INITIO CALCULATIONS ON Ag_2, Au_2 AND AgAu INCLUDING POLARIZATION FUNCTIONS AND EXTENDED ELECTRON CORRELATION...................................15 min.(2:30)

R. B. ROSS and W. C. ERMLER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

RG5. VIBRATIONAL-ROTATIONAL ANALYSIS OF THE HYDROGEN PEROXIDE CATION FROM AB INITIO POTENTIAL ENERGY AND DIPOLE MOMENT SURFACES...........................15 min.(2:46)

SUSAN KRAUT, Citroil Aromatic, Inc., 320 Veterans Boulevard, Carlstadt, New Jersey, 07072; HSIUCHIN C. HSIEH, and WALTER C. ERMLER, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

Intermission

RG6. AN AB INITIO STUDY OF CS AND H ADSORPTION ON Be METAL...........................15 min.(3:15)

M. M. MAKINO, M. SAWAMURA, and W. C. ERMLER, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

RG7. AB INITIO CALCULATIONS OF POLARIZABILITIES INCLUDING RELATIVISTIC EFFECTS FOR ELEMENTS OF GROUPS IA AND IB...15 min.(3:31)

J. M. POWERS, R. B. ROSS, and W. C. ERMLER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

RG8. CHARGE STABILIZATION OF EXCITED ELECTRONIC STATES OF CN^-......................15 min.(3:47)

C. S. EWIG and J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

RG9. AN APPROXIMATE AB-INITIO THEORY OF LARGE MOLECULAR SYSTEMS......................15 min.(4:03)

G. P. DAS, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

RG10. ELECTRONIC STATES OF Na_3^+ AND Na_3: CALCULATED PE SURFACES AND MOLECULAR STRUCTURES....................Late Paper....................10 min.(4:19)

G. H. JEUNG, Laboratoire de Chimie Quantique, Université Louis Pasteur, 4 rue Pascal, 67000 Strasbourg, France; M. BROYER, and P. LABASTIE, Laboratoire de Spectrométrie Ionique et Moléculaire, Université de Lyon I, 43 bd du 11 Novembre 1918, 69622 Villeurbanne, France.

RG11. EMISSION SPECTRUM OF SUPERSONICALLY COOLED BENZYL RADICAL......Late Paper........10 min.(4:30)

P. G. CARRICK, Air Force Astronautics Laboratory/YSX, Edwards Air Force Base, California, 93523; and J. I. SELCO, Department of Chemistry, University of Redlands, Redlands, California, 92373.

RG12. FLUORESCENCE SPECTROSCOPY OF PREDISSOCIATED LEVELS OF ELECTRONICALLY EXCITED S_2..............................Late Paper...............................10 min.(4:41)

WAFAA FAWZY and M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, Georgia, 30322.

RG13. WAVELENGTH-RESOLVED FLUORESCENCE STUDIES OF THE COLLISION DYNAMICS OF $Br_2(B)$
....Late Paper..............................10 min.(4:52)

M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, Georgia, 30322; E. A. DORKO, G. P. PERRAM, and L. HANKO, AFWL, Kirtland AFB, New Mexico, 87117.

RG14. ELECTRONIC SPECTROSCOPY OF RARE GAS ISOLATED I_2 AND IBr.........................10 min.(5:03)

M.A.P. MACLER and M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, Georgia, 30322.

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, 1988 -- 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 POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee.

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

> W. F. MURPHY, Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

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)

> F. DEVLIN and P. J. STEPHENS, Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482.

RH5. VIBRATIONAL CIRCULAR DICHROISM OF β-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-^{16}O AND -^{18}O.........................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 1-CHLOROCYCLOBUTENE......................................10 min.(3:37)

> NORMAN C. CRAIG and STEVEN S. BORICK, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074.

RH9. VIBRONIC STATES OF PuF_6 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 CO_2 AND SF_6 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.

FA1. FOURIER TRANSFORM INFRARED SPECTROSCOPY OF NITRIC OXIDE IN ELECTRIC AND
MICROWAVE DISCHARGES...10 min.(8:30)

K. L. McNESBY and R. A. FIFER, US Army Ballistic Research Laboratory,
SLCBR-IB-I, Aberdeen Proving Ground, Maryland, 21005-5066.

FA2. FOURIER TRANSFORM DETECTION OF THE ν_3 FUNDAMENTAL OF THE N_3 RADICAL...............10 min.(8:41)

C. R. BRAZIER, P. F. BERNATH, Department of Chemistry, University of
Arizona, Tucson, Arizona, 85721; J. B. BURKHOLDER, and C. J. HOWARD,
NOAA Aeronomy Laboratory, R/E/AL2, 325 Broadway, Boulder, Colorado,
80303, and Department of Chemistry and Biochemistry and CIRES,
University of Colorado, Boulder, Colorado, 80309.

FA3. DIODE LASER SPECTROSCOPY OF ALKALI HALIDES......................................15 min.(8:52)

C. R. BRAZIER, M. DOUAY, 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 N-H 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 μm 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 $s2\nu_2 \leftarrow a\nu_2$ 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 2-3μm...10 min.(9:41)

N. TU, K. NARAHARI RAO, Department of Physics, The Ohio State University,
Columbus, Ohio, 43210; S. URBAN, Czechoslovak Academy of Sciences,
J. Hevrovsky 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. EGGERS 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 μm REGION............................15 min.(10:21)

YASUHIRO OHSHIMA, KOZO KUCHITSU, Department of Chemistry, Faculty of
Science, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan;
YOSHIYASU 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)

YOSHIYASU MATSUMOTO, MICHIO TAKAMI, The Institute of Physical and
Chemical Research(RIKEN), Wako, Saitama, 351-01, Japan;
YASUHIRO OHSHIMA 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)

A.R.W. McKELLAR and J.W.C. JOHNS, Herzberg Institute of Astrophysics,
National Research Council of Canada, Ottawa. Ontario, Canada, K1A OR6.

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

A.R.W. McKELLAR, Herzberg Institute of Astrophysics, National Research
Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

FRIDAY, JUNE 17, 1988 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chairman: DAVID PERRY, Department of Chemistry, University of Akron, Akron, Ohio.

FB1. THE MICROWAVE SPECTRUM OF DIFLUOROMETHANIMINE, $CF_2=NH$..............................10 min.(8:30)

    P. GRONER, H. NANAIE, J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208; and D. D. DESMARTEAU, Department of Chemistry, Clemson University, Clemson, South Carolina, 29631.

FB2. MICROWAVE SPECTRUM AND STRUCTURE OF DIMETHYLAMINODIFLUOROPHOSPHINE..............10 min.(8:42)

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

FB3. MILLIMETER AND SUBMILLIMETER SPECTROSCOPY OF SMALL INTERNAL ROTORS..............15 min.(8:54)

    S. L. SHOSTAK, T. ANDERSON, R. L. CROWNOVER, E. HERBST, F. C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706, and E. C. SUTTON, Department of Physics and Space Sciences Laboratory, University of California, Berkeley, California, 94720.

FB4. PRESSURE BROADENING OF MILLIMETER WAVE TRANSITIONS OF HNO_3, NO_2, CF_2Cl_2, HDO, AND HOOH BY NITROGEN AND OXYGEN...15 min.(9:11)

    T. M. GOYETTE W. L. EBENSTEIN, S. L. SHOSTAK, F. C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706; and P. HELMINGER, Department of Physics, University of South Alabama, Mobile, Alabama, 36688.

FB5. THE MICROWAVE SPECTRUM OF DIFLUOROMETHANIMINE, F_2CNH..............................15 min.(9:28)

    K. MOELLER, M. WINNEWISSER, Physikalisch-Chemisches Institut, Justus Liebig Universität, D-6300 Giessen, West Germany; G. PAWELKE, and H. BÜRGER, FB 9, Anorganische Chemie, Gesamthochscule Wuppertal, D-5600 Wuppertal 1, West Germany.

FB6. MICROWAVE SPECTRUM OF $^{13}CD_3OH$...15 min.(9:45)

    I. MUKHOPADHYAY, K.V.L.N. SASTRY, and R. M. LEES, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada, E3B 5A3.

Intermission

FB7. THE SUBMILLIMETER-WAVE SPECTRUM OF THE $^{12}CH_3O$ AND THE $^{13}CH_3O$ RADICALS...........15 min.(10:15)

    TAKAMASA MOMOSE, TADAMASA SHIDA, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan; YASUKI ENDO, Department of Pure and Applied Science, College of Arts and Science, University of Tokyo, Tokyo, Japan; and EIZI HIROTA, Institute for Molecular Science, Okazaki 444, Japan.

FB8. MICROWAVE SPECTRUM AND STRUCTURE OF CYCLOBUTADIENE OZONIDE......................10 min.(10:32)

    P. LORENCAK and R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109-1055.

FB9. MILLIMETER WAVE ABSORPTION AND FAR INFRARED LASER MAGNETIC RESONANCE SPECTROSCOPY OF FO_2...15 min.(10:44)

    M. BOGEY, C. DEMUYNCK, J. L. DESTOMBES, Universite de Lille I, Laboratoire de Spectroscopie Hertzienne, CNRS, 59655 Villeneuve d'Ascq, France; P. B. DAVIES, Physical Chemistry Laboratory, Lensfield Road, Cambridge, CB2IEP England; and T. J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973.

FB10. THE DETERMINATION OF THE COMPLETE CHLORINE NUCLEAR QUADRUPOLE COUPLING TENSOR IN CHLOROTRIFLUOROETHYLENE...15 min.(11:01)

    W. LEWIS-BEVAN, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois, 62901; M.C.L. GERRY, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6; E. BITTNER, K. W. HILLIG, II, and R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

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FB11. THE MICROWAVE SPECTRUM OF KR•PF$_3$...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
Chemistry, University of Connecticut, Storrs, Connecticut, 06268.

FB12.　Σ4 WILL BE PRESENTED HERE (R. H. PETRMICHL).................................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 THE CIRCULAR DICHROISM MEASUREMENTS IN THE $800-600$ 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 DICHROISM 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. Σ9 WILL BE PRESENTED HERE (G. M. ROBERTS)....................................15 min.(11:20)

FC13. Σ10 WILL BE PRESENTED HERE (M. DIEM)...15 min.(11:37)

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.

Σ1. THE 5 μm INFRARED SPECTRUM OF NH_3 COLLISION-BROADENED BY H2..................10 min. (FA16)

C. CHAPADOS, Département de Chimie-Biologie, Université du Québec à Trois-Rivières, Trois-Rivières, Québec, Québec, Canada, G9A 5H7; and G. BIRNBAUM, National Bureau of Standards, Washington, D.C., 20899.

Σ2. LOW FREQUENCY INTERMOLECULAR VIBRATIONS IN VARIOUS BINARY COMPLEXES FROM NEAR INFRARED SPECTROSCOPY...10 min. (TA11)

D. DAYTON, K. W. JUCKS, and R. E. MILLER, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27599.

Σ3. SUB-DOPPLER RESOLUTION INFRARED SPECTROSCOPY OF WATER DIMER....................10 min. (TA12)

Z. S. HUANG and R. E. MILLER, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27599.

Σ4. THE MICROWAVE SPECTRUM OF SiF^+..15 min.(FB12)

R. H. PETRMICHL, K. A. PETERSON, and R. C. WOODS, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, 53711.

Σ5. TUNABLE FAR INFRARED LASER SPECTROSCOPY OF HYDROGEN BONDS: THE $K_a = 0_u \rightarrow 1_g$ ROTATION TUNNELING SPECTRUM OF THE HCl DIMER.................................10 min. (RE14)

G. A. BLAKE, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, 91125; K. L. BUSAROW, R. C. COHEN, K. B. LAUGHLIN, Y. T. LEE, and R. J. SAYKALLY, Department of Chemistry and Lawrence Berkeley Laboratories, University of California, Berkeley, California, 94720.

Σ6. TUNABLE FAR INFRARED LASER SPECTROSCOPY OF VAN DER WAALS AND HYDROGEN BONDED CLUSTERS FORMED IN A PLANAR SUPERSONIC JET...................................10 min. (RC13)

K. BUSAROW, 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.

Σ7. TUNABLE FAR INFRARED LASER SPECTROSCOPY OF VAN DER WAALS BONDS: TUNNELING-ROTATIONAL AND VIBRATION-ROTATION SPECTRA OF $Ar-H_2O$..................10 min. (RC14)

R. C. COHEN, K. L. BUSAROW, 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.

Σ8. SUB-DOPPLER DIRECT ABSORPTION IR LASER SPECTROSCOPY IN FAST ION BEAMS............10 min. (RE15)

J. V. COE, J. C. OWRUTSKY, E. R. KEIM, N. V. AGMAN, and R. J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.

Σ9. VIBRATIONAL CIRCULAR DICHROISM OF SMALL PEPTIDES AND PEPTIDE MODELS IN SOLUTIONS : EXPERIMENTAL DATA AND CALCULATIONS..................................15 min. (FC12)

G. M. ROBERTS, O. LEE, and M. DIEM, Department of Chemistry, City University of New York, Hunter College, New York, New York, 10021.

Σ10. VIBRATIONAL CIRCULAR DICHROISM OF OLIGO-NUCLEOTIDES: EXPERIMENTAL DATA AND CALCULATIONS..15 min. (FC13)

M. GULOTTA 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.

TI1. 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.

TI2. THE FUNDAMENTAL AND OVERTONE SPECTROSCOPY OF PYRROLE IN THE BULK GAS AND
IN A MOLECULAR BEAM..15 min.(TI2)

> C. DOUKETIS and J. P. REILLY, Department of Chemistry,
> Indiana University, Bloomington, Indiana, 47405.

TI3. OBSERVATION OF A NEW RO-VIBRONIC BAND OF OOH FREE RADICAL GENERATED
FROM H_2O_2 DECOMPOSITION ON GLASS SURFACES...................................15 min.(TI3)

> C. DOUKETIS and J. P. REILLY, Department of Chemistry,
> Indiana University, Bloomington, Indiana, 47405.

TI4. 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.

TI5. Λ-DOUBLING 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.

TI6 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.

TI7. INFRARED SPECTROSCOPY IN SLIT SUPERSONIC EXPANSION...........................15 min.(TI7)

> 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.

TI8. 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.

TI9. 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.

TI10. THE ROTATIONAL RKR 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.

TI11. 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.

TI12. ABSOLUTE INFRARED ABSORPTION INTENSITIES FOR OH $X^2\Pi(v=1\leftarrow0)$....................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 Astro-
> physics, National Bureau of Standards, Boulder, Colorado,
> 80309-0440.

TI3. 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.

TI4. RESTRICTED HARTREE-FOCK WAVEFUNCTIONS AND EXCITATION ENERGIES OF
ALKOXY RADICALS..15 min.(TD'1)

STELLA M. SUNG and RUSSELL M. PITZER, Department of Chemistry,
The Ohio State University, Columbus, Ohio, 43210.

TI5. AN AB INITIO STUDY OF CS AND H ADSORPTION ON Be METAL.........................15 min.(TD'2)

M. M. MARINO, M.SAWAMURA, and W. C. ERMLER, Stevens Institute
of Technology, Hoboken, New Jersey, 07020.

TI6. AB INITIO CALCULATIONS ON Ag_2, Au_2, 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.

TI7. 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.

TI8. VIBRATIONAL-ROTATIONAL ANALYSIS OF THE HYDROGEN PEROXIDE CATION FROM
AB INITIO POTENTIAL ENERGY AND DIPOLE MOMENT SURFACES.......................15 min.(TD'5)

SUSAN KRAFT, Citroil Aromatic, Inc., 320 Veterans Boulevard,
Carlstadt, New Jersey, 07072; and HSIUCHIN C. HSIEH and
WALTER C. ERMLER, Stevens Institute of Technology, Hoboken,
New Jersey, 07030.

TI9. EXPERIMENTAL AND THEORETICAL WORK 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, Frescativägen 24, S-104 05,
Stockholm, Sweden.

TI20. FOURIER TRANSFORM SPECTROSCOPY OF $^7Li_2$: THE $1^3\Sigma_g^+-1^3\Sigma_u^+$ 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 BUJIN, C. H. CHENG,
and E. STAD, Physics Department, University of New
Brunswick, P.O. Box 4400, Fredericton, N.B., Canada E3B 5A3.

TI21. INFRARED SPECTRAL ANALYSIS OF THE PRODUCTS AND MECHANISM OF THE
LASER-INITIATED OXIDATION OF SIMPLE HYDROCARBONS............................10 min.(MH15)

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

TI22. INFRARED MATRIX ISOLATION STUDIES OF THE 1:1 MOLECULAR COMPLEXES OF
THE HYDROGEN HALIDES, AND ClF 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.

TI23. ULTRAFAST TRANSIENT SOLVATION OF POLAR DYE MOLECULES IN SIMPLE
POLAR SOLVENTS..10 min.(TD'7)

MICHAEL A. KAHLOW, TAI JONG KANG, WLODZIMEIRZ JARZEBA, and
PAUL F. BARBARA , Department of Chemistry, University of
Minnesota, Minneapolis, Minnesota, 55455.

TA4. AB INITIO CI STUDY OF THE MAGNETIC CIRCULAR DICHROISM SPECTRUM OF
ACETYLENE FOR THE X $\rightarrow$ $\tilde{B}(^1B_u)$ AND X $\rightarrow$ $\tilde{C}(^1\Pi_u)$ 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.

TA5. THEORETICAL STUDY OF THE RADIATIVE LIFETIME FOR THE SPIN-FORBIDDEN
TRANSITION $X^1 \Sigma_g^+ \leftarrow a^3\Sigma_u^+$ 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 DYNAMICS AND PHASE-COHERENT CHEMISTRY

KEITH A. NELSON

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.[1,2] 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 α-perylene crystals, in which the excited-state reaction path is closely related to a single lattice phonon coordinate, will be presented.

[1] Y.-X. Yan, L.-T. Cheng, and K.A. Nelson, in Advances in Nonlinear Spectroscopy, ed. by R.J.H. Clark and R.E. Hester, (Adv. in Spectrosc. vol. 15, Wiley, 1988).
[2] S. Ruhman, A.G. Joly, B. Kohler, L.R. Williams, and K.A. Nelson, Revue de Phys. Appl. 22, 1717 (1987).

Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

ME1.

OPTICAL DESIGN OF EFFICIENT ABSORPTION SAMPLING SYSTEMS FOR FTIR SPECTROMETERS

Wm. B. Olson

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 20899

ME2.

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 μm. 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.

ME3.

SELECTIVE FOURIER TRANSFORM SPECTROSCOPY OF RADICALS

M. Elhanine, R. Farrenq 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.

Laboratoire d'Infrarouge, Associé au C.N.R.S., Bât. 350, Université Paris XI, 91405 Orsay-Cedex, France.

ME4

HIGH PRECISION IR 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 on what can be expected for precision and accuracy of line parameters.

Address of Henry and Valentine: Laboratoire de Physique Moleculaire et Atmospherique, C.N.R.S. et Universite Pierre et Marie Curie, 4 place Jussieu, Paris 75005, France.

ME5.

ANALYSIS OF FERMI RESONANCES AND LOCAL MODES IN CH_2Cl_2 AND CD_2Cl_2 USING AN INTERNAL COORDINATE HAMILTONIAN

L. HALONEN

A curvilinear internal coordinate Hamiltonian is used to analyze Fermi resonances between CH two stretching and CH_2 (CD_2) scissoring vibrations in CH_2Cl_2 and CD_2Cl_2. The Hamiltonian is constructed by expanding the g matrix elements and the potential energy function in terms of the Morse variable $y = 1 - \exp(-ar)$ 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 CH_2Cl_2 and CD_2Cl_2 are reproduced well with a single potential energy surface.

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ROTATIONAL PARTITION FUNCTIONS FOR SYMMETRIC-TOP MOLECULES

ROBIN S. McDOWELL

It has recently been shown that improved closed-form expressions for the rotational partition functions of linear[1] and spherical-top[2] 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

$$Q_r = \sigma^*(\pi m)^{1/2} \exp[\beta(4-m)/12]\beta^{-3/2}[1 + \beta^2(1-m)^2/90 + \ldots](1+\delta)(1 + \rho_0 + \rho_1\beta^{-1} + \ldots),$$

where $\beta = hcB/kT$; $m = B/A$ for prolate tops or B/C for oblate tops; and for XY_n molecules $\sigma^* = (2I_Y+1)^n/\sigma$, where I_Y is the nuclear spin of the Y nuclei and σ 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

$$\delta = [2\exp(-\pi^2 m/9\beta)\exp(\pi^2 m^2/54)/(2I_Y+1)^2]\{1 + \pi^2 m^2[\pi^2 m^2 + 72(1-m)\beta]/14580\}.$$

The final factor gives the centrifugal distortion correction in the form derived by Wilson,[3] where in terms of the usual spectroscopic distortion constants D_J, D_{JK}, D_K, the parameters are

$$\rho_2 = -[(8+2m-4m^2+3m^3)D_J + m(2-2m+3m^2)D_{JK} + 3m^3 D_K]/12B,$$

$$\rho_1 = [(8+4m+3m^2)D_J + m(2+3m)D_{JK} + 3m^2 D_K]/4B.$$

The accuracy of this expression will be demonstrated with calculations on NH_3, CH_3D, and CHD_3.

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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

Vl.G. TYUTEREV

The problem of processing of experimental vibration-rotation spectra in
the case of strongly interacting vibrational states are discussed. Among them
two aspects of convergence problems are considered in more details: a) con-
vergence 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 extrapo-
lation 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 simultaneous-
ly good fit of experimental data and unambiguous physically meaningful values
of spectroscopic parameters?

1. Vl.G.Tyuterev, V.I.Starikov, V.I.Tolmachev, Dokl. Akad.Nauk, v.297,No.2,
   p.345, 1987.

2. Vl.G.Tyuterev, J.P.Champion, G.Pierre, V.I.Perevalov, J.M.S., 120, 49 (1986).

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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.[1] Perturbation theory through third order yields
algebraic expressions for transition wavenumbers. These formulas give wavenumbers in terms of
diagonal tensor functions (the F^4- and F^6- coefficients of Moret-Bailly[2] and the $\tilde{g}$-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)[4,5] have been
developed to give order-of-magnitude comparisons of contributions to the wavenumber shifts.

Fits of the formulas to the ν_3 and ν_4 spectra of SiF_4 are examined to test the accuracy.
reliability. and convergence of perturbation theory.

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MF 11.   (4:35)

ROVIBRONIC ENERGY LEVELS AND INTENSITIES OF ROVIBRONIC TRANSITIONS OF NONLINEAR TRIATOMIC
OPEN-SHELL RARE GAS COMPLEXES

WAFAA FAWZY AND JON T. HOUGEN

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
$^2\Pi$ or a $^2\Sigma$ electronic state. Previously, Mills et al. have discussed pure rotational spectra
of ArNO for the $^2\Pi$ case[1].

The model system used in this work is an ArOH Van der Waals complex, where the OH
internuclear axis can be at any angle (θ) relative to the line connecting the Ar atom to the
center of mass of the OH. The electronic states under consideration are the $X^2\Pi$ and the $A^2\Sigma$
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.[1], the spin-orbit coupling, the spin-rotation interaction, and a quenching
parameter, which allows the degeneracy of the Π_x and Π_y orbitals existing in the diatomic
radical to be split upon complex formation. We have also derived the electronic dipole
transition moment matrix elements for rovibronic transitions of the type $^2\Pi \leftrightarrow ^2\Pi$ and a $^2\Pi \leftrightarrow ^2\Sigma$
respectively, where the $^2\Pi$ and $^2\Sigma$ 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 (θ).
Both the theory and examples of calculated spectra with different values of the various
parameters will be presented.

---

[1] Paul D. Mills, Colin M. Western, and Brian J. Howard, J. Phys. Chem. 90, 3331 (1986).

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MF12.   (4:51)

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 unkown 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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ME13.   (5:02)

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 ν_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_o = 0.477cm^{-1}, C_1 = 0.370 cm^{-1}, and C_2 = 0.254 cm^{-1}.

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MF1.   (1:30)

SPECTROCOPY 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 $\approx 2\%$ 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 $E^1\Sigma^+-X^1\Sigma^+$ 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}, $\omega_e x_e = 1.6$ 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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MF2.   (1:41)

NEW INFRARED ELECTRONIC SPECTRA OF C_2 AND SiC

M. DOUAY, R. A. NIETMANN, S. A. ROGERS, C. R. BRAZIER, L. C. O'BRIEN, A. D. McLEAN AND P. F. BERNATH

Two new low-lying electronic states of C_2, $B^1\Delta_g$ and $B'^1\Sigma_g^+$, were discovered by Fourier transform emission spectroscopy. The $B^1\Delta_g$-$A^1\Pi_u$ and $B'^1\Sigma_g^+$-$A^1\Pi_u$ 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 $d^1\Sigma^+$-$b^1\Pi$ transition SiC was observed[1] near 6000 cm^{-1} by Fourier transform emission spectroscopy. The $d^1\Sigma^+$-$b^1\Pi$ transition of SiC corresponds to the $B'^1\Sigma_g^+$-$A^1\Pi_u$ transition of C_2. There are no previous spectroscopic observations of the SiC molecule.

[1]P. F. Bernath, S. A. Rogers, L. C. O'Brien, C.R. Brazier and A. D. McLean, Phys. Rev. Lett. 60, 197 (1988).

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MF3.   (1:56)

HIGH RESOLUTION LASER SPECTROSCOPY OF OH$^+$

D.J. RODGERS AND P.J. SARRE

The first observation of transitions in the $c^1\Pi-b^1\Sigma^+$ 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 $c^1\Pi$ state by repulsive $^5\Sigma^-$ 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 $A^3\Pi-X^3\Sigma^-$ emission spectrum.

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

1. A.J. Merer, D.N. Malm, R.W. Martin, M. Horani and J. Rostas,
   Can. J. Phys. 53 (1975) 251
2. D.M. Hirst and M.F. Guest, Molec. Phys. 49 (1983) 1461

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MF4.   (2:12)

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 HCCS, HCCO 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 specta 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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MF5.   (2:28)

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

A diatomic molecule in the vibronic state $|\Lambda S\Sigma;v\rangle$ has a dominant magnetic moment given by $(\Lambda+2\Sigma)$ (eh/4mc) due to which weak rotational transitions within this state are possible. Magnetic dipole transitions of this kind are known[1] in the $X^3\Sigma_g^-$ state of O_2. Extending the results to other electronic states, expressions for the intensity factors are derived for rotational transitions in $^2\Lambda$ and $^3\Lambda$ 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 $|\Lambda S\Sigma;r\rangle$ 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 $^1\Lambda$ ($\Lambda \neq 0$) 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] L.R. Zink and M. Mizushima, J.Mol. Spectrosc. 125, 154 (1987).

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MF6.   (2:39)

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[1]. Most of these rules[2] seem intuitively plausible and their validity is readily demonstrated[3]. 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[1] 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 H_2 molecule[2]. 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] E. Wigner and E.E. Witmer, Z. Physik 51, 859 (1928).

[2] G. Herzberg, Molecular Spectra and Molecular Structure Vol.1 (Spectra of Diatomic Molecules) Van Nostrand, New York (1950).

[3] L.D. Landau and E.M. Lifshitz, Quantum Mechanics , Pergamon Press, London (1965).

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(3:00)

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/H_2 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 $^5\Sigma$ - $^5\Sigma$ transition. The 480 nm spectrum, which is extremely complex with dense
rotational structure, arises from a $^5\Pi$ - $^5\Sigma$ 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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(3:16)

VUV 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 spectrograph/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 spectrograph. 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.

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MF9. (3:27)

LEVEL SHIFTS IN THE $B^3\Sigma_u^-$ STATE OF MOLECULAR OXYGEN

R.S. FRIEDMAN AND A. DALGARNO

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

[1]P.S. Julienne and M. Krauss, J. Mol. Spectrosc. 56, 270 (1975).

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MF10. (3:43)

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

R.S. FRIEDMAN

Band oscillator strengths of the Schumann-Runge ($B^3\Sigma_u^-$ - $X^3\Sigma_g^-$) 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.

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MF11. (3:59)

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 Ω = 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]1 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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MF12. (4:10)

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 Ω-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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MF13. (4:26)

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 (809nm-1.1μ). The vibrational band heads were spectrally resolved with a resolution of 0.2nm at 650-890nm and 1.0nm at 890nm-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$\longrightarrow$v"=5 to v'=0$\longrightarrow$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.

1. J.A. Coxon, J. Mole. Spectry., 50, 142-165 (1974).
2. D.L. Albritton, A.L. Schmeltekopf, and R.N. Zare, "An Introduction to the Least-Squares Fitting of Spectroscopic Data," in Modern Spectroscopy, Modern Research II, K.N. Rao, ed, Academic Press, NY, 1976.

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MF14.   (4:37)

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(1), to predissociaton 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.

1. M.C. van Hemert, H. Dohmann and S.D. Peyerimhoff, Chem. Phys. 110, 55 (1986).
2. R.L. Brooks and B.G. Nickel, Chem. Phys. Lett. 139, 503 (1987).

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MF15.   (4:48)

THE COMET-TAIL AND BALDET-JOHNSON SYSTEMS OF $^{13}C^{18}O^+$[1]

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

The emission spectra of the comet-tail ($A^2\Pi_i - X^2\Sigma^+$) and the Baldet-Johnson ($B^2\Sigma^+ - A^2\Pi_i$) 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 1-0) bands of the B-X system were photographed in the 2nd and/or 3rd orders of 2 m and 3.4 m grating spectrographs. 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 $^2\Pi_{1/2} - X^2\Sigma^+$) 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 $X^2\Sigma^+$, $A^2\Pi_i$ and $B^2\Sigma^+$ states of $^{13}C^{18}O^+$ was obtained.

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MF16.   (5:04)

FOURIER TRANSFORM SPECTROSCOPY OF $^7Li_2$: THE $1^3\Sigma_g^+ - 1^3\Sigma_u^+$ TRANSITION

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

Fluorescence resulting from excitation of $^7Li_2$ 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 $1^3\Sigma_g^+ - 1^3\Sigma_u^+$ 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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MG1.   (1:30)

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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[1] J. L. Hardwick, J. Mol. Spectrosc. 109, 85 (1985).

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MG2.   (1:46)

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 obtaineu by monitoring photo-induced changes in their neutralization-reionization mass spectra will be discribed. 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_3O, and H_2F will be discussed.

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MG3.   (2:02)

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 $\tilde{A}$ $\leftarrow$ $\tilde{X}$ 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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M54.   (2:18)

LASER EXCITATION AND DISPERSED FLUORESCENCE SPECTRA OF METHOXY PRODUCED BY PHOTODISSOCIATION IN A PULSED SUPERSONIC JET EXPANSION

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

Methoxy is a highly reactive organic free radical that is a key intermediate in the combustion of hydrocarbon fuels and in atmospheric reactions. It has nominal C_{3v} symmetry and an electronically degenerate ^2E ground state and is therefore subject to Jahn-Teller distortion and also split by a moderately large (~ 60 cm^{-1}) spin-orbit coupling. The origin of the electronic transition $\tilde{A}$ $^2A_1$ $\leftrightarrow$ $\tilde{X}$ ^2E of methoxy in the ultraviolet has been reported in the literature to have several different values over the years. Extensive laser-induced fluorescence excitation spectra and wavelength resolved emission spectra have been recorded at low temperatures for methoxy, CH_3O, and its perdeutero analog, CD_3O. A detailed analysis of the vibronic spectrum of methoxy has yielded a new reliable value for the electronic origin and an essentially complete set of significantly revised vibrational frequencies for both the $\tilde{X}$ and $\tilde{A}$ states. These results have been used to determine the vibronic structure of the ground state and in the elucidation of several ambiguous excited state vibronic assignments.

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IONIC CLUSTERS [$(NO)_n^+Ar_y$ and $(C_6F_6)_n^+R_m$, R=He, Ne or Ar] IN A SUPERSONIC JET

C.-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 invloving NO^+ and $C_6F_6^+$.

Resonantly enhanced multiphoton ionization of NO produces cleanly NO^+ 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^+ seed.

For the van der Waals molecules $(C_6F_6)_n^+R_m$, 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_1 MANIFOLD

SUDHIR S KULKARNI AND JONATHAN. E. KENNY

Absorption spectra of azulene from S_1 manifold are obtained in a pulsed planar supersonic jet. Line profiles of single vibrational levels, starting from S_1 origin up to 2417 cm^{-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_1 and S_2 state are compared

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66

PRERESONANCE RAMAN INTERFERENCE IN LINEAR POLYENES

I. SZTAINBUCH and G. E. LEROI

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 1 for a diphenyldecapentaene (DPDP) to locate the lowest-lying excited gerade singlet state (^1A_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 1445 cm^{-1}. The technique has been applied to other polyenes, and results for all systems investigated to date will be described.

[1]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.[1]

We have prepared and investigated spectroscopically $(bpy)_2Ru(II)(bpm)$, $(phen)_2Ru(II)(bpm)$, $[(bpy)_2Ru(II)]_2(bpm)$, 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 complexes 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.

[1]D. G. Whitten, Accts. Chem. Res. 13, 83 (1980).

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MG9.   (3:46)

FLUORESCENCE EXCITATION SPECTROSCOPY OF $p-C_6H_4Cl_2$ AND $p-C_6D_4Cl_2$ IN A SUPERSONIC FREE JET
EXPANSION W. D. SANDS AND R. MOORE

The spectra of $p-C_6H_4Cl_2$ and $p-C_6D_4Cl_2$ have been assigned over the range of 0 - 2500 cm^{-1}.
The spectra are dominated by totally symmetric vibrations and vibronically allowed b_{3g} vibra-
tions. Overtones of several out of plane bending modes are observed. The S_1 frequencies are
markedly reduced from S_0 values, indicating that the molecules are significantly less rigid
in S_1. 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
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MG10.   (4:C2)

ULTRA HIGH-RESOLUTION ELECTRONIC SPECTROSCOPY IN MOLECULAR BEAMS.   THE $S_1 \leftarrow S_0$ 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", con-
sisting 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 $S_1 \leftarrow S_0$ fluorescence excitation spectrum of 1-fluoronaphthalene, at ca.
310 nm, permitting tests of the instrumental bandwidth and sensitivity as well as a deter-
mination 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 S_1 and S_0 states and the orientation of the optical tran-
sition moment relative to the inertial frame. Future applications of this instrument to
problems in chemical dynamics will be discussed.

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

J. L. TOMER, 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. S_1 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 T_1 acetophenone exhibits no such change, a fact that can be attributed to subtle dif
ferences in the orbital character of the two excited states.   In contrast, both S_1 and T_1
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.

[1]For a review, see A. E. Dorigo, D. W. Pratt, and K. N. Houk, J. Am. Chem. Soc. 109,
6591 (1987).

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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 $^3A_u \leftarrow {}^1A_g$ electronic transition.[1]   The rota
tional structure of this band will be presented and shown to be inconsistent with assignment
of A_u 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.

[1]Hollas, J. M., Spectrochim. Acta 20, 1563 (1964).

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MG13.   (4:50)

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 inensities of the molecular eigenstate spectra. It is concluded that substantial differences exist between both spectra.

[1] J. Kommandeur, W.A. Majewski, W.L. Meerts and D.W. Pratt, Ann. Rev. Chem. Phys. 38 (1987) 433

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MG14.   (5:06)

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 $S_1 \leftarrow S_0$ 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 indentified. We found the intersystem crossing rate to be independent of the rotational quantum numbers and depending on the vibrational state.

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MH1.   (1:30)

INFRARED SPECTRUM AND STRUCTURE OF THE AlC_2H_4 MOLECULE IN SOLID ARGON

Laurent Manceron and Lester Andrews

AlC_2H_4, aluminum monoethylene, has been synthesized by cocondensation of Al atoms and ethylene molecules in solid argon. Analysis of the isotopic shifts (using C_2H_4, C_2D_4, $^{13}C_2H_4$ and CH_2CD_2) for the 7 observed fundamentals, shows that the metal forms a symmetrical π complex of C_{2v} symmetry. A normal-coordinate analysis for the Al block motions estimates the perturbations of the C=C and 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 C=C bond, AlC_2H_4 presents two noteworthy characteristics: i) a relatively large Al-C force comstant and ii) the relative intensities of the observed fundamentals are very different from other π complexes. This second point is analysed through estimates of some of the electro-optical parameters of AlC_2H_4, linked to the variation of charge flow between the metal center and the π bond through CC distance or CH_2 bond angle variations. Comparison with the same parameters in LiC_2H_4 reveals a significant difference. This fact might be more indicative of differences in the nature of the bonding between the metals and the C=C double bond, than is a simple comparison of the vibrational frequencies or even C=C force constant perturbations.

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MH2.   (1:46)

MATRIX REACTIONS OF OXYGEN ATOMS WITH P_4. INFRARED SPECTRA OF P_4O, P_2O, PO and PO_2

Lester Andrews and Robert Withnall

Oxygen atoms (^{16}O and ^{18}O) 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_4O exhibited a strong terminal P=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_4O before relaxation by the matrix: the first absorbed at 1197 cm^{-1}, photolysed with red light, and is probably P_2O; 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_4O structural isomer. Higher discharge power gave O atoms and vacuum ultraviolet radiation; these conditions favored the bridge-bonded P_4O species and the simple oxides PO and PO_2, which were observed at 1218 and 1319 cm^{-1}, respectively. The matrix efficiently quenched the large exothermicity (130 ± 10 kcal/mole) for the P_4 + O reaction and allowed the lowest oxide of phosphorus P_4O to be trapped for the first time as a molecular species.

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MH3.   (2:02)

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[1,2]. 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.

[1]R. Gevirzman, Y. Kozirovski, M. Folman, Trans. Faraday Soc., _65_ (1969).

[2]H.H. Richardson, C. Baumann, and G.E. Ewing, Sur. Sci. _185_, 15 (1987).

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MH4.   (2:18)

"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.[1] They were all found to have $^2\Sigma$ 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 ^{45}Sc, ^{89}Y, and ^{105}Pd nuclei were determined. The $^2\Sigma$ ground state of YPd found here is among the three lowest states calculated by Shim and Gingerich.[2]

[1] R. J. Van Zee and W. Weltner, Jr., High Temperature Science _17_, 181 (1984).
[2] I. Shim and K. A. Gingerich, Chem. Phys. Lett. _101_, 528 (1983).

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MH5.   (2:29)

S = 4 and S = 5 SPIN STATES OF THE "ANTIFERROMAGNETIC" Mn_2 MOLECULE

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

Mn_2 has been shown to be a van der Waals molecule with the two Mn atoms $(3d^54s^2)$ antiferromagnetically coupled (J = -10 cm^{-1}) to form a $^1\Sigma_g$ lowest state.[1] Mn_2 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.

[1] C. A. Baumann, R. J. Van Zee, S. V. Bhat, and W. Weltner, Jr., J. Chem. Phys. _78_, 190 (1983); J.-C. Rivoal, J. Shakhs-Emampour, K. J. Zeringue, and M. Vala _92_, 313 (1982).

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MH6.

ESR OF TRANSITION METAL DIATOMIC IONS: Mn_2^+

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The molecular cation $^{55}Mn_2^+$ has been generated in an argon matrix at 4 K by simultaneous laser vaporization of manganese metal and open tube argon discharge photoionization.[1] 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 $^{12}\Sigma$ molecule with a zero-field splitting parameter, D, of about 0.06 cm^{-1}. This contrasts sharply with Mn_2 which has an "antiferromagnetic" $^{1}\Sigma$ ground state,[2] but also a much weaker bond than Mn_2^+.[3]

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[1] Similar to the procedure pioneered by L. B. Knight, Jr., Acc. Chem. Res. 19, 313 (1986).
[2] R. J. Van Zee, C. A. Baumann, and W. Weltner, Jr., J. Chem. Phys. 78, 6977 (1981).
[3] K. Ervin, S. K. Loh, N. Aristov, and P. B. Armentrout, J. Phys. Chem. 87, 3593 (1983).

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MH7.

FTIR ISOTOPIC STUDY OF THE C_3H RADICAL IN AN ARGON MATRIX AT 9 K[*]
JIUNWOEI HUANG and W.R.M. GRAHAM

The rotational spectrum of C_3H observed in two astronomical sources and in the laboratory showed that it has a linear structure with a $^2\Pi$ ground state. *Ab initio* calculations by Green[1] 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 C_3H, and the same mode of C_3D 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 C_3H and C_3D will be reported.

[1] S. Green, Astrophys. J. *240*, 962 (1980).
[2] M. E. Jacox and D. E. Milligan, Chem. Phys. *4*, 45 (1974).

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·JH8.

HIGH RESOLUTION, HIGH DILUTION SPECTRA OF OCS IN Ar, N_2, 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 N_2 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 N_2. 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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MH9.

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 illucidate 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 splayed 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 illucidate 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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MH10.

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[1] in a study of the vacuum-ultraviolet photolysis of H_2O 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.

[1]D. E. Milligan and M. E. Jacox, J. Chem. Phys. 54, 927 (1971).

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MH11.

INFRARED SPECTRA OF H_2O AND D_2O 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. H_2O 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 D_2O consists of unstructured bands at 2350 cm-1 and 1165 cm-1, with no apparent structure on the wings.

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MH12.   (4:20)

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_o = -18±2 kJ mol^{-1}).
At high coverages, multilayer adsorption was noted: spectral features attributed to the 'glassy liquid' phase observed by Gordon and coworkers[1] were seen in the visible and infrared.

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[1] R.D. Gordon, S. C. Dass, J. R. Robins, H. F. Shurvell, and R. F. Whitlock, Can. J. Chem., 54 2658 (1976).

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MH13.   (4:36)

INFRARED SPECTROSCOPY OF CO ON NaCl(100)

H.-C. CHANG, H.H. RICHARDSON, AND G.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 α-CO. This structure is a consequence of the near perfect match of the α-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.

[1] H.H. Richardson and G.E. Ewing, J. Phys. Chem., 91, 5833 (1987).

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MH14.   (4:52)

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[1] with the model for the electrostatic potential above the surface
taking into account the continuous distribution of charge within the
crystal[2]. The present results are compared to previous calculations and
experiments involving HCN adsorbed on NaCl films[3].

[1]Dykstra, C.E.; Liu, S.-Y.; Malik, D.J. Adv. Chem. Phys. in press.

[2]Ben-Ephraim, A.; Folman, M. J. Chem. Soc., Faraday Trans. 2 1984, 80, 681.

[3]Kozirovski, Y.; Folman, M. Trans. Faraday Soc. 1966, 62, 808.

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MH15.   (5:08)

**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 O_2 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 N_2O 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 + C_3H_4 are interpreted in terms of an undetected ethylidene intermediate.

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MH16.   (5:19)

**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 Hebi 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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TA2.   (9:03)

OPTOTHERMAL-INFRARED AND PULSED-NOZZLE FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY OF RARE GAS-CO_2 COMPLEXES

G. 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 3715 cm^{-1}, in the region of the $2\nu_2^0+\nu_3/\nu_1+\nu_3$ 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 $K_a=1\leftarrow0$ subband by as much as 500 MHz

---

[1]J. M. Steed, T. A. Dixon, and W. Klemperer, J. Chem. Phys. 70, 4095 (1979).

Address of Fraser, Pine, and Suenram: Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland 20899.

TA3.   (9:19)

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 $\nu_1+\nu_3/2\nu_2^0+\nu_3$ 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[1-3], there is a marked vibrational dependence to the vibrational
predissociation rate in the HF dimer with the "free"-H stretching mode, ν_1, much longer
lived than the "bound"-H stretching mode, ν_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 ν_1 band with high precision
($\pm$ 0.5 MHz). We observe a substantial K, but negligible J, dependence for the ν_1
predissociation linewidths, and a smaller, but statistically significant, dependence on the
tunneling state. For the symmetric lower tunneling level of ν_1, the K=1 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 ν_2 band predissociation
linewidths with reduced spectral congestion and blending[1,2] afforded by the low effective
temperatures of the adiabatic expansion.

[1] A. S. Pine and W. J. Lafferty, J. Chem. Phys. _78_, 2154 (1983).
[2] A. S. Pine, W. J. Lafferty, and B. J. Howard, J. Chem. Phys. _81_, 2939 (1984).
[3] Z. S. Huang, K. W. Jucks and R. E. Miller, J. Chem. Phys. _85_, 3338 (1986).

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OPTOTHERMAL SPECTROSCOPY OF HF COMPLEXES WITH CO_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_2, OCS, and NO have
been recorded with an optothermal (bolometer-detected) molecular-beam color-center laser
spectrometer. As with the CO_2 complex observed previously,[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_2 and $OC^{32}S$ 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).

[1] C. M. Lovejoy, M. D. Schuder and D. J. Nesbitt, J. Chem. Phys. _86_, 5337 (1987).

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INFRARED AND MICROWAVE INVESTIGATIONS OF INTERCONVERSION TUNNELING IN THE ACETYLENE DIMER

G. T. FRASER, R. D. SUENRAM, F. J. LOVAS, A. S. PINE, J. T. HOUGEN, W. J. LAFFERTY, AND J. S. MUENTER

A sub-Doppler infrared spectrum of $(HCCH)_2$ has been obtained in the region of the acetylene C-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.[1] and the perpendicular band to a C_{2h} complex by Bryant et al.[2] 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.[1], 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 cm^{-1} barrier separating the four minima.

[1] D. G. Prichard, R. N. Nandi, and J. S. Muenter, J. Chem. Phys. (to be published).
[2] G. W. Bryant, D. F. Eggers, and R. O. Watts, J. Chem. Soc. Farad. II, (to be published).

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Address of Muenter: Department of Chemistry, University of Rochester, Rochester, New York, 14627.

LASER-INDUCED FLUORESCENCE MOLECULAR-BEAM OBSERVATIONS OF THE HYPERFINE STRUCTURE
IN THE NO_2 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 calbration 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 NO_2 (bands 99 and 115 of Smalley et
al.[1]). 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 compon-
ents. The calibration system allowed the hyperfine splittings of a rotational line
to be measured to ±1 MHz, while giving agreement to ±10 MHz between $\Delta_2F''(N)$
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 para-
meters were obtained for the $^2B_2$ upper levels with N=1,3,...,9. Good agreement was
obtained with literature values[2] 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.[3] and Demtroder
et al.[2] are not inconsistent with each other, but represent different viewpoints of
the same perturbed system.

[1] R.Smalley, L.Wharton and D.Levy. J.Chem.Phys. 63, 4977(1975).
[2] (a)T.Tanaka and D.Harris. J.Mol.Spectrosc. 59, 413(1976). (b)G.Persch, H.
Vedder and W.Demtroder. J.Mol.Spectrosc. 123, 356(1987).
[3] S.Coy, K.Lehmann and F.DeLucia. J.Chem.Phys. 85, 4296(1986).

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MOLECULAR BEAM OBSERVATIONS OF HYPERFINE TRANSITIONS IN KOH
J. CEDERBERG, D. RIOUX, 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 l 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.

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TA9.

OBSERVATION OF $(H_2O)_2$ 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 $(H_2O)_2$. As anticipated from group
theoretical arguments[1] and similar to K=0 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.

[1]T.R. Dyke, J. Chem. Phys. 66, 492 (1977).

Department of Chemistry, University of Oregon, Eugene, Oregon, 97403.

TA10.

ROTATIONAL SPECTRA OF CARBOXYLIC ACID DIMERS

W. KRESA AND A. BAUDER

Rotational transitions of the dimers $HCOOH \cdot \cdot CF_3COOH$ and $CH_3COOH \cdot \cdot CF_3COOH$ 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 CF_3 groups were too small to be observed. Only the internal rotation of the CH_3 group
led to splittings of the order of 1 - 40 MHz.

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Hochschule, CH-8092 Zürich, Switzerland.

(11:39)

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 $(HCN)_2$ 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
$(HCN)_2$ for comparison.

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(11:50)

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 $K_a=0\leftarrow1$
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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TP1.

ANALYSIS OF THE ν_6 BAND IN CH_2DF, AND ASSIGNMENT OF SOME SMMW LASER LINES

D.F. Eggers, W. Lewis-Bevan, M.C.L. Gerry, 'I.S. Tobin and T.W. Daley

A sample of CH_2DF was prepared in high isotopic purity and the IR spectrum was run on a Bomem instrument at 0.005 cm^{-1} resolution. The ν_6 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 $K_a = 10$ in this band with $K_a = 8$ in the ν_5 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 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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Address of Tobin and Daley: U.S. Army Electronics, Research and Development Command, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783

TP2.

THE INFRARED SPECTRUM OF AMINODIFLUOROBORANE, NH_2BF_2: PARTIAL ASSIGNMENT OF THE FUNDAMENTALS AND ANALYSIS OF THE 2^1_0 BAND NEAR 1608 cm^{-1}

W. LEWIS-BEVAN, H.M. JEMSON AND M.C.L. GERRY

The infrared spectrum of gas phase aminodifluoroborane, NH_2BF_2, has been observed for the first time. A partial assignment to the fundamental vibrations has been made. The 2^1_0 band has been recorded at high resolution, and the rotational and centrifugal distortion constants of $NH_2{}^{11}BF_2$ have been obtained in both the ground and 2^1 levels. 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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Address of Gerry: Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver B.C. V6T 1Y6 Canada.

HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CH_2F_2: THE ν_8 BAND AT 1435 cm^{-1}

R. D'CUNHA, P. K. WAHI, V. B. KARTHA, AND A. WEBER

Fourier transform infrared spectra of methylene fluoride were recorded with the NBS BOMEM DA3.002 spectrometer with an apodized resolution of 0.004 cm^{-1}. Detailed assignments up to $J_{max} = 25$ have been made for the ν_8 parallel A type band centered at 1435 cm^{-1}. Watson's A type reduced Hamiltonian in the 1^r 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 NH_3[1]

Yukari Matsuo, Sang K. Lee, and R. H. Schwendeman

Infrared-infrared four-level double resonance has been observed in NH_3 by using a CO_2 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 100% 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 asR(2,0) transition in the ν_2 band of $^{15}NH_3$ has been pumped while transitions in the $\nu_2 = 2a \leftarrow \nu_2 = 1s$ 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 $\Delta K=0$ four-level double resonance, whereas a broader velocity-conserving effect is seen in a $\Delta K=3$ 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.

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TB5.   (9:24)

LINEAR AND NONLINEAR SPECTROSCOPY BY USE OF MICROWAVE MODULATION SIDEBANDS IN THE CO LASER REGION[1]

Shin-Chu Hsu and R. H. Schwendeman

The analysis of infrared microwave sideband laser spectra of the ν_2 band of D_2CO at 1700 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 $K_a < 9$ to an absolute accuracy of approximately 10 MHz. The transitions for $K_a = 9-11$ show evidence for a resonance.

An infrared radio-frequency double resonance effect has been observed by pumping an R-band transition in the ν_2 band of H_2CO 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 asymmetry doublets.

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TB6.   (10:00)

HIGH RESOLUTION INFRARED STUDY OF THE ν_2 BAND OF CD_3I[1]

Han-G. Cho and R. H. Schwendeman

The infrared spectrum of the ν_2 band of CD_3I 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 ν_5 state will be presented and compared to previous results.

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TB7.   (10:16)

STARK EFFECT OBSERVATIONS WITH IR LASER SIDEBANDS

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

Linear Stark effect has been resolved on several ro-vibrational transitions in the ν_4 fundamental of $^{13}CD_4$. 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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TB8.   (10:32)

COLOR CENTER LASER SPECTROSCOPY OF C_2H AND $^{13}C_2H$

J. W. STEPHENS, M. L. RICHNOW, AND R. F. CURL

Transient absorption spectra of C_2H and $^{13}C_2H$ 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_2H 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_2H and $^{13}C_2H$ 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_2H bands of $^2\Sigma^+$-$^2\Sigma^+$ symmetry, three $^{13}C_2H$ bands of $^2\Sigma^+$-$^2\Sigma^+$ symmetry, and one $^{13}C_2H$ band of $^2\Pi^+$-$^2\Sigma^+$ symmetry. Three of the $^{13}C_2H$ bands have been assigned as analogues of $^{12}C_2H$ bands observed here and in previous works. The assignment of the CH stretch is still uncertain, however two of the three $^2\Sigma^+$-$^2\Sigma^+$ ground state C_2H bands are possible candidates.

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TB9.   (10:48)

INFRARED-RADIOFREQUENCY DOUBLE RESONANCE SPECTROSCOPY OF CH_3F 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-radiof quency double resonance spectroscopy possible [1].

We have used this technique to study the A_1-A_2 splitting of CH_3F in the ν_4 (J, $K=1$, $l=1$ and J, $K=2$, $l=-1$) state. This splitting can be represented by

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

where the second and third terms are centrifugal distortion terms. We determined $q=16.04466(53)$ MHz, $q_J=3.523(29)$ KHz and $q_{JJ}=2.53(36)$ Hz for $K=1$, $l=1$; and $q=6.88835(72)$ KHz, $q_J=4.6124(70)$ Hz and $q_{JJ}=2.444(16)\times10^{-3}$ Hz for $K=2$, $l=-1$.

We also measured the electric dipole moment of CH_3F in the ν_4 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 ν_4 states. Using the ratio of this splitting (when $J'' = K''$ and $J' = K'$) the dipole moment can be calculated according to

$$\mu' = \mu'' \frac{\Delta\nu'}{\Delta\nu''} \frac{(J'+1)}{(J''+1)}$$

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 stuuy 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.

[1] R. L. Deleon, P. H. Jones, and J. S. Muenter, *Appl. Opt.* 20, 525(1981)

[2] S. C. Wofsy, J. S. Muenter, and W. Klemperer, *J. Chem. Phys.* 55, 2014(1971)

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TB10.   (11:04)

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

A. G. MAKI, WM. 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 (HNO_3). The two in-plane vibrations, ν_6 at 646.83 cm^{-1} and ν_7 at 580.30 cm^{-1}, are found to be nearly 100% A-type bands and the intensity of ν_7 has been measured relative to that of ν_6. The two out-of-plane fundamentals, ν_8 and ν_9, have band-centers at 763.15 cm^{-1} and 458.23 cm^{-1} respectively. The R-branch of ν_8 is considerably stronger than the P-branch and appropriate Herman-Wallis-like constants were determined in order to allow one to accurately calculate the spectrum. 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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Address of Goldman: Department of Physics, University of Denver, Denver, CO, 80208.
Address of Burkholder and Howard: NOAA Aeronomy Laboratory, 325 Broadway, Boulder, CO, 80303.

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

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

The far infrared spectrum of HCNO exhibits a widely spread set of perpendicular transitions in the manifold of the quasilinear bending mode, ν_5, and the combination manifold $\nu_4 - n\nu_5$, where ν_4 is the skeletal bending mode. We have analyzed the spectrum of the ^{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 $(\nu_1\nu_5)^\ell = (02)^{0e} - (11)^{01}$ and $(02)^{0e} - (11)^{00}$, respectively. These transitions are only allowed due to a Coriolis interaction between the levels $(02)^{0e}$ and $(10)^{1e}$, which was observed as a relatively weak interaction in the parent species.

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THE LOWEST SKELETAL BENDING MODE OF N_2O_3 IN THE GAS PHASE

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

The search for the lowest bending mode of N_2O_3 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_2 which severely limits the possibility of locating rotational structure due to N_2O_3. 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_2O_3.

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TB13.   (11:47)

HIGH RESOLUTION INVESTIGATION OF CH3CHO IN THE INFRARED

I. KLEINER, M. GODEFROID, M. HERMAN

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

The v_4 infrared band of CH3CHO, C-O stretch centered around 1743 cm^{-1}(1), is studied at high resolution. Different experimental approaches were carried on 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 developped 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

(1) H.Hollenstein and Hs.H.Günthard, Spectrochim. Acta vol.27A, p.2027 (1971).
(2) E.Herbst, J.K.Messer, F.De Lucia and P. Helminger, J. Mol. Spectrosc., 108, 42 (1984).
(3) K U.L Sastry, E.Herbst, R.A.Booker and F.De Lucia, J. Mol. Spectrosc., 116, 120 (1986)
(4) W. Liang, J.G. Baker, E.Herbst, R.A.Booker and F.De Lucia, J. Mol. Spectrosc., 120, 298 (1986).

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Address of Marshall : Amherst College, Department of Chemistry, Amherst, MA 01002, USA
Address of Johns and McKellar : Herzberg Institute of Astrophysics, National Research Council, K1A OR6 Ottawa, Canada.

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 ν_1 of CHF_3 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 ν_1 (species A_1) and the combinations $\nu_4^{\pm}+\nu_5^{\pm}+\nu_6^{\pm}$ (A_1+A_2) located only 1.45 cm^{-1} above ν_1, whose origin is at 3033.52 cm^{-1}. The coupling constant of the resonance is $k_{1456}/2\sqrt{2} = 3.67$ cm^{-1}. Additional severe perturbations by the E components of $\nu_4+\nu_5+\nu_6$ as well as by $\nu_2+\nu_4+\nu_6$ have been identified in the spectrum.

Since the ν_1 vibration is known to be in global Fermi resonance with the overtone $2\nu_4^0$, we have also recorded the 2680 - 2815 cm^{-1} region, containing the $2\nu_4^0$ and $2\nu_4^2$ bands, under Doppler-limited conditions using a difference-frequency laser spectrometer. This has yielded much improved spectroscopic constants, in particular for the strongly perturbed $2\nu_4^{-2}$ state.

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TC1.   (8:30)

PHOTOFRAGMENTATION OF JET-COOLED ACETIC ACID

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

Acetic acid cooled in a free jet expansion photodissociates following $n \rightarrow \pi^*$ excitation at 218 nm. The nascent internal energy distribution of the OH X $^2\Pi$ 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.

Address: Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221

TC2.   (8:47)

PHOTOFRAGMENTATION OF KETENE AT THE SINGLET THRESHOLD

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

Ketene (CH_2CO) 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, CH_2 (ã $^1A_1$). CH_2 was detected by laser-induced fluorescence (LIF). The appearance threshold and yield curve of individual $^1CH_2$ 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 $CH_2CO \rightarrow {}^1CH_2 + CO$ 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 7×10^7 s^{-1} 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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TC3.   (9:04)

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
polypyridyl 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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TC4.   (9:21)

INVESTIGATION OF THE RESPONSE OF THE $NO/NO_2/N_2O_4$ 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 $NO/NO_2/N_2O_4$ 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 NO_2 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
NO_2 and N_2O_4 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.

(1)M.Carleer, M.Herman, J.Vander Auwera and M.Van Roozendael, Chem. Phys. Letters 127, 13-18
     (1986).
(2)J.Vander Auwera and M.Herman, J. Photochem., 38, 15-33 (1987).

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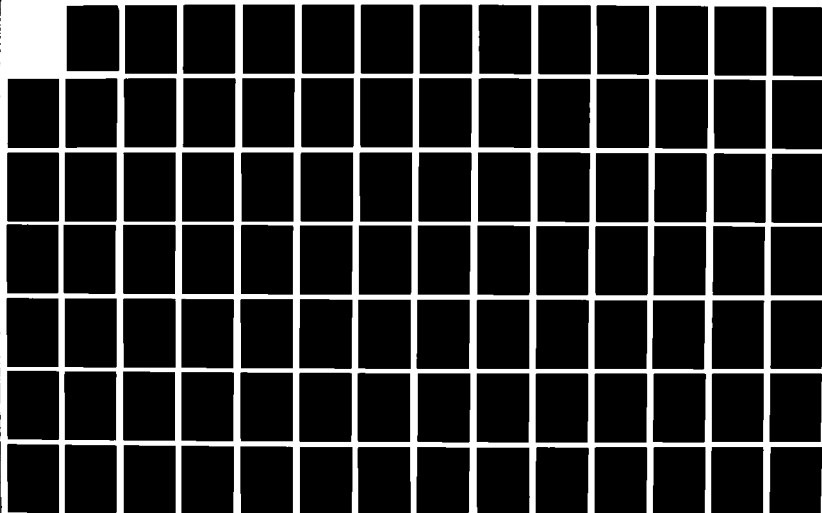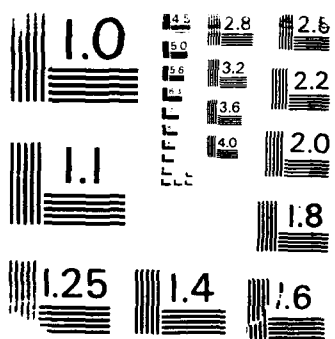
HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF THE SINGLET MOLECULAR OXYGEN-IODINE REACTION AND POPULATIONS OF THE $B O_u^+$ AND A 1u STATES THROUGH NON LINEAR INVERSION OF EMISSION SPECTRA

D. CERNY, R. BACIS, and J. VERGES

The dissociation of molecular iodine I_2 by metastable oxygen O_2 ($^1\Delta_g$) 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 ($^1\Delta_g$) is obtained from a microwave discharge in oxygen. The flow of less than 10 % of O_2 ($^1\Delta_g$) is mixed with pure iodine. The reaction gives a flame emitting from 3 700 cm^{-1} to 20 000 cm^{-1}. We observe this flame along the axis with a high resolution Fourier Transform spectrometer. The 10 000 - 20 000 cm^{-1} emission is due to the $B O_u^+ \rightarrow X O_g^+$ transition and allows to determine the populations of the $B O_u^+$ rovibrational levels. The Infra-Red region comes from A 1u $\rightarrow$ X O_g^+ 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 $B O_u^+$ has a maximum population around v = 30 - 35. The rotational distribution in A 1u or $B O_u^+$ 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 ($^1\Delta_g$) 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 $\rightarrow$ 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_2CO $\tilde{A}$ $^1A_2$ 4^1 $1_{0,1}$ 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 $\tilde{A}$ $^1A_2$ $v_4=1$, $J=1$, $K_a=0$. Previous rotational state-to-state measurements in the H_2CO $\tilde{A}$ 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 $1_{0,1} \rightarrow (0_{0,0}$ or $2_{0,2}) \rightarrow 1_{0,1}$ processes. The transient response within the $1_{0,1}$ 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 $5^2P_{1/2}$ - $5^2P_{3/2}$ TRANSITION

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

The pressure broadening of the hyperfine lines of the $^2P_{1/2}$ - $^2P_{3/2}$ 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 n m Ar^+ lines. Pressure broadening of 1.95 MHz/torr, 3.9 MHz/torr and 19.3 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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adress of Vergès: Laboratoire Aimé Cotton, CNRS II , bâtiment 505, 91405 Orsay, France

RS9. (10:50)

INTERMEDIATE CASE LEVEL STRUCTURE IN INFRARED SPECTRA: EVIDENCE FOR BOTH
ANHARMONIC AND CORIOLIS COUPLING IN THE C-H REGION OF 1-BUTYNE

A. M. DE SOUZA, DEVINDER KAUR, S. A. HAMMAD, G. A. BETHARDY, AND <u>DAVID S. PERRY</u>

Infrared spectra of jet-cooled (3 K) 1-butyne were recorded by the direct
absorption method. A two-spherical-mirror multiple pass cell was used to enhance
the absorption of the F-center laser beam.

For the lower rotational levels (J'≤3) of the a-type band near 3333 cm^{-1},
discrete features are rigorously assigned by comparing ground state combination
differences to accurate microwave data. While the $K_a'=1$ features appear
unperturbed, the $K_a'=0$ transitions are split into multiplets of at least 5
lines. These multiplets arise from strong interactions of the zero-order
acetylenic C-H stretch with the bath of background vibrations. The measured
density of eigenstates at 87 per cm^{-1} is comparable to the appropriate
calculated density of vibrational states. For J'=0-2, the matrix elements are
0.01 cm^{-1} and are anharmonic in origin.

For J'=3-7, the spectral complexity increases rapidly with J and individual
eigenstates are no longer discernible. Because redundant information occurs in
the P and R branches, it was possible to make a qualitative separation of the
contribution of $K_a'=1$ from $K_a'=0,2$. The width of the $K_a'=0$ multiplets is
approximately constant for all J' at a value near 0.05 cm^{-1}. Mixing of the $K_a'=1$
levels with the bath is apparent for J'>4 and the matrix elements, attributed to
Coriolis coupling, are <0.008 cm^{-1}.

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TC10. (11:02)

A MODIFIED RRKM APPROACH TO THE VIBRATIONAL PREDISSOCIATION DYNAMICS
OF THE S_1 p-DIFLUOROBENZENE-Ar VAN DER WAALS COMPLEX

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

The vibrational predissociation (VP) dynamics of the S_1 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 data[1] for the pDFB-Ar vdW complexes. Recently,
Kelley and Bernstein[2] 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 satisfactory. 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 S_1 complex levels. In
agreement with the data, it predicts that VP is highly selective
among the possible final levels. The selectivity has several
characteristics: i) VP does not favor nearby resonant monomer
levels, ii) VP does favor small vibrational quantum number changes,
iii) the monomer 0^0 level is a common final state for VP from all
initial levels. It also predicts the intramolecular vibrational
relaxation (IVR) observed in our experiments.

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

[2]D.F. Kelley and E.R. Bernstein, J. Phys. Chem. <u>90</u>, 5164 (1986).

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TC11.

OBSERVATIONS OF ROTATIONALLY AND VIBRATIONALLY INELASTIC SCATTERING
FROM AN EXCITED STATE POLYATOMIC: S_1 GLYOXAL

K.W. BUTZ, H. DU, D. KRAJNOVICH AND C.S. PARMENTER

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 ^1Au (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 ± 1 quantum changes in the lowest frequency mode, the torsion ν_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. ΔK 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 ΔE exponential scaling law, and where similar ΔE occurs, they are the same size. In contrast, the ΔK state-resolved cross sections from 7^2 are quite different. Some $\Delta v_7 = -1$ cross sections with small ΔK 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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TC12.

ENERGY DEPENDENCE OF THE INELASTIC COLLISION CROSS SECTION OF VIBRATIONALLY EXCITED I_2^* ($v' = 35$, 15) WITH He.

K.W. BUTZ, H. DU, D. J. KRAJNOVICH, AND C.S. PARMENTER

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 $v' = 35$ or 15 of the B 0_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 Δv UP versus Δv 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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TC13.   (11:53)

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.

(1) H.H. Richardson and G.E. Ewing, J. Phys. Chem. **91**, 5833(1987).
(2) R.J. Anderson and P.R. Griffiths, Anal. Chem. **47**, 2339(1975).

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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 LN_2 - 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 (T_1) 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.

[1] J.D. Simpson and H. W. Offen, J. Chem. Phys. 55, 1323 (1971) and earlier work cited therein.
[2] C.J. Sandroff, I.Y. Chan and W.M. Chung, ibid, 84, 2424 (1987).

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OPTICALLY DETECTED MAGNETIC RESONANCE OF Mn(IV) HEXAFLUORIDE IN Cs_2GeF_6 AND K_2GeF_6

E. LIFSHITZ AND A. H. FRANCIS

The photoexcitation and luminescence spectra ($^2E \dashrightarrow {}^4A_2$) of MnF_6^{2-} diluted in Cs_2GeF_6 and K_2GeF_6 host lattices have been recorded at liquid helium temperature. The manganese coordination geometry is O_h in Cs_2GeF_6 and D_{3d} in K_2GeF_6. 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 O_h site {$g(^2E)=2.0$} is as predicted theoretically; however, the value obtained for the D_{3d} site is unexpectedly large {$g(^2E)=2.95$}. The data obtained is compared with theoretical predictions and the results of similar studies of d^3 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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TD3.   (9:34)

ANALYSIS OF THE MID-IR ELECTRONIC ABSORPTION SPECTRUM OF $Fe_2P_2S_6$ AND $Co_2P_2S_6$

N. NAGASUNDARAM AND A. H. FRANCIS

Single crystal FTIR spectra of $Fe_2P_2S_6$, $Co_2P_2S_6$, $Cd_2P_2S_6$, and $Mn_2P_2S_6$ were recorded at room temperature. The $Fe_2P_2S_6$ and $Co_2P_2S_6$ 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 $Fe_2P_2S_6$ intercalated with pyridine was analyzed in terms of intercalation induced changes in the crystal-field parameters.

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TD'1.   (10:00)

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 ($OH\cdot$), methoxy ($CH_3O\cdot$), ethoxy ($C_2H_5O\cdot$), isopropoxy ($C_3H_7O\cdot$), and vinoxy ($C_2H_3O\cdot$) 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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100

TD'2.   (10:16)

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 of 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]

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TD'3.   (10:32)

Ab Initio Calculations on Ag_2, Au_2, 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_2, Au_2, 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 consts ts are compared to experiment and to previous ab intio
all-electron and REP studies.

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ID'4.   (10:48)

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.

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TD'5.   (11:04)

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 Å, R_{OH}=1.00 Å, $\angle_{HOO}$=104°). 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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EXPERIMENTAL AND THEORETICAL WORK ON DOUBLY CHARGED MOLECULAR IONS: N_2^{2+} AND CO^{2+}

A. Pinkvall, M. Larsson, B.J. Olsson and P. Sigray

Only a few doubly charged molecular ions are known to possess emission spectra. The $D\ ^1\Sigma_u^+ - X\ ^1\Sigma_g^+$ transition of N_2^{2+} was rotationally analyzed by Carroll already 1958 and more recently by Cossart and coworkers. We have used the high frequency deflection technique to perform the first direct vibrationally resolved measurement of a fluorescence lifetime of a doubly charged molecular ion.[1] Furthermore, we have used the complete active space SCF (CASSCF) method to calculate the electronic transition moment function of the D-X transition. The contracted CI (CCI) method was used to improve the potential curves obtained at the CASSCF level and the radiative lifetime was obtained with help of these potential curves and the electronic transition moment function. The experimental and theoretical lifetimes, 6.0 ± 0.5 and 8.0 ns respectively, are in good agreement.

No emission from the CO^{2+} ion has yet been observed. The CASSCF and CCI methods have been used to obtain potential curves of low lying triplet states of CO^{2+}. With these curves as guidance, emission from CO^{2+} following electron impact on jet cooled CO have been searched for. We also plan to search for a laser induced predissociation spectrum of CO^{2+} with the fast ion beam laser technique.

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[1] B.J. Olsson, G. Kindvall and M. Larsson, J. Chem. Phys. (in press).

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ULTRAFAST TRANSIENT SOLVATION OF POLAR DYE MOLECULES IN SIMPLE POLAR SOLVENTS

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

Recently we constructed a time resolved fluorescence apparatus with a resolution of less than 300 femtoseconds[1]. We have used this instrument to measure the microscopic solvation dynamics of three simple polar solvents (propylene carbonate, propiontrile, 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 τ_1 of the solvents. Results will be discussed in terms of several recent theoretical models[2-3].

---

[1] M.A. Kahlow, T.J. Kang and P.F. Barbara, J. Chem. Phys. 88, 2372 (1988); M.A. Kahlow, W. Jarzeba, T.P. DuBruil and P.F. Barbara, Rev. Sci. Instrum. (in press).
[2] E.W. Castner, G.R. Fleming and B. Bagchi, Chem. Phys. Lett. (in press).
[3] P.G. Wolynes, J. Chem. Phys. 86, 5133 (1987).

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Ab Initio CI study of the Magnetic Circular Dichroism Spectrum of
Acetylene for the $X \rightarrow \tilde{B}(^1B_u)$ and $X \rightarrow \tilde{C}(^1\Pi_u)$ Electronic Transitions

C. 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:

$$1. \quad (\tilde{H}^0 - E)\psi_i^1 = -\tilde{H}^P\psi_i^0 \quad ; \quad (\tilde{H}^1 = \text{some perturbing Hamiltonian})$$

over Configuration State Functions (CSF's) to obtain the first-order correction ψ_i^1 to
the electronic state ψ_i. This partially alleviates the impossible task of attempting
to calculate explicitly the infinite manifold of perturbing states represented in the
usual expression for a first-order perturbation:

$$2. \quad \psi_i^1 = \sum_{\substack{j \neq i}}^{\infty} |\psi_j^0\rangle \langle \psi_j^0|\tilde{H}^P|\psi_i^0\rangle \, \hbar \omega_{ji}$$

The MCD B term, which acquires it's 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 this
new application of the method to the singlet $X \rightarrow \tilde{B}(^1B_u)$ and $X \rightarrow \tilde{C}(^1\Pi_u)$ transitions
in acetylene.

----

1 D. R. Yarkony. J. Chem. Phys. 86, 1642 (1987): and references therein.

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Theoretical Study of the Radiative Lifetime for the Spin-forbidden Transition
$X^1\Sigma_g^+ \leftarrow a^3\Sigma_u^+$ in He2* Using Ab Initio State Averaged MCSCF Plus CI Methods

Cary F. Chabalowski, D. R. Yarkony, B. H. Lengfsfield III, J. O. Jensen

The radiative lifetime for the $a^3\Sigma_u^+$ state in neutral He2* was calculated
including spin-orbit (SO) interactions between the $a^3\Sigma_u^+$ and $^1\Pi_u$ manifold of
states, and the repulsive ground state $X^1\Sigma_g$ and the $^3\Pi_g$ 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 $X^1\Sigma_g^+$ or $a^3\Sigma_u^+$
wavefunctions, and the list of Configuration State Functions generated by a
second-order CI for the states of $^3\Pi_g$ or $^1\Pi_u$ symmetries, respectively (1). This
partially alleviates the problem of solving explicitly for many eigenstates of
the $^3\Pi_g$ or $^1\Pi_u$ symmetries. The results show a rapidly changing electric
transition dipole moment over the bound region of the $a^3\Sigma_u^+$, i.e. r(He-He) = 1.5
to 4.0 bohr. A vibrational analysis gives the lifetime of the v=0 level of $a^3\Sigma_u^+$
to be around 18 secs, which is consistent with a recent experimental estimate of
10 secs (v=?) as a lower bound.

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1. D. R. Yarkony. J. Chem. Phys. 86, 1642 (1987); and references therein.

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TE1.   (1:30)

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 concen-
tration in the field conditions based on researches carried out at the Ins-
titute of Atmospheric Optics SB USSR Academy of Sciences.

High resolution laser spectrometers, including intracavity laser spec-
trometers, laser spectrophotometers, opto-acoustic laser spectrometers,
fluorescence laser spectrometer are described. Using these spectrometers,
some thousands of new absorption lines, tens of previously unknown H_2O, CO_2,
C_2H_2, N_2O, NH_3, CH_4, HBr molecular absorption bands and their isotopes
were recordered, 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 atmos-
pheric pollutants. A new approach to the development of the differential
technique in the trace gas analyzers is discussed.

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* 6

TE2.   (2:05)

DIODE LASER SPECTROSCOPY OF TRIFLUOROHALOMETHANES (CF_3X) IN THE 9-9.5 μm REGION

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

Diode laser spectra of CF_3X 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 v_1 fundamental (CF_3 symmetric stret-
ching and the $2v_5$ overtone; of the latter, only the parallel component ($2v_5^0$) has been observed.
The measurements were carried out at low temperature (∿ 200 K) in order to simplify the com-
plex 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 transi-
tions to the energy expression including the quartic centrifugal distortion coefficients was per-
formed. Some lines were found to be rotationally perturbed by $2v_5^{\pm 2}$ and the different mechanisms
involving $\Delta l = \Delta k = \pm 2$, and $\Delta l = \pm 2$, $\Delta k = \mp 1$ interactions have been considered in the interpre-
tation. Accurate molecular parameters of v_1 and $2v_5^0$ bands of the two different isotopic species
of CF_3Cl and CF_3Br have been determined.

Work on the spectrum of CF_3I 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_3 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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Address of Solomon: Fabrication Division, Mail Stop 390, NASA Langley Research Center, Hampton, Virginia, 23665-5225

LINE POSITIONS AND INTENSITIES OF THE $2\nu_3$, $\nu_1 + \nu_3$, AND $2\nu_1$ BANDS OF $^{16}O_3$

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 $2\nu_3$, $\nu_1 + \nu_3$, and $2\nu_1$ bands of $^{16}O_3$, 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 $^{16}O_2$ 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$\approx$55, K_a=14 for the $2\nu_3$, J=64, K_a=17 for the $\nu_1 + \nu_3$, and J$\approx$55, K_a=14 for the $2\nu_1$ 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.[1] 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.

[1]J. M. Flaud et al., J. Mol. Spectrosc. 124, 209-217 (1987).

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TE5.   (2:46)

LINE INTENSITY AND COLLISION-BROADENED LINE WIDTH MEASUREMENTS IN THE ν_1-FUNDAMENTAL OF $^{14}N_2O$ 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 ν_1- fundamental of $^{14}N_2O$ 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 N_2-broadened, O_2-broadened and air-broadened line width data at several temperatures between 150 and 296 K.

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TE6.   (3:03)

LINEWIDTH NARROWING IN THE INFRARED BAND OF N_2O PERTURBED BY N_2

CAI PEIPEI , SHEN SHANXIONG , 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 N_2O perturbed by N_2.

Using R(16) line of a grating tunable N_2O laser and a White type long cell with variable lengths from 40 to 1000 m, the absorption spectrum of N_2O are obtained. The pressure of N_2O is varied from 10 to 20 Torr. The variation of linewidths is to plot the peak height of absorption as a function of N_2 gas pressure. The peak absorption constant increases with the N_2 gas pressure, reaches a maximum and then decreases. The maximum appears at the N_2 gas pressure of 300 Torr and 250 Torr when N_2O pressures are 10 and 20 Torr, respectively.

The conclution that[1] a collision partner with equal mass is most effective in changing the velocity through collisions is not exactly obvious in our case, since N_2O and N_2 have quite defferent masses.

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[1] D. Ramachandra Rao et al, J.Mol.Spectrosc., 122,16-27(1987)

Address: Department of Physics, East China Normal University, Shanghai,200062, People's Republic of China.

IF. (3:30)

ABSOLUTE INTENSITIES IN THE ν_2 REGION OF CO_2

J.W.C. JOHNS

Absolute intensities and pressure broadening parameters have been measured in the region of the ν_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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IFS. (3:47)

STUDIES CONCERNING THE OPTIMUM HAMILTONIAN FOR USE IN LARGE AMPLITUTUDE, 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 disassociation. Many important advances have occured 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.

1. R.B. Wattson and L.S. Rothman, J. Mol. Spectrosc. 119, 83-100 (1986).
2. E.B. Wilson, Jr. J.C. Decius, and P.C. Cross, Molecular Vibrations (McGraw-Hill, New York, 1955); J.K.G. Watson, Mol. Phys. 15, 479 (1968); J.K.G. Watson, Mol. Phys. 19, 465 (1970).

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CALCULATIONS OF ENERGIES AND INTENSITIES FOR THE ASYMMETRIC SPECIES OF CO_2

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 CO_2 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.

1. A.R. Hoy, I.M. Mills, and G. Strey, Mol. Phys. 24, 1265 (1972).
2. R.B. Wattson and L.S. Rothman, J. Mol. Spectrosc. 119, 83-100 (1986).

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CO_2 SPECTROSCOPIC CONSTANTS DETERMINED BY GLOBAL LEAST-SQUARES FITTING AND DIRECT NUMERICAL DIAGONALIZATION

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

The $^{12}C^{16}O_2$ 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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TE11.

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 near 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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TE12.

TEMPERATURE DEPENDENCE OF LINE BROADENING OF CO_2 LASER BAND

CAI PEIPEI , SHEN SHANXIONG , XU JIDONG AND I-SHAN CHENG

The broadening of CO_2 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 CO_2 laser is used as a source. The sample CO_2 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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TF1. (1:30)

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.[1] 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 ~8 x 8 x 10", 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.

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TF2. (1:47)

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[1] 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_4X particles. However, the rotational spectrum of vapor over heated solid NH_4Cl (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_0 and D_J 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.

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TF3.   (2:04)

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 μ and the electric field gradients χ_o 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[1] and trimer.[2] A dipole moment of 6.552(35) D has been reported for the dimer[3] and we have found 10.6(2) D for the trimer.[2] 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 $\Delta\chi_o(^{14}N)$.

A mutual polarization model was used to predict the induced dipole moments from the four 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 $\Delta\chi_o$'s. Equations are derived for calculation of $\Delta\mu$ of an infinite H-bonded chain and are applied 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.

[1] R. S. Ruoff, T. Emilsson, C. Chuang, T. D. Klots, and H. S. Gutowsky, Chem. Phys. Letters 138, 553 (1987).
[2] R. S. Ruoff, T. Emilsson, T. D. Klots, C. Chuang, and H. S. Gutowsky, J. Chem. Phys., submitted.
[3] E. J. Campbell and S. G. Kukolich, Chem. Phys. 76, 225 (1983).

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TF4.   (2:21)

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[1] 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) Å respectively, both about 0.05 Å shorter than the r for the dimer, 4.448 Å.[2] The overall shrinkage in OC-HCN-HCN is a bit less, 0.083(3) versus 0.106(1) Å, but it is highly asymmetric, 0.07(1) Å for r_1 and only 0.010(5) Å for r_2. The figures for N$_2$-HCN-HCN are comparable, an overall shrinkage of 0.075(3) Å with 0.065(10) and 0.009(6) Å for r_1 and r_2 respectively. The results for these and other hydrogen-bonded trimers will be presented and discussed.

[1] R. S. Ruoff, T. D. Klots, C. Chuang, T. Emilsson, and H. S. Gutowsky, Abstract MG14, 42nd Symposium on Molecular Spectroscopy, The Ohio State University, June 15-19, 1987, p. 69.
[2] R. S. Ruoff, T. Emilsson, T. D. Klots, C. Chuang, and H. S. Gutowsky, J. Chem. Phys., submitted.

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112

(2:35)

EMISSION FREQUENCY OF THE 496 μm LINE IN $^{12}CH_3F$ 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_3 excited vibrational state of this species; the implications of those results to the question of pressure shift will be discussed.

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(3:05)

A COLLISIONAL ENERGY TRANSFER MAP INCLUDING ΔK PROCESSES IN CH_3F

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 $^{13}CH_3F$, 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 ΔJ rates and vibrational relaxation rates. The first ΔK 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 ΔK=3n. We have also obtained preliminary results on a similar study of $^{12}CH_3F$.

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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 $^{12}CH_3F$ 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, $C_2H_3-O-C_2H_3$, 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, x_p, θ_p and ϕ_p.

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.

[1] C. Hirose and R. F. Curl, Jr., J. of Mol. Spectrosc. **38**, 358-366 (1971).
[2] C. Hirose and S. Maeda, J. of Mol. Spectrosc. **72**, 62-85 (1978).
[3] J. T. Hougen, J. Mol Spectrosc. **114**, 395-426 (1985).
[4] W. Pyckhout, C. Van Alsenoy, H. J. Geise, B. Van Der Veken and G. Pieters, J. of Mol. Structure. **130**, 335-353 (1985)

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

TF9.

TWO-DIMENSIONAL MICROWAVE FOURIER TRANSFORM SPECTROSCOPY

B. VOGELSANGER, M. ANDRIST, AND A. BAUDER

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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TF10.

ROTATIONAL SPECTRUM AND RING PUCKERING OF CYCLOBUTANE-1,1-d_2

B. VOGELSANGER, W. CAMINATI, R. MEYER, AND A. BAUDER

The pure rotational spectrum of cyclobutane-1,1-d_2 has been measured between 12-40 GHz with a pulsed microwave Fourier transform spectrometer. The assignment for transitions with $J \leq 40$ 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-d_2 and cyclobutane-d_1 and the vibrational transition frequencies of the ring puckering of the parent and the d_8 species.

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TF11.   (4:30)

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 ± 8.59, B = 2541.16 ± 0.05 and C = 2309.62 ± 0.04 MHz. From the Stark effect the dipole moment components were determined to be $|\mu_a|$ = 1.91 ± 0.02, $|\mu_b|$ = 1.07 ± 0.01, $|\mu_c|$ = 0.31 ± 0.01 and $|\mu_t|$ = 2.21 ± 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 ab initio calculations as well as those for trans-1-fluoro-2-butene and methacryloyl fluoride.

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TF12.   (4:42)

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 methylfluoroformate-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 ab initio calculations at the 6-31G* level.

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THE $\tilde{A}-\tilde{X}$ BAND SYSTEM OF C_2D_2 :
IR CONSTANTS OF THE TRANSBENDING LEVELS

T R HUET and M.HERMAN

The conventional rovibrational analysis of the $\tilde{A}-\tilde{X}$ band system of acetylene, already performed on C_2H_2 (1-4), is extended to other isotopomers. Results are presented in this first communication, concerning the $nv_4''(n=0-4)$ ground levels of C_2D_2, involved on the absorption spectra. Improved and new rovibrational constants are provided for $2v_4''$ and $3v_4''$ respectively. Perturbations encountered on the spectrum, arising because of the proximity of ω_4 and ω_5 in C_2D_2, $\tilde{X}^1\Sigma_g^+$, are briefly discussed.

(1)C.K.Ingold and G.W.King, J. Chem. Soc. 2702-2755 (1953).

(2)K.K.Innes, J. Chem. Phys., 22, 863-876 (1954).

(3)J.K.G.Watson, M.Herman, J.C.Van Craen and R.Colin, J. Mol. Spectrosc. 95, 101-132 (1982).

(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 $\tilde{A}-\tilde{X}$ BAND SYSTEM OF C_2D_2 :
ROVIBRONIC INFORMATION ON THE $\tilde{A}$ STATE

T.R. HUET and M. HERMAN

The conventional rovibrational analysis of the $\tilde{A}-\tilde{X}$ band system of acetylene, already performed on C_2H_2 (1-4), is extended to other isotopomers. This second communication concerns the information derived on the $\tilde{A}$ state of C_2D_2. Original rovibrational constants are presented and compared to those of C_2H_2 (1-4).

(1)C.K.Ingold and G.W.King, J. Chem. Soc. 2702-2755 (1953)

(2)K.K.Innes, J. Chem. Phys., 22, 863-876 (1954)

(3)J.K.G. Watson, M.Herman, J.C.Van Craen and R.Colin, J. Mol. Spectrosc. 95, 101-132 (1982)

(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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TG3.

HIGH RESOLUTION INVESTIGATION OF THE $\tilde{a}^3A_u$ STATE OF GLYOXAL

F VANHORENBEKE, J VANDER AUWERA, M VERVLOET and M.HERMAN

The $\tilde{a}^3A_u-\tilde{x}^1A_g$ transition of $C_2H_2O_2$, 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.

(1) J Vander Auwera, M.Godefroid, M.Herman, T.R.Huet and J.W.C.Johns, Can J Phys 66 (1988)
(2) J.Vander Auwera and M.Herman, Chem. Phys. Letters, 135, 432 (1987)

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TG4.

ZEEMAN STUDIES OF MICROWAVE-OPTICAL DOUBLE RESONANCE SIGNALS IN THE $\tilde{A}$ $^1A_2$ – $\tilde{X}$ $^1A_1$ SYSTEM OF THIOFORMALDEHYDE

W. HÜTTNER , 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_0 rotational levels of the 4^1 $\tilde{A}$ $^1A_2$ excited state and terminate in highly excited rovibronic levels of the $\tilde{X}$ $^1A_1$ 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 $\tilde{X}$ $^1A_1$ ground state support the earlier proposition that K_a is not a good quantum number for these levels.

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THE VIBRONIC SPECTRUM OF SELENOFORMALDEHYDE IN THE NEAR INFRARED

R. H. JUDGE, D. J. CLOUTHIER, D.C. MOULE

The polymers of CH_2Se and CD_2Se 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 CD_2Se was observed at 13631.5 cm^{-1} while that of CH_2Se 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 CH_2Se/CD_2Se 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 thioformaldehyde.

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THE INTERNAL ROTATION AND INVERSION MOTIONS OF THIOACEALDEHYDE IN ITS FIRST TRIPLET $\tilde{a}^3A''$ ELECTRONIC STATE

D.C.MOULE, Y.G.SMEYERS, A. NINO

Thioacetaldehyde, CH_3CHS displays a banded absorption spectrum at 615 nm which is attributed to the $T_1 \leftarrow S_0, \tilde{a}^3A'' \leftarrow \tilde{X}^1A'$ 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 ν_{15}. Substitution of deuterium for the aldehyde hydrogen produces an isotope shift which demonstrates that a strong coupling exists between the aldehyde wagging mode ν_{14} and the methyl torsion ν_{15}.

Ab initio SCF methods were used to generate the potential surface defined by θ(internal rotation) and α(hydrogen wagging) in both electronic states from which the potential $V(\theta,\alpha)$ was derived as a Fourier expansion. The band spectrum of CH_3CHS 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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ON THE ASSIGNMENT OF THE EXCITED SINGLET STATES
IN THE CO$_2$ MOLECULE

P. J. Knowles, P. Rosmus and H. J. Werner

High accuracy electronic structure calculations (contracted MRCI wavefunctions with the quality of several 10^7 uncontracted configurations) for the energies of CO$_2$ in the lowest states in each of $^1\Sigma_g^+$, $^1\Pi_g$, $^1\Delta_u$ and $^1\Sigma_u^-$ 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 $^1\Sigma_u^-$, $^1\Delta_u$ and $^1\Pi_g$ states have been calculated. The results show that the electronically excited states $^1\Sigma_u^-$ and $^1\Delta_u$ of linear CO$_2$ cross in the Franck–Condon region of the absorption spectrum with the $^1\Pi_g$ state. It has been found that the $^1\Delta_u$ 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 CO$_2$ photodissociation will be discussed.

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CHEMILUMINESCENCE SPECTRA OF SMALL MOLECULES CONTAINING SULFUR, 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 F$_2$ with CS$_2$, the reaction of F$_2$ with CSe$_2$ 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 Se$_2$(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 F$_2$/CS$_2$ feature.

Reactions of F$_2$ with CH$_3$ X CH$_3$, where X = Se, Se$_2$, Te, and Te$_2$, are being studied as sources for emission spectra of CH$_2$Se and CH$_2$Te. Fruitful chemical trends and analogies are being exploited in effort to identify new spectra of hard-to-study small molecules in chemiluminescence.

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STEADY STATE PRODUCTION OF THE HNCN IN THE GAS PHASE BY HYDROGEN ABSTRACTION FROM CYANAMIDE

P. E. FLEMING, C. W. MATHEWS, AND M. WINNEWISSER

The cyanamidyl radical HNCN was first observed and identified by Herzberg and Warsop[1] 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

$$X + H_2NCN \longrightarrow HX + HNCN$$
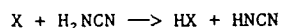
The efficiency of the mechanism is monitored by the intensity of the 0 - 0 band of the $\tilde{A}$ - $\tilde{X}$ transition near 3440 Å. The best results are obtained using discharges in CF_4, SF_6 or CCl_2F_2 as hydrogen scavenger sources.

[1]G. Herzberg and P. A. Warsop, Can. J. Phys., 41, 286, (1963).

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TG10.   (3:31)

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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TG11.   (3:47)

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 $C_6F_6^+$, $C_6F_3H_3^+$ and C_5H_5 will be presented.

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TG12.   (4:03)

ANALYSIS OF ROTATIONALLY RESOLVED SPECTRA OF THE $^2A_2'' \leftarrow {}^2E_1''$ BAND OF CYCLOPENTA-DIENYL RADICAL

LIAN YU, STEPHEN C. FOSTER, JAMES M. WILLIAMSON, AND TERRY A. MILLER

Rotationally resolved LIF spectra of the $^2A_2'' \leftarrow {}^2E_1''$ band ($\nu_{00}=29{,}572.166$ cm^{-1}) of cyclopentadienyl radical (C_5H_5) were taken in a supersonic free-jet expansion. An effective Hamiltonian appropriate for C_5H_5 in $^2E_1''$ vibronic state is constructed. A least square fit of the 0_0^0 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 $^2E_1''$ state may indicate a large Jahn-Teller effect. The spin effects (spin-orbit and spin-rotation interactions) in C_5H_5 are also discussed.

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TG13.   (4:19)

ROTATIONAL ANALYSIS OF THE $\tilde{A}\ ^2A \leftarrow \tilde{X}\ ^2E$ TRANSITION OF $CH_3O\cdot$ AND $CH_3S\cdot$

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

Rotationally resolved spectra of both $CH_3O\cdot$ and $CH_3S\cdot$ $^2A \leftarrow {}^2E$ transition have been obtained by both cw and pulsed supersonic free jet expansion and LIF techniques. Rotational spectra of the 0_0^0 and 3_0^1 bands of $CH_3O\cdot$ and 0_0^0 band of $CH_3S\cdot$ 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 $\tilde{A}$ 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 $T \approx 25$ K.

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TG14.   (4:35)

Fast Ion Beam Laser Spectroscopy of N_2O^+ : Effects of Orbital Angular Momentum and Vibrational Anharmonicity

M.Larzilliere*,**and Ch.Jungen**

Fast ion beam laser spectroscopy has been used to study the $\tilde{A}^2\Sigma^+$ - $\tilde{X}^2\pi$ 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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TG15.   (4:46)

LASER SPECTROSCOPY OF ALKALINE EARTH MONOCARBOXYLATES AND MONOFORMAMIDE

A.M.R.P. BOPEGEDERA, C.R. BRAZIER, S. KINSEY-NEILSEN, T.W.M.L. FERNANDO,
                  L.C. O'BRIEN AND P.F. BERNATH

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 $M^+ - \overset{O}{\underset{O}{\subset}} C-R$ and $M^+ - \overset{O}{\underset{O}{\subset}} C-R$ (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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TG16.

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 $\tilde{A}^2A_1-\tilde{X}^2A_1$ 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 $^3P_1-^1S_0$ atomic line of calium (at 6573 A) 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 $^2E_{1/2}-^2A_1$ component and one from the $^2E_{3/2}-^2A_1$ 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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TH1.   (1:30)

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 X^1A_g glyoxal. The polarization methods allowed detection of a stimulated emission signal as small as 10^{-6} 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 3473.2 ± 0.2 cm^{-1}, and the vibrational constants for the v_2 mode were determined as $\omega_2^0 = 1745.8(5)$ cm^{-1} and $X_{22} = -4.6(5)$ cm^{-1}. It was observed that the $K_a \neq 0$ 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}.

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TH2.   (1:47)

VIBRATION-ROTATION SPECTROSCOPY BY STIMULATED EMISSION PUMPING IN A SUPERSONIC BEAM: a-AXIS CORIOLIS COUPLED $v_4=1$ and $v_8=1$ LEVELS OF $\tilde{X}^1A_g$ 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 X^1A_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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TH3.   (2:04)

SELECTIVE EXCITATION AND SPECTROSCOPY OF HIGH VIBRATIONAL LEVELS OF $\tilde{a}^1A_1$ 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 a^1A_1 CH$_2$. The methylene radical was produced by photolysis of the ketene molecule. The pump laser pulse excites the $\tilde{b} \leftarrow \tilde{a}\ 2_0^{16}$ transition and the dump laser stimulates emission through the $\tilde{a} \leftarrow \tilde{b},\ 2_1^{16}$ 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 $\tilde{a} \longleftrightarrow \tilde{b}$ transitions originates in the $\tilde{a}$ or $\tilde{b}$ state. The double minima in the bending potential can also be characterized.

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TH4.   (2:21)

VAN DER WAALS VIBRATIONAL LEVELS OF THE GLYOXAL($\tilde{X}^1A_g$)·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($\tilde{X}^1A_g$)·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 $\tilde{X}$ 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 $\bar{4}_1$ and $\bar{8}_1$ levels and <0.04 cm^{-1} for the $\bar{5}_1$ level. These widths arise from vibrational predissociation of the complex.

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TH5.   (2:38)

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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(3:05)

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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(3:22)

THE INERTIAL DEFECTS OF VIBRATIONALLY EXCITED ORTHO-RHOMBIC MOLECULES AS SOURCE FOR INFORMATION ON HARMONIC FORCE FIELDS: CALCULATIONS ON 1,1 DI-FLUOROETHYLENE

Dines 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^{γ} (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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TH8.

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-d_1, has been recorded and used along with the infrared and Raman data for the d_0 and d_2 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-d_4 species in terms of a two-dimensional surface is underway.

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TH9.

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 expeected to have two-dimensional potential energy surfaces of the form

$$V = a(x_1^4 + x_2^4) + b(x_1^2 + x_2^2) + cx_1^2 x_2^2,$$

where x_1 and x_2 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 funciton and the energy levels approach those of a free pseudorotor. The calculaitons are such systems will be discussed.

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TH10.

INTERNAL ROTATION OF CYCLOPROPYLGERMANE AND CYCLOPROPYLSILANE-d_3

M. B. KELLY, M. DAKKOURI, and J. LAANE

The mid-infrared combination band spectra resulting form the internal rotation of the GeH_3 group of cyclopropylgermane and the SiD_3 group of cyclopropylsilane-d_3 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 cylopropyl ring and the silicon atom. The barrier of 455 cm^{-1} determined for the cyclopropylgermane is similar to values previously determined for other organogermanes.

[1] J. Laane, E. M. Nour, and M. Dakkouri, J. Mol. Spectrosc., 102, 38 (1983).

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TH11. (4:25)

ASYMMETRIC TOP CONTOUR SIMULATION AND VIBRATIONAL SPECTRA OF ISOPROPYL FORMATE

R. S. LEE, J. LAANE, 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-$10,000$ 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_0 compound and the isolated isopropyl C-H stretch of the d_7 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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TH12. (4:42)

APPLICATIONS OF MOLECULAR MECHANICS TO THE CONFORMATIONAL ANALYSIS OF RING MOLECULES

R. S. LEE, C. COOPER, and J. LAANE

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_2, C_s, 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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TH13. (4:59)

VIBRATIONAL SPECTROSCOPY AND POTENTIAL ENERGY SURFACES FOR THE OUT-OF-PLANE MOTIONS OF CYCLOHEXENE AND SOME ANALOGUES

J. LAANE, 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 (90-180 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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TI1.

THE OVERTONE SPECTROSCOPY OF HYDROGEN PEROXIDE ON A MOLECULAR BEAM

C. DOUKETIS AND J.P. REILLY

The $4 \leftarrow 0$ stretching overtone region of H_2O_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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TI2.

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 (C_4H_4NH) 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 $4 \leftarrow 0$ 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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130

TI3.   (2:04)

OBSERVATION OF A NEW RO-VIBRONIC BAND OF OOH FREE RADICAL
GENERATED FROM H_2O_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 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.

[1] Jue Wang, Vasgen A. Shamamian, Bruce R. Thomas, James M. Wilkinson, Joelle Riley, Clayton
F. Giese, and W. Ronald Gentry, Phys. Rev. Lett. 60, 696(1988)

[2] E. P. Wigner, Phys. Rev. 73, 1002(1948)

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Λ-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 Λ-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 Λ-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 $X^2\Pi_{1/2}$ ($J=1.5$) Λ-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.

[1] M.C.L. Gerry, A.J. Merer, U. Sassenberg and T.C. Steimle, 86 4754 (1987).

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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 ^{63}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.

[1] T.C. Steimle and Y. Azuma, J. Mol. Spectrosc. 118, 237 (1986).
[2] F. David, M. Douay and Y. Lefebvre, J. Mol. Spectrosc. 112, 115 (1985).

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INFRARED SPECTROSCOPY IN SLIT SUPERSONIC EXPANSIONS

C. M. LOVEJOY, A. MCILROY, AND D. J. NESBITT

A 50 cm absorption pathlength, 40 MHz sub-Doppler linewidths, 5 K rotational temperatures, 10^{17}/cm^3 number density, and detection limits of 5×10^7 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 μsec duration, 60 Hz repetition rate pulsed valve with a 4 cm long by 75 μm wide slit nozzle and multipass optics. Examples are presented from the near-IR (2-4 μm) spectra of hydrocarbons and van der Waals complexes.

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TI8.   (3:32)

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 ArHF to encompass all of the low-frequency (≤ 75 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 (00^00), the van der Waals stretch (00^01), the HF stretch (10^00), and combinations of the HF stretch with the van der Waals stretch (10^01), the Σ bend (12^00), the Π bend (11^10), and the van der Waals stretch overtone (10^02), listed in order of increasing energy.

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[1]C. M. Lovejoy, M. D. Schuder and D.J. Nesbitt, J. Chem. Phys. 85, 4890, (1986).
[2]G. T. Fraser and A. S. Pine, J. Chem. Phys. 85, 2502, (1986).

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TI9.   (3:49)

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 Π 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 Π^f 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 ≥ 25 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 Π^e 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 Π^e levels with the Σ bend, which is not directly observed but which is inferred to have a predissociation lifetime of ≤ 8 psec. Scattering calculations[1] on a recently obtained ab initio potential energy surface[2] predict the observed results nearly quantitatively.

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[1]D. C. Clary, S. V. ONeil, C. M. Lovejoy, and D. J. Nesbitt, to be published.
[2]S. V. ONeil, H.-J. Werner, and P. Rosmus, J. Chem. Phys. (submitted).

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(4:06)

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[1] 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 H_2 $X^1\Sigma_g^+$) molecules.

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[1] M. S. Child and D. J. Nesbitt, Chem. Phys. Lett. (in press).

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TI11.

(4:23)

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[1] 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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[1] M. S. Child and D. J. Nesbitt, Chem. Phys. Lett. (in press).

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TI12.

(4:40)

ABSOLUTE INFRARED ABSORPTION INTENSITIES FOR OH $X^2\Pi$ (v=1←0)

ARAM 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 $X^2\Pi$ (v=1←0) via infrared laser light absorption. The OH radicals were produced by photolysis of HNO_3 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 linestrengths.

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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.

[1]G. V. Hartland and P. M. Felker, J. Phys. Chem. 91, 5527 (1987).

[2]P. M. Felker, B. F. Henson, T. C. Corcoran, L. L. Connell, and G. V. Hartland, Chem. Phys. Lett. 142, 439 (1987).

[3]See, for example, M. D. Levenson, Introduction to Nonlinear Laser Spectroscopy (Academic, New York, 1982).

[4]D. E. Reisner, P. H. Vaccaro, C. Kittrell, R. W. Field, J. L. Kinsey, and H.-L. Dai, J. Chem. Phys. 77, 593 (1982).

Address of Felker: Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024-1569.

FTIR Studies of Wood Chemistry

N.L. Owen, 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:

$$R-NCO + H-O-Wood \rightarrow R-\underset{\underset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-O-Wood$$
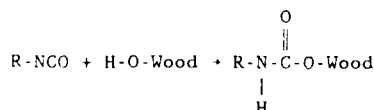
and consequently distinguish between surface and bulk reaction. The formation of an allophanate upon extensive reaction of the isocyanate can also be detected from the spectra. I.R. work on the powdered samples of isolated lignin and holo-cellulose show that the rate and extent of reaction with isocyanate is different for the two components.

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RA4. (9:30)

BEND-STRETCH INTERACTIONS IN THE CH OVERTONE SPECTRUM OF ACETYLENE

BRIAN C. SMITH AND JOHN S. WINN

High resolution FTIR spectra of C_2H_2 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 $(v_2 + v_4 + v_5)^0$ were analyzed, and an unperturbed value of v_3 was determined. This was combined with other data to obtain ω_m, x_m, and λ 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 $2v_4^0$. 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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RA5. (9:46)

ANALYSIS OF WEAKER BANDS OF ACETYLENE IN THE 1.1 μm REGION

M. HERMAN, T.R. HUET and M. VERVLOET

The absorption spectrum of C_2H_2 was recorded in the 1.1 μm 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.

(1) S.Ghersetti, J.E.Adams and K.N.Rao, J. Mol. Spectrosc. 64, 157-161 (1977).

Address of Herman and Huet : Laboratoire de Chimie Physique Moléculaire – CP.160, Université Libre de Bruxelles, Faculté des Sciences, 50,av.F.D. Roosevelt, B-1050 Bruxelles, Belgium.
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RA6. (9:52)

SPECTROSCOPIC CONSTANTS OF CS_2 DERIVED FROM THE v_3 SPECTRAL REGION

D. CHRIS BENNER, V. MALATHY DEVI, GUY GUELACHVILI AND K. NARAHARI RAO

Spectroscopic constants for carbon disulfide have been derived from molecular constants obtained from our analysis of over 30 bands of CS_2 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 ^{34}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 au CNRS, Orsay Cedex, France.
Address of Narahari Rao: Department of Physics, Ohio State University, 174 W. 18th Avenue, Columbus, OH 43210.

RA7.

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 $\cdot_e$, $\cdot_e x_e$, and $\cdot_e y_e$, 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_2O 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.

[1] G. Thompson, A. G. Maki, and A. Weber, J. Mol. Spectrosc. 118, 540 (1986).

[2] P. L. Clouser and W. Gordy, Phys. Rev. A 134, 863 (1964).

Address of Uehara, Horiai, Nakagawa, and Konno: Department of Chemistry, Josai University, Keyakidai, Sakado, Saitama 350-02, Japan.
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RA8.

INFRARED SPECTRUM OF THE ν_3 BAND OF $C_2H_2^+$ 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 ν_3 fundamental vibration-rotation band of $C_2H_2^+$ ($^2\Pi_u$) 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 ν_3 band of $^{13}C_2H_2^+$. 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 : $C_2H_2/^{13}C_2H_2$ or in a liquid nitrogen-cooled discharge of He : H_2 : $CH_4/^{13}CH_4$ (700:20:1) with a total pressure of ≈ 6 torr. Our attempt to observe $HCCD^+$ is in progress.

[1] M. W. Crofton, M-F. Jagod, B. D. Rehfuss, and T. Oka, J. Chem. Phys., 86, 3755(1987).
[2] M.-F. Jagod, M. W. Crofton, B. D. Rehfuss, and T. Oka, paper ME16, 42nd Symposium on Molecular Spectroscopy, Columbus, Ohio.

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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 $C_2H_3^+$ 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 $C_2H_3^+$ 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: $B = 1.1422(5)$ cm^{-1}, $C = 1.0467(4)$ cm^{-1}. These rotational constants agree well with those predicted from *ab initio* calculations.[1,2,3] 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}C species will be discussed.

[1] T. J. Lee and H. F. Schaefer III, *J. Chem. Phys.*, **85**, 3437(1986).

[2] J. A. Pople, *Chem. Phys. Lett.*, **137**, 10(1987).

[3] R. Lindh, B. O. Roos, and W. P. Kraemer, *Chem. Phys. Lett.*, **139**, 407(1987).

[4] J. T. Hougen, *J. Mol. Spectrosc.*, **123**, 197, (1987).

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OBSERVATION OF HOT BANDS OF H_3^+ USING AN EXTENDED DIFFERENCE FREQUENCY SPECTROMETER

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$_3$ [1] 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 H_3^+ . We have observed many transitions of H_3^+ not assignable to the $\nu_2 \leftarrow 0$ fundamental band using a liquid nitrogen cooled AC discharge with 600 mTorr H_2 and 7 Torr He. Many of the lines have been assigned to the $2\nu_2$, $\ell=2$ $\leftarrow \nu_2$, $\ell=1$ band based on the recent calculation of Miller and Tennison[2]. We expect most of the remaining lines to belong to the $2\nu_2$, $\ell=0 \leftarrow \nu_2$, $\ell=1$ and $\nu_1 + \nu_2 \leftarrow \nu_1$ hot bands.

[1] S. Yu. Volkov *et al.*, *Sov. J. Quantum Electron.*, **11**, 135 (1981).

[2] S. Miller and J. Tennison, *J. Mol. Spect.*, **126**, 183 (1987), and private communication.

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RA11.   (11:18)

IS THE DISSOCIATIVE RECOMBINATION OF H_3^+ 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^3s^{-1} for most positive molecular ions. These rates are important in model calculations of the interstellar chemical evolution. H_3^+ in particular occupies a key role. The dissociative recombination rate constant of H_3^+ was measured to be $(2.9\pm0.3)\times 10^{-7}$ cm^3s^{-1} at 205 K by using the stationary afterglow method[1]. 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($\sim 10^{-11}$ cm^3s^{-1}) by using the flowing afterglow/ Langmuir probe(FALP) technique[2]. A theoretical calculation also suggested a small rate constant[3]. Also very recently Hus et al[4] 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_3^+.

Considering the astrophysical impact of these low values, we have carried out direct measurements of the decay of the infrared absorption signals of H_3^+, 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 $(1.8\pm0.2)\times 10^{-7}$ cm^3s^{-1}, which disagrees with the recent values[2,4].

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RA12.   (11:34)

A SEARCH FOR THE C-H (BRIDGE) STRETCH VIBRATION-ROTATION BAND OF $C_2H_3^+$

T. Amano, N. Moazzen-Ahmadi, and A. R. W. McKellar

Oka and coworkers[1] have detected $C_2H_3^+$ by high-resolution infrared spectroscopy around 3 μm; 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 (v_2) of non-classical $C_2H_3^+$ around 5 μm.

An initial search was made in 2020-2080 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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FIR LASER SIDEBAND SPECTROSCOPY OF H_3O^+

P. VERHOEVE, D.B. McLAY, J.J. TER MEULEN, A. DYMANUS AND W. LEO MEERTS

The tunable FIR-laser sideband system has been used to study the H_3O^+ 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_3O^+

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RB1.

Dissociation Of H_2 In A Fast Beam
Optical Translational Spectroscopy

S.C.Laperriere,M.Larzilliere,J.Tremblay,J.P.Moreau and A.Alikacem

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(2l) 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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RB2.

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) $^3\Sigma_g^+$,i (3d) $^3\Pi_g$ and j (3d) $^3\Delta_g$
and the nearby h (3s) $^3\Sigma_g^+$ state, has been performed.   3s,3d <--- 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) $^3\Sigma_g^+$ state to
describe the complex for lower v values. Molecular constants are also given.

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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^{-4}, R^{-6}, and R^{-8}, under more restrictive assumptions.[1] Good agreement is found with accuracte 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 $j^3\Delta_g$ 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 $j^3\Delta_g$ state of H_2. Vibrational levels $v' = 7 - 14$ and $v" = 7 - 12$ 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 $j^3\Delta_g$ state arises from coriolis interaction with the vibrational continuum of the $i^3\Pi_g$ 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 $^3\Pi_g$ 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 $X\,\Sigma \to A\,\Pi$ 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, A_D, A_H of fine structure splitting and p, p_D of λ-type doubling have been determined with high precision for the vibrational states $8 \leq v' \leq 14$ of the A Π-state and $0 \leq v'' \leq 2$ for the X Σ -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 λ-doubling parameter p decreases with increasing v' and changes sign near v' = 13. The interatomic potential of the A Π- and of the X Σ-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 ($>10^4$ 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 $Ca^{2+}O^{2-}\,X\,^1\Sigma^+$ state, the electronic structure of CaO may be understood as a weakly interacting electron/hole pair, the electron localized on Ca^+ (in $X\sigma, A\pi, B\sigma$ orbitals borrowed from the corresponding $X^2\Sigma^+, A^2\Pi, B^2\Sigma^+$ states of CaF) and the hole localized on $O^-\,2p^{-1}$ (σ^{-1} or π^{-1} as for NaO). We report here the previously unknown $C''^1\Sigma^+$ state, belonging to the $A\pi\pi^{-1}$ configuration. This completes the characterization of the CaO Orange Bands which consist of transitions between all six $A\pi\pi^{-1}$ ($^{1,3}\Delta, \,^{1,3}\Sigma^{\pm}$) upper states and the two $X\sigma\pi^{-1}$ ($A'^1\Pi, a^3\Pi$) lower states.[1,2] Experimental knowledge of the four lowest $^1\Sigma^+$ states ($X^1\Sigma^+ \sim Ca^{2+}O^{2-}, A'^1\Sigma^+ \sim X\sigma\sigma^{-1}, C''^1\Sigma^+ \sim A\pi\pi^{-1}, C^1\Sigma^+ \sim B\sigma\sigma^{-1}$) should provide stringent tests of ab initio calculations as well as an opportunity to extract deperturbed, integer-valence, $Ca^{2+}O^{2-}$ and $Ca^+O^-\,^1\Sigma^+$ 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 $C''^1\Sigma^+ \leftarrow A'^1\Pi$ 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 $^1\Sigma^+$ identity of the upper state in this transition was confirmed by observation of resolved fluorescence spectra in the $C''^1\Sigma^+ \to X^1\Sigma^+$ transition. The preliminary molecular constants for the $C''^1\Sigma^+$ state T_e, B_e, α_e, and ω_e are 24 635.546, 0.3456, 2.4×10^{-3}, 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.[1] 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$\leftarrow$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$\approx$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 ns, we observe an 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 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.SCHRÖDER AND A.J.MERER

A hyperfine analysis of the sub-Doppler intermodulated fluorescence spectrum of gaseous niobium nitride (NbN) from 5700 Å to 6300 Å has been completed. Two triplet systems, the $\delta\pi\ ^3\Phi$ - $\sigma\delta\ X^3\Delta$ in the orange region and the $\delta\pi\ ^3\Pi$ - $\sigma\delta\ X^3\Delta$ 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_β) Hamiltonian where the isotropic hyperfine parameters in the matrix elements off-diagonal in Ω 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 Å, assigned as $\delta\pi\ ^3\Pi$ - $\delta^2\ ^3\Sigma^-$ and $\delta\pi\ ^3\Pi$ - $\sigma\delta\ ^1\Delta$, 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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RB9.

HIGH RESOLUTION LASER SPECTROSCOPY OF MANGANESE OXIDE, MnO

Y.AZUMA, T.CHANDRAKUMAR AND A.J.MERER

The $(0,0)$ band of $A^6\Sigma^+$ - $X^6\Sigma^+$ 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 $\Delta N=5$), 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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RB10.

FIRST OBSERVATION OF BOUND-CONTINUUM TRANSITIONS IN THE LASER INDUCED $A^1\Sigma_u^+$ - $X^1\Sigma_g^+$ 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 $A^1\Sigma_u^+$ ← $X^1\Sigma_g^+$ 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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POLARIZATION OF ATOMIC POTASSIUM FLUORESCENCE EXCITED BY LASER PHOTODISSOCIATION OF K_2

V. Zafiropulos, X. Zeng, A. M. Lyyra, P. Kleiber, K. Sando and W. C. Stwalley

A tunable dye laser was used to excite K_2 from the ground $X(^1\Sigma_g^+)$ state into the continuum of the $B(^1\Pi_u)$ state. This results in dissociation of the molecule producing an excited $K(^2P_{3/2})$ 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 $15 + 2\%$ 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.

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LASER INDUCED FLUORESCENCE OF Cs_2 BY ARGON ION LASER LINES IN THE PRESENCE OF NOBLE BUFFER GASES

J. J. Ho, Chongye Wang, 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 satelite 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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RB13.   (11:30)

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[1] for the
reduction of spectroscopic line positions to effective radial Hamiltonian operators. The
method is applied to the $X^1\Sigma^+$ and $B^1\Sigma^+$ states of $H^{35}Cl$, $H^{37}Cl$, $D^{35}Cl$, and $D^{37}Cl$.

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
isotopically invariant radial functions U(H) and U(Cl) which result in effective potential
functions U(eff) for each isotopomer according to Eq. (1).

$$U(eff) = U(BO) + U(H)/M_a + U(Cl)/M_b, \tag{1}$$

where M_a and M_b are the atomic masses of H/D and $^{35}Cl/^{37}Cl$, 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),

$$H(rot) = (\hbar^2/2\mu R^2)[1 + q(R)][J(J+1)]. \tag{2}$$

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.

[1]J.A. Coxon, J. Mol. Spectrosc. 117, 361-387 (1986).

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RB14.   (11:46)

PARITY SELECTED EXCITATION SPECTROSCOPY OF $ArCl_2$

K. C. Janda, D. D. Evard and J. I. Cline

Parity selected excitation spectra have been recorded of the B-X transition of
$ArCl_2$ 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. $ArCl_2$ 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 Cl_2 molecule. This compares to ArClF which is a
linear molecule with only a 3.3 Å Ar-Cl separation. By measuring the vibrational
predissociation threshold, the Ar-Cl_2 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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RC1. (8:30)

VIBRATION-ROTATION SPECTRUM OF CARBONYL SULFIDE DIMER

R. W. RANDALL, J. M. WILKIE, C. E. JAMES, B. J. HOWARD, AND J. S. MUENTER

The infrared spectrum of carbonyl sulfide dimer, $(OCS)_2$, has been recorded by observing the absorption of diode laser radiation in a pulsed molecular beam. The observed signals, in the carbonyl stretching region of the infrared spectrum, are from a perpendicular band of a quite asymmetric prolate rotor. Energy levels in the ground state with odd K_0 values are missing, which requires $(OCS)_2$ to have a center of symmetry. The vibrational origin occurs at 2072.007 cm^{-1}, and the rotational constants are A"=3075, B"=1263, C"=894, A'=3068, B'=1259, and C'=892 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 10 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 3.636 Å, and the monomer centers of mass are nearly opposite one another. The horizontal separation of the centers of mass is ± 0.294 Å.

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RC2. (8:46)

VIBRATION-ROTATION SPECTRUM OF CARBON DIOXIDE-ACETYLENE

DIANA G. PRICHARD, R. N. NANDI, J. S. MUENTER, 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"=8876, B"=2859, C"=2155, A'=8864, B'=2855, and C'=2154 MHz. The axes of the two monomer molecules are parallel and the complex has C_{2v} symmetry. The separation of the monomer units is 3.285 Å. 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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RC3. (9:02)

VIBRATION-ROTATION SPECTRUM OF ACETYLENE-NITROGEN

R. N. NANDI, DIANA G. PRICHARD, AND J. S. MUENTER

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 3283.093 cm^{-1}, with B"=1502 MHz and B'=1507 MHz. These rotational constants give a centers of mass separation for the monomers of 4.822 Å and 4.815 Å, respectively. Low frequency bending vibrations will be discussed in terms of a distributed multipole potential function.

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RC4. (9:18)

VIBRATION ROTATION SPECTRUM OF ACETYLENE-CARBON MONOXIDE

MARK J. MARSHALL, DIANA G. PRICHARD, AND J. S. MUENTER

The infrared absorption spectrum of acetylene-carbon monoxide, obtained in the three micron wavelength region from a pulsed molecular beam, indicates that this is a linear van der Waals complex. The spectrum is quite similar to that of acetylene-nitrogen. Excited state perturbations are present, but acetylene-carbon monoxide does not exhibit the hot bands found in HCCH-NN. The vibrational origin is at 3279.9 cm^{-1} and the ground state B value is 1497 MHz. This corresponds to a separation of 5.011 A for the monomer centers of mass. The spectrum cannot directly distinguish between the HCCH-CO and the HCCH-OC configurations. However, the HCCH-CO geometry produces a van der Waals bond 0.1 A shorter than the sum of van der Waals radii, while the HCCH-OC structure would have a bond length 0.3 A longer than the sum of van der Waals radii. Distributed multiple analysis also strongly favors the HCCH-CO configuration.

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RC5. (9:34)

STRUCTURAL STUDY OF THE H_2O-H_2O-CO_2 TRIMER

K. I. 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:

	Lower State	Upper State
A	6163.576(5) MHz	6164.068(7) MHz
B	2226.156(3) MHz	2226.677(3) MHz
C	1638.972(2) MHz	1638.839(3) MHz
Δ	-0.66197 uA^2	-0.57724 uA^2

The electric dipole moment has also been measured yielding μ_a=1.57D, μ_b=0.76D and μ_c <0.1D. Several isotopically substituted species have been studied including various ^{13}C, ^{18}O 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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RC6. (10:00)

ROTATION SPECTRUM AND STRUCTURE OF CO_2-CO_2-H_2O

K. I. PETERSON, R. D. SUENRAM, AND F. J. LOVAS

The microwave spectrum of the trimeric species CO_2-CO_2-H_2O 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 H_2O-H_2O-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:

	symmetric	antisymmetric
A	3313.411(1)	3313.419(2)
B	1470.548(1)	1470.545(1)
C	1308.851(1)	1308.849(1)

The dipole moment for the complex is μ_b=1.989(2)D. These observations imply that the complex has a two-fold axis of symmetry with the H_2O subunit oriented such that its C_{2v} axis is aligned with the b-axis of the complex. The magnitude of the rotational constants along with information obtained from ^{13}C substitution suggest that the CO_2 subunits lie in a plane perpendicular to the b-axis separated by a distance similar to that observed in the CO_2-CO_2 dimer. It is expected that the oxygen of the H_2O is oriented toward the plane of the two 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 H_2O subunit. The levels are shifted rather than split because of the involvement of the CO_2 oxygens which have a spin quantum number of 0.

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RC7. (10:16)

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 (NH_2-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., $2q_{aa}-q_{bb}-q_{cc}$, $q_{bb}-q_{cc}$, q_{ab}, q_{ac}, and 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 N_2D_4 by Harmony and Baron[1]. 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 $<\cos^n\theta>^{1/n}$, should be significantly better than the fits obtained for loosely bound complexes, unless our understanding of the tunneling apects of this problem is seriously flawed.

[1] M. D. Harmony and P. A. Baron, J. Molecular Structure, **38**, 1-8 (1977).

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QUADRUPOLE HYPERFINE SPLITTING IN THE $J = 1 \leftarrow 0$ ROTATIONAL TRANSITION OF CCl_3F

M.D. MARSHALL, H.O. LEUNG, AND R.D. SUENRAM

The hyperfine structure of the $J = 1 \leftarrow 0$ transition of CCl_3F 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[1] for this molecule it is shown that the hyperfine splitting is qualitatively, but not quantitatively predicted using the classic method of Wolf, et. al.[2] and the effective hyperfine constants, $\epsilon qQ_{zz} = 29.047$ MHz and $\epsilon qQ_{xx} - \epsilon qQ_{yy} = -110.95$ 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 $\epsilon qQ_{xx} - eqQ_{yy}$ term in the hyperfine Hamiltonian, but also those which find their origin in the usually ignored eqQ_{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.

[1] J. H. Carpenter, P. J. Seo, and D. H. Whiffen, *J. Mol. Spectrosc.* **123**, 187-196 (1987).
[2] A. A. Wolf, Q. Williams, and T. L. Weatherly, *J. Chem. Phys.* **47**, 5101-5109 (1967).

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MICROWAVE SPECTRUM OF THE OZONE-WATER COMPLEX

R. D. SUENRAM, F. J. LOVAS, J. GILLIES, 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, $H_2^{18}O$, and one deuterated species have been assigned. Both $\underline{a}$- and $\underline{c}$-type transitions have been observed and fit using a centrifugal distortion Hamiltonian. For the O_3-H_2O species the rotational constants are A=11960.584(5), B=4174.036(8) and C=3265.173(8) MHz. The measured dipole moment components for the complex are μ_a=1.014(2)D, μ_b=0D, and μ_c=0.52(3)D which gives μ_T=1.14(1)D. From the available data several structural conclusions can be made, but details of the conformation are, at present, somewhat uncertain. The inertial defect ($\Delta \equiv I_c$-I_b-I_a) is -8.55uÅ^2 which indicates that the complex has a non-planar heavy atom structure. From Ray's asymmetry parameter $\kappa \equiv (2B-A-C)/(A-C)$ ($\kappa \equiv -0.8$) we conclude that the observed conformation must have a sandwich (H_2O and O_3 monomer planes parallel) or T-shaped (H_2O and 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 μwater = 1.85D and μozone = 0.53D. This is also consistent with a sandwich or T-shaped structure. Additional work is in progress involving the second deuterated isotope and $H_2^{17}O$. It is hoped that these additional isotopes will allow a more detailed determination of the structure of the complex.

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RC10.   (11:04)

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 ($\Delta\mu$) are (in D):

	HCl		HCN		HF[1,2]	
	μ	$\Delta\mu$	μ	$\Delta\mu$	μ	$\Delta\mu$
Acetylene	1.6032(29)	0.57	3.4130(42)	0.50	2.3681(28)	0.65
Ethylene	1.6167(15)	0.58	3.4023(27)	0.49	2.3839(45)	0.67
Benzene	1.688(10)	0.67			2.244(4)	0.59
Cyclopropane	1.7405(16)	0.71	3.5875(41)	0.67	2.5084(28)	0.78

The dipole moments for the HF complexes have been measured previously[1,2] 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.[3] 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.

1.   D.D. Nelson, Jr., G.T. Fraser, and W. Klemperer, J.Chem.Phys. 82, 4483 (1985).
2.   F.A. Baiocchi, J.H. Williams, and W. Klemperer, J.Am.Chem.Soc. 87, 2079 (1983).
3.   S. R. Gandhi and R.B. Bernstein, Chem.Phys.Lett. 143, 332 (1988).

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RC11.   (11:20)

DETERMINATION OF THE STRUCTURE OF $H_2CO\ CO_2$

T. A. BLAKE, S. E. NOVICK, R. D. SUENRAM, F. J. LOVAS

The rotational spectrum of the $H_2CO\ CO_2$ 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 C_2 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 $(CO_2)_2$ and $CO_2\ OCS$, with the oxygen of H_2CO interacting with the carbon of CO_2. The structural parameters and dipole moments of both the A and B states are the same within the stated uncertainties. The C-O (formaldehyde)-C (carbon dioxide) angle is 102.90(5)°, the O (formaldehyde)-C-O (carbon dioxide) angle is 83.23(3)°, and the O (formaldehyde)-C (carbon dioxide) distance is 2.980(1) A. The measured dipole moments are μ_a=1.661(2) D, and μ_b=1.671(2) D.

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RC12.   (11:36)

DETERMINATION OF THE STRUCTURE OF Ar H_2CO

S.E. NOVICK, R.D. SUENRAM, F.J. LOVAS, and G.T. FRASER

The rotational spectrum of the weakly bound complex Ar H_2CO 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 formalde-
hyde with an Ar--C distance of 3.66 A 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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RC13.   (11:52)

TUNABLE FAR INFRARED LASER SPECTROSCOPY OF van der WAALS AND HYDROGEN BONDED CLUSTERS FORMED IN
A PLANAR SUPERSONIC JET

K. BUSAROW, G. A. BLAKE, K. B. LAUGHLIN, R. C. COHEN, Y. T. LEE, AND R. J. SAYKALLY

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 spectro-
scopy. 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 provices 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 Σ bend of 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 ArH_2O and $(HCl)_2$.

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RC14.   (12:03)

TUNABLE FAR INFRARED LASER SPECTROSCOPY OF VAN DER WAALS BONDS: TUNNELING-ROTATIONAL AND
VIBRATION-ROTATION SPECTRA OF Ar-H_2,O

R. C. COHEN, K. L. BUSAROW, K. B. LAUGHLIN, G.A. BLAKE, M. HAVENITH, Y. T. LEE, AND R. J.
SAYKALLY

The upper component of the ground state perpendicular tunneling-rotation spectrum of the
Ar-H_2O dimer has been observed near 21cm^{-1} using a cw planar supersonic jet and a tunable far
infrared laser system. Analysis of this sub-band suggest 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, $(1,K_a=0 \leftarrow 0,K_a=1)$ near 24 cm^{-1} goves 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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RD1.   (8:30)

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 partioning 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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RD2.   (8:42)

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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RD3.

THE MICROWAVE SPECTRUM OF ^{13}C SUBSTITUTED METHYL CYANIDE FOR THE FREQUENCY RANGE 17-95 gHz[1]

J. A. ROBERTS AND H. TAM[2]

The microwave spectrum of ^{13}C substituted methyl cyanide $CH_3C^{14}N$ was studied for the $v_8 = 1, 2$, for both single and double ^{13}C substitutions, vibrational states in the frequency range of 17 to 95 gHz.

The frequencies of the $1 \leq J \leq 5$ 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, $v_8 = 1, 2$, up to an accuracy of 100 kHz.

Previously obtained experimental data, available from the literature for the naturally occuring 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 $K\ell = 1$, $K = \ell = -1$ and $K = \ell = +1$ spectral components will be discussed.

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RD4.

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 μ_a- and μ_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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RD5.   (9:23)

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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RD6.   (9:35)

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. SJØGREN AND G. O. SØRENSEN

Microwave spectra of the parent and the $^{15}N_3$ species show the molecule to exist as a mixture of two planar tautomers: a 1H-form with C_s symmetry and a 2H-form with C_{2v} symmetry. The dipole moments of the tautomers have been measured as $\mu_{1H} = 4.38$ D and $\mu_{2H} = 0.218$ D in the $^{15}N_3$ species. The relative abundance, estimated from rough intensity measurements, is 1H:2H ∿ 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 2H-form to be the more stable, with $\Delta E_{1H \to 2H} = -14.7$ kJ mol^{-1}.

Structural refinements of a planar C_{2v} model of the 2H-tautomer was carried out based on the electron diffraction data in combination with the measured rotational constants (corrected to A_z, B_z and C_z).

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RD7.   (10:05)

STRUCTURAL DETERMINATIONS USING SCALED MOMENTS OF INERTIA

RAJIV J. BERRY AND <u>MARLIN D. HARMONY</u>

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_s 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.

[1] M.D. Harmony and W.H. Taylor, J. Mol. Spectrosc. <u>118</u>, 163-173 (1986).
[2] M.D. Harmony, R.J. Berry and W.H. Taylor, J. Mol. Spectrosc. (In press).
[3] J.K.G. Watson, J. Mol. Spectrosc. <u>48</u>, 479-502 (1973).
[4] R.J. Berry and M.D. Harmony, J. Mol. Spectrosc. (In press).

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RD8.   (10:22)

ROTATIONAL SPECTRUM, RING PUCKERING, AND NH INVERSION OF 3-PYRROLINE

J. DOMMEN, W. CAMINATI, <u>R. MEYER</u>, AND A. BAUDER

The microwave spectra of the unsaturated five-membered ring molecule 3-pyrroline (C_4H_7N) and its N-deuterated species have been reinvestigated between 26.5-40 GHz. The spectra were dominated by μ_a-type transitions which showed small splittings due to the intramolecular motion. A few μ_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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RD9.   (10:39)

TUNNELING MOTION IN ArH 3 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 ArH_3^+ were investigated. The ionic clusters were produced inside a negative glow extended by a magnetic field, in $Ar/H_2/D_2$ 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 H_3^+ 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_3^+ and ArD_3^+.

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RD10.   (10:56)

INFRARED DIODE LASER SPECTRA OF MgH, MgD, CaH AND CaD $(X \, ^1\Sigma^+)$

B. LEMOINE, C. DEMUYNCK and J.L. DESTOMBES

Rotation-vibration spectra of MgH, CaH and their deuterated forms in the $X \, ^1\Sigma^+$ state have been measured using tunable infrared diode lasers. The hydrides were produced in a D.C. discharge of H_2 or D_2 over heated magnesium or calcium. Transitions from the fundamental bands and from hot bands ($v=2\leftarrow 1$ for MgH, and up to $v=4\leftarrow 3$ 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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(1:30)

MICROWAVE SPECTRUM OF THE N_2-H_2O COMPLEX

H. O. LEUNG, M. D. MARSHALL, R. D. SUENRAM, AND F. J. LOVAS

The a-type K=0 microwave spectrum of the N_2-H_2O 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 N_2-H_2O complex exhibits tunneling motions similar to the 1 → 2 tunneling motion of the H_2O-DOD complex[1] which gives rise to four components for each rotational transition. The molecular constants obtained for $^{14}N_2$-HOH are (in MHz):

State	B_1	A_1	A_2	B_2
(B + C)/2	2906.362(1)	2906.925(1)	2914.146(1)	2914.252(1)
D	0.04181(2)	0.04349(2)	0.04263(2)	0.04300(2)
$eQq(^{14}N)$		-4.253(2)		-4.227(3)

The structure has a nearly linear N-N-HO geometry with a N-H distance of 2.42(4)Å and an OHN angle of 168° (R_{O-N} = 3.37(4)Å). The electric dipole moment along the principal axis was determined for the $^{15}N_2$-H_2O species with μ_a=0.833(3) Debye.

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[1] L. H. Coudert, F. J. Lovas, R. D. Suenram, and J. T. Hougen, J. Chem. Phys. **87**, 6290 (1987).

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(1:46)

ROTATIONAL SPECTRA AND STRUCTURES OF THE H_2S-H_2O AND $(H_2S)_2$ 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 H_2S-H_2O and $(H_2S)_2$. The a-type K=0 rotational transitions of both species have been observed in the 6-21 GHz range. The spectrum of H_2S-H_2O is expected to be analogous to that of $H_2^{18}O$-H_2O and $^{15}N_2$-H_2O (described in the previous papers) for which two tunneling motions,[1] give rise to four components for each transition. For H_2S-H_2O and its ^{34}S and ^{18}O isotopic forms, 3 of the 4 components have been resolved. The molecular parameters for H_2S-H_2O are:

State		1	2	3
(B+C)/2	(MHz)	3443.899(1)	3450.712(1)	3450.777(2)
D	(kHz)	28.71(5)	21.20(4)	24.67(4)
μ	(D)	0.551(3)	0.702(3)	0.697(6)

The energy levels of H_2S dimer and its isotopic forms are expected to be similar to those of water dimer.[1] 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 $(H_2S)_2$, $(H_2^{34}S)$ and $(D_2S)_2$, and the similar levels of the mixed isotopic forms have been observed. For $(H_2S)_2$ the rotational constants are: B (E^+) = 1749.310(1) MHz and B (E^-) = 1748.109(1).

The structures of both complexes will be presented based on 9 isotopic species of H_2S-H_2O and 7 species of $(H_2S)_2$. Comparisons of the hyperfine structure, dipole moments and structural implications will be presented.

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[1] L. H. Coudert, F. J. Lovas, R. D. Suenram, and J. T. Hougen J. Chem. Phys. **87**, 6290 (1987).

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STUDIES OF ISOTOPICALLY ENRICHED WATER DIMER SPECIES

R. 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.[1] We have now observed spectra for $(HOD)_2$, two singly substituted ^{18}O species, two singly substituted ^{17}O species and the doubly substituted ^{17}O species.

For $(HOD)_2$, 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 ^{17}O species have been determined from measurements on the $J = 1-0$ transitions. The values determined are reported below.
Quadrupole Coupling Constants for ^{17}O Water Dimer Species (in MHz)

Species State	$H_2O \cdot H^{17}OH$ A_1	$H_2^{17}O$-HOH A_1	A_2	$(H_2^{17}O-)_2$ E
eQq_1	-5.190(16)			-5.171(25)
eQq_2		1.942(8)	-1.522(8)	1.954(44)

[1]L. H. Coudert, F. J. Lovas, R. D. Suenram, and J. T. Hougen, J. Chem. Phys., 87, 6290 (1987).

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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 ($\Delta\nu_{1/2} \approx 10$ 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) $\rightarrow$ 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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RF7.   (2:34)

VIBRATIONAL PREDISSOCIATION STUDIES OF Cs$^+$(MeOH)$_n$ AND Cs$^+$(EtOH)$_m$ SOLVATED ION CLUSTERS

KWANG-YUL LIU AND JAMES M. LISY

Vibrational predissociation spectra of mass-selected Cs$^+$(MeOH)$_n$, n = 1 - 16, and Cs$^+$(EtOH)$_m$, m = 1 - 11, solvated ion clusters have been observed by exciting the OH stretching mode of the solvent molecules in the 3.0 μ range. The solvated ions are produced by combining a thermionic Cs ion source and supersonic nozzle.

From the spectral dependence on the solvent number surrounding the Cs ion, we have observed the formation of solvation shells. Ten MeOH or six EtOH molecules are required to complete the first solvation shell around the Cs ion in the gas phase. The relationship between neutral methanol and ethanol clusters and the solvated cesium ions will be discussed.

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RF4.   (2:50)

SOLVATION OF ALKALI IONS WITH NON-POLAR SOLVENTS

JEFFREY A. DRAVES AND JAMES M. LISY

The combination of a thermionic ion source and a supersonic nozzle molecular beam has been used to produce solvated ion clusters. The core ion M can be solvated by a number of different solvents both polar and non-polar. For example, the solvated ion has the form M(S)$_n$ where M=Cs$^+$ and S=C$_6$H$_6$ (benzene). The clusters are focused with an electrostatic lens system and resolved with a quadrupole mass filter.

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.

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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 more narrow 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.

[1] K.D. Kolenbrander, C.E. Dykstra, and J.M. Lisy, J. Chem. Phys. 88, xxxx (1988).

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THE PHOTODETACHMENT SPECTRA OF NEGATIVE CLUSTER IONS OF WATER

G.H. Lee, C. Ludewigt, J.G. Eaton, H.W. Sarkas, H. Haberland, and K.H. Bowen

We have recorded the photoelectron spectra of the water negative cluster ions; $(H_2O)^-_{n=2,6,7,10-25,30,34,37,40}$, $(D_2O)^-_{n=2,6,7,11-23}$, $Ar(H_2O)^-_{n=2,6,7}$, and $Ar(D_2O)^-_{n=2,6,7}$, 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 $(H_2O)^-_2$ to 1.79 eV for $(H_2O)^-_{40}$. 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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RE9.   (3:51)

THE PHOTODETACHMENT SPECTRA OF HOMOGENEOUS ALKALI METAL CLUSTER ANIONS: $Na^-_{n=2-6}$, $K^-_{n=2-8}$, $Rb^-_{n=2-4}$, and $Cs^-_{n=2,3}$

K.M. McHugh, J.G. Eaton, H.W. Sarkas, L.H. Kidder, G.H. Lee, J.T. Snodgrass, M.F. Maria, and K.H. Bowen

The alkali metals are the simplest of metals. We have recorded the photoelectron spectra of $Na^-_{n=2-5}$, $K^-_{n=2-8}$, $Rb^-_{n=2-4}$, and $Cs^-_{n=2,3}$ using 2.540 eV photons. These highly structured spectra chart both the electron affinities vs. cluster size for those 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 our 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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RE10.   (4:07)

PHOTODETACHMENT STUDIES OF HETEROGENEOUS ALKALI METAL DIMER AND TRIMER ANIONS

D. Patel-Misra, J.G. Eaton, H.W. Sarkas, G.H. Lee, S.T. Arnold, and K.H. Bowen

In our laboratory, we have generated several mixed alkali dimer and trimer anions including: NaK^-, KRb^-, $RbCs^-$, Na_2K^-, and K_2Na^-. 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.

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(4:23)

PRODUCTION AND PHOTODETACHMENT STUDIES OF Li_2^-

H.W. Sarkas, S.T. Arnold, K.M. McHugh, D. Patel-Misra, J.G. Eaton, G.H. Lee,
and K.H. Bowen

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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(4:39)

THE PHOTODETACHMENT SPECTROSCOPY OF HYDRATED AND DEUTERATED NITRIC OXIDE ANIONS

S.T. Arnold, J.G. Eaton, G.H. Lee, D. Patel-Misra, and K.H. Bowen

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 $NO^-(H_2O)_{n=1,2}$ and $NO^-(D_2O)_{n=1,2}$ 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 $NO^-(Ar)$, $NO^-(Kr)$, $NO^-(Xe)$, and $NO^-(N_2O)_{n=1,2}$.

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RE13.

THE STRUCTURE AND DYNAMICS OF Ne_2Cl_2

C. R. Bieler, S. R. Hair, J. I. Cline, K. C. Janda

The structure, bond energy, and photodissociation dynamics of the $NeCl_2$ van der Waals molecule are studied by a laser pump-probe technique. Analysis of excitation spectra reveals the structure to be nearly tetrahedral. The Cl_2 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_2 to Cl_2 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 suprisal analysis.

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RE14.

TUNABLE FAR INFRARED LASER SPECTROSCOPY OF HYDROGEN BONDS: THE $K_a = 0_u \to 1_g$ ROTATION TUNNELING SPECTRUM OF THE HCl DIMER

G. A. BLAKE, K. L. BUSAROW, R. C. COHEN, K. B. LAUGHLIN, Y. T. LEE, AND R. J. SAYKALLY

The ground state $K=0_u \to 1_g$ b-type sub-band of the rotational tunneling spectrum of the symmetric $^{35}Cl-^{35}Cl$, $^{37}Cl-^{37}Cl$ and the mixed $^{35}Cl-^{37}Cl$ 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 $(H^{35}Cl)_2$ center-of-mass separation of 3.814(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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RE15.

SUB-DOPPLER DIRECT ABSORPTION IR LASER SPECTROSCOPY IN FAST ION BEAMS

J. V. COE, J. C. OWRUTSKY, E. R. KEIM, N. V. AGMAN, AND R.J. SAYKALLY

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 HN_2^+ and H_3O^+ will be discussed.

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U(ΔJ = +4) TRANSITIONS AND OVERLAP PARAMETERS FOR H_2-Ar MIXTURES*

C. T. W. HSIEH and S. PADDI REDDY

Collison-induced enhancement absorption spectra of the fundamental band of H_2 in H_2 - 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 $U_1(1)$ corresponding to the rotational selection rule $\Delta J = +4$ 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 H_2, characteristic half-width parameters δ_d and δ_c of the short-range overlap-induced transitions and δ_{q2} and δ_{q4} of the quadrupole-induced transitions have been determined. The overlap parameters of the induced dipole moment of H_2 - Ar pairs have also been determined. The absorption coefficient of the $U_1(1)$ transition is also estimated.

[1]See, for example, Reddy, S. P. in "Phenomena Induced by Intermolecular Interactions" ed. G. Birnbaum, Plenum Press, New York, 1985, pp. 129-167.

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INFRARED SPECTRUM OF SOLID HYDROGEN: THEORY OF THE INTEGRATED ABSORPTION COEFFICIENTS OF W(ΔJ=6) TRANSITIONS

T.K. BALASUBRAMANIAN, R.D'SOUZA and K. NARAHARI RAO

The present work has been motivated by the efforts[1] to observe W(ΔJ=6) transitions in the induced infrared spectrum of solid H_2. Transition with ΔJ=6 should occur due to the part of the dipole moment induced by the 2^6th electric multipole moment of H_2. Starting with the expressions[2,3] for the dipole moment induced in a molecule by the 2^lth multipole moment of its neighbour, expressions for the integrated absorption coefficients are derived for the $W_{v\leftarrow0}(0)$, $W_{v\leftarrow0}(1)$ single transitions and the $W_{v\leftarrow0}(0)+Q_{v\leftarrow0}(0)$ 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 2^6th moment of H_2.

We have also calculated the possible satellite structure around the $W_{v\leftarrow0}(0)$ line when the para-H_2 crystal contains traces of ortho impurity.

[1]K. Narahari Rao (private communication).
[2]C.G. Gray, J. Phys B $\underline{4}$,1661 (1971).
[3]R.H Tipping and J.D. Poll, Molecular spectroscopy: Modern Research, Vol.III (Editor, K. Narahari Rao) Academic Press, N.Y., (1985).

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RF3.

ABSOLUTE RO-VIBRATIONAL INTENSITIES FOR THE $\Delta V = 1$ VIBRATIONAL BANDS OF $^3\Sigma^-$ NH

C. Chackerian Jr., G. Guelachvili, A. Lopez-Pineiro and R. H. Tipping

We determine absolute ro-vibrational line intensities for $\Delta V = 1$ (V'=1-4) vibrational bands of the astrophysically important species, NH, indepently 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.

[1] C. Chackerian, Jr. J. Chem. Phys. **85**, 1200 (1986).

[2] C. Chackerian, Jr., C. W. Bauschlicher, S. R. Langhoff, A. Lopes-Pineiro and R. H. Tipping (to be published)

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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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RF5.   (2:24)

HIGH RESOLUTION OBSERVATIONS OF STARS, PLANETS AND THE SUN USING AN
FTS/POSTDISPERSER

D. E. JENNINGS AND G. R. WIEDEMANN

Infrared spectrosocpy in astronomy at mid-infrared wavelengths often requires resolving powers $\nu/\Delta\nu$ as high as 10^5. 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 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 astronomy. This instrument, a cryogenic grating monochromator, permits 0.01 cm^{-1} resolution on a variety of sources. By narrowing the spectral bandwidth to $0.6 - 3$ cm^{-1}, the background noise is greatly reduced. Examples will be shown of Mg lines in stars[1], C_2H_2 and HCN in circumstellar shells[2], $^{13}CCH_6$ detected in Jupiter[3] and Zeeman splitting in sunspots[4]. Observations were performed using the facility FTS's at the McMath and Mayall telescopes at Kitt Peak.

[1] D. E. Jennings, D. Deming, G. R. Wiedemann and J. J. Keady 1986, Ap. J. (Letters), 310, L39.

[2] R. J. Boyle, D. E. Jennings, G. R. Wiedemann and J. J. Keady, in preparation.

[3] G. L. Bjoraker, D. E. Jennings and G. R. Wiedemann, in preparation.

[4] D. Deming, R. J. Boyle, D. E. Jennings and G. R. Wiedemann 1988, Ap. J., submitted.

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RF6. (2:40)

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 ν_3 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 straight forward radiation transfer model of the cometary coma, we have analyzed the ν_3 fluorescence data. A rotationally equilibrated, aperature-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

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[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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RF7. (2:56)

AIR-BROADENED HALFWIDTHS AND PRESSURE SHIFTS IN THE ν_3 BAND OF $^{13}CH_4$

V. MALATHY DEVI, MARY ANN H. SMITH, D. CHRIS BENNER AND CURTIS P. RINSLAND

Ultra-resolution 0.01 cm^{-1}, room-temperature spectra of $^{13}CH_4$ diluted with dry air were studied in the 3000-3100 cm^{-1} spectral region using the McMath Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. A 99% ^{13}C-enriched methane diluted to a mixing ratio of approximately 0.1 was used in a 5 cm absorption path to record the data. The total sample pressures used were approximately 75, 150, 300 and 500 Torr. A nonlinear least-squares spectral fitting technique was used in determining the halfwidth coefficients and positions. The derived halfwidth coefficients and pressure shifts will be compared to values obtained for identical transitions in the ν_3 band of $^{12}CH_4$ as well as to those in the ν_4 band of $^{12}CH_4$.

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(3:47)

INTENSITY AND LINE WIDTH MEASUREMENTS IN THE ν_4-FUNDAMENTAL OF $^{13}CH_4$ AT PLANETARY ATMOSPHERIC TEMPERATURES[†]

P. VARANASI, and S. CHUDAMANI

Observation of the spectral lines belonging to $^{13}CH_4$ and comparison of their intensities and collision-broadened half-widths with those of $^{12}CH_4$ 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 H_2, He, Ar, N_2, O_2 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.

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(3:58)

MEASUREMENT OF INTENSITIES AND COLLISION-BROADENED LINE WIDTHS IN THE ν_4-FUNDAMENTAL OF $^{12}CH_4$ AT LOW TEMPERATURES[†]

P. VARANASI, and S. CHUDAMANI

In the analysis of the observed $^{12}CH_4$ 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 ν_4 lines broadened by H_2, He, N_2 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 O_2 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.

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RF12. (4:14)

PRESSURE SHIFT MEASUREMENTS ON THE INFRARED LINES OF $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$ AND $^{14}N_2O$ AROUND 7.85 μm 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 N_2O, 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 $^{12}CH_4$, $^{13}CH_4$, $^{12}CH_3D$ and $^{14}N_xO$ located between 1265 and 1275 cm^{-1}. The temperature dependence of the shifts is also pres ted for collisions of the absorbers with H_2, He, Ar, N_2, O_2 and air.

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RF13. (4:25)

INFRARED BAND STRENGTH MEASUREMENTS OF CF_2 AND CH_3

J. WORMHOUDT 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 CF_2 radical, of interest in plasma etching systems, and the CH_3 radical, important in metalorganic and diamond chemical vapor deposition systems. CF_2 concentrations are determined by ultraviolet absorption of 248.4 nm radiation from a KrF excimer laser. CH_3 radicals are generated by reaction of CH_4 with F atoms. They are quantified using the known 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]

[1]C. Yamada and E. Hirota, J. Chem. Phys. 78, 669 (1983).
[2]J.J. Orlando, J. Reid, and D.R. Smith, Chem. Phys. Lett. 141, 423 (1987).

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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[1] has been used to evaluate far wing absorption for the 404-515 self-broadened H_2O 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,[2] will be presented.

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[1] R.W. Davies, R.H. Tipping and S.A. Clough, Phys. Rev. A 26, 3378 (1982).
[2] A. Nauts and R.E. Wyatt, Phys. Rev. A 30, 872 (1984).

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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 $C''^5\Pi_u$ and $A'^5\Sigma_g^-$ 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 $A^2\Sigma^-$ 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 rovibronic (or spin-rovibronic) 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

$$A' \text{ levels have parity} \cdot (-1)^N,$$
$$A'' \text{ levels have parity} \cdot (-1)^N.$$

This gives a useful characterization even when N is not a perfect quantum number. The classification of case (d) rovibronic levels in terms of the symmetries of the levels of the core will also be considered briefly.

[1] J. M. Brown et 9 al., *J. Mol. Spectrosc.* **55**, 500-503 (1975).

[2] M. H. Alexander et 28 al., to be published.

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R63.

ON THE ESR OF SMALL CARBON CLUSTERS

D. W. EWING

Electron spin resonance (ESR) signals attributed to the linear C_4, C_6, C_8, and C_{10} molecules in their lowest $^3\Sigma$ states, presumably their ground states, have recently been observed in solid neon and argon matrices at 4K[1]. Hyperfine interaction in the $^{13}C_n$ molecules was small, indicating cumulene-like bonding with the unpaired spins in pπ 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 C_8 is attributed to a corresponding variation in the spin-orbit coupling with low lying states, principally the $^1\Sigma_g^+$ as the chains lengthen. Gross orbital spin populations and $^1\Sigma_g^+ - X^3\Sigma_g^-$ energy differences were obtained from Hartree-Fock calculations in order to interpret the hfs and $|D|$ data, respectively. For C_4 and C_6 electron correlation was included via second (MP2) and third (MP3) order Moller-Plesset perturbation theory.

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[1] R. J. Van Zee, R. F. Ferrante, K. J. Zeringue, W. Weltner, Jr., and D. W. Ewing, J. Chem. Phys., submitted.

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R64.

Ab Initio Calculations on Ag$_2$, Au$_2$, 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$_2$, Au$_2$, 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 intio all-electron and REP studies.

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RG5.   (2:46)

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 Å, R_{OH}=1.00 Å, $\angle_{HOO}$=104°). 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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RG6.   (3:15)

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 of 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]

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[1]G.S. Tompa, M. Seidl, W.C. Ermler and W.E. Carr, Surf. Sci. 185 (1987) L453.

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RG7. (3:31)

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.

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RG8. (3:47)

CHARGE STABILIZATION OF EXCITED ELECTRONIC STATES OF CN⁻

C. S. EWIG 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[1] to emission from an excited triplet state of CN⁻ to the $^1\Sigma^+$ 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 ($\tau \sim 100$ ms.) species has previously been labeled $^3\Pi$ in analogy with CO, there is some evidence it may be $^3\Sigma^+$ as in N_2.

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 $^1\Sigma^+$ state and for the low-lying $^3\Pi$ and $^3\Sigma^+$ 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.

[1]M. Mendenhall et al., Chem. Phys. Letters (submitted).

RG9. (4:03)

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_2^+ and Na_3: Calculated PE surfaces and molecular structures

G. H. Jeung, M. Broyer, and P. Labastie

All electronic states of Na_3^+ dissociating into $2Na(3s) + Na^+$ and some lowest states dissociating into $Na(3s) + Na(3p) + Na^+$ are calculated in full valence CI using a flexible basis set. D_e of the ground state $^1A_1$ with respect to $Na_2(X^1\Sigma_g^+) + Na^+$ is 1.376 eV. A strong Jahn-Teller effect for the first excited state $^1E'$ leads to a linear $^1\Sigma_u^+$ and an acute-angle $^1A_1$ geometries. These states are stable with respect to dissociation into $Na_2(X^1\Sigma_g^+) + Na^+$. Other three states are repulsive. Among the molecular states which can be made from $Na(3s) + Na(3p) + Na^+$, only the $^1A_2$ state is quite stable $(D_e = 0.958eV)$ with respect to dissociation into $Na_2(a^3\Pi_u) + Na^+$. The two Jahn-Teller partner states of $(2)^1E'$ are very weakly bound.

The lowest states of Na_3 are also calculated in full VCI. The ground state $(^2B_2)$ is stable by 0.290 eV with respect to dissociation into $Na_2(X^1\Sigma_g^+) + Na(3s)$. The $^2B_1$ state is only 0.021 eV lower than the $^2A_1$ state and the conic intersection $(^2E')$ lies 0.093 eV higher than the $^2B_1$ 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_3^+ and Na_3. 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 ($^1B_2 \rightarrow {}^1A_1$) and the benzyl radical ($^2A_2 \rightarrow {}^2B_2$) 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 ($2^2B_2 \rightarrow 1^2B_2$) in benzyl radical were observed, although greatly reduced in intensity compared to the ($^2A_2 \rightarrow {}^2B_2$) transition and previous gas phase emission spectra[1]. The high degree of mixing[1] between 2^2B_2 and vibronic states of 1^2A_2 introduces a mechanism that allows collisional electronic quenching to occur during the expansion via removal of vibrational energy.

[1] C. Cossart-Magos and S. Leach, J. Chem. Phys., 64, 4006 (1976).

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RG12.

FLUORESCENCE SPECTROSCOPY OF PREDISSOCIATED LEVELS OF

ELECTRONICALLY EXCITED S_2

Wafaa Fawzy and M. C. Heaven

We have re-examined the laser induced fluorescence spectrum of jet-cooled 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, λ=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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RG13.

WAVELENGTH - RESOLVED FLUORESCENCE STUDIES OF THE COLLISION

DYNAMICS OF 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 Br_2 (B). A self-quenching rate of 4×10^{-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 6×10^{-11} cm^3 molecule^{-1} s^{-1}. An upper bound of 5×10^{-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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RG14.

ELECTRONIC SPECTROSCOPY OF RARE GAS ISOLATED I_2 AND IBr

M.A.P. MACLER and M.C. HEAVEN

The electronic spectroscopy of I_2 and IBr, isolated in solid rare gas matrices has been studied using time and wavelength resolved fluorescence techniques.

Argon isolated I_2, excited at a wavelength of 193 nm, showed a broad feature at about 380 nm, that has a very short life-time ($\simeq$ 20 ns). This transition has been tentatively assigned as the $D'(^3\Pi_{2g})-A'(^3\Pi_{2u})$ system.

Ar, Kr and Xe isolated IBr, excited at a wavelength of 532 nm, exhibited both $A(^3\Pi_1)-X(^1\Sigma)$ and $A'(^3\Pi_2)-X(^1\Sigma)$ systems. The life-times of these transitions decrease with increasing atomic number of the host.

Spectral and temporal analyses will be discussed.

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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,[1] a number of fluorinated and alkylated derivatives of H_3PO and H_2POH,[2] and several cytosine tautomers and methylated and fluorinated derivatives.[3] Hence, we may examine the values calculated for force constants and dipole moment derivatives for chemically similar bonds (C-H, 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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[3] M. Szczesniak, J. S. Kwiatkowski, K. KuBulat, K. Szczepaniak and W. B. Person, J. Am. Chem. Soc., submitted for publication; A. Jaworski, unpublished results.

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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, $P_{\alpha\beta}^{\lambda}$, and atomic axial tensors, $M_{\alpha\beta}^{\lambda}$ [1,2]. Ab initio calculations of $P_{\alpha\beta}^{\lambda}$ and $M_{\alpha\beta}^{\lambda}$ 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 $P_{\alpha\beta}^{\lambda}$ and $M_{\alpha\beta}^{\lambda}$ tensors. We report a previously unnoted representation of $P_{\alpha\beta}^{\lambda}$ tensors, involving the electronic momentum operator, and its implementation using CHF perturbation theory. Alternative representations of both $P_{\alpha\beta}^{\lambda}$ and $M_{\alpha\beta}^{\lambda}$ tensors in terms of nuclear electromagnetic shielding tensors, $\aleph_{\alpha\beta}^{\lambda}$ and $\xi_{\alpha\beta}^{\lambda}$ [9,10] are discussed. $\aleph_{\alpha\beta}^{\lambda}$ exists in length, momentum and force representations; $\xi_{\alpha\beta}^{\lambda}$ exists in angular momentum and torque representations. The calculation of $\aleph_{\alpha\beta}^{\lambda}$ and $\xi_{\alpha\beta}^{\lambda}$ 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 $P_{\alpha\beta}^{\lambda}$ and $M_{\alpha\beta}^{\lambda}$ 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-methylcyclohexanone and α-pinene. New VCD spectra of several molecules will also be reported.

1. F. Devlin and P.J. Stephens, Appl. Spectry. 41, 1142 (1987).

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RH5.   (2:33)

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 $P^\lambda_{\alpha\beta}$ and $M^\lambda_{\alpha\beta}$ tensors calculated $\underline{ab}$ $\underline{initio}$ at the SCF level, are compared to the experimental spectra.

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RH6.   (2:50)

VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF MOLECULES CONTAINING SECOND-ROW ELEMENTS

R. Bursi and P.J. Stephens

The accuracy of $\underline{ab}$ $\underline{initio}$ 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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RH7.   (3:20)

VIBRATIONAL SPECTRA OF TETRAFLUOROOXIRANE-^{16}O AND -^{18}O

NORMAN C. CRAIG, DIANE GESTY, AND ALLEN G. KASTELLE

The Raman spectrum of tetrafluorooxirane-^{16}O (tetrafluoroethylene oxide-16: TFEO-16) has been obtained at -80°C. From this spectrum and a previous infrared study[1] we have developed a complete assignment of the vibrational fundamentals. These fundamentals in cm^{-1} are: (a_1) 1610, 1161, 792, 502, 320; (a_2) 1240, 516, 234; (b_1) 1128, 776, 696, 528; (b_2) 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_6 and v_8.[1] The assignments for v_5, v_8, 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.[2]

From the infrared and Raman spectra of TFEO-18 the fundamentals in cm^{-1} are: (a_1) 1607, 1136, 789, 494, 321; (a_2) 1240, 516, 234; (b_1) 1127, 777, 679, 516; (b_2) 1282, 539, 185. Because v_1 shifts very little with ^{18}O substitution, this mode is not "ring breathing"[1] 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 ^{18}O substitution are v_2 (sym CO stretching), v_{11} and v_{12} (asym CO stretching), and v_{14} (COC flappping).

[1] N. C. Craig, Spectrochim. Acta, 28A, 1195 (1972).

[2] J. W. Agopovich, J. Alexander, C. W. Gillies, and T. T. Raw, J. Am. Chem. Soc., 106, 2250 (1984).

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RH8.

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 C_S symmetry. The axis of least moment of inertia, I_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, 916, 890, 869, 493, 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 itself,[1] 261 cm^{-1} in 1-fluorocyclobutene,[2] 132 cm^{-1} in 3,3,4,4-tetrafluorocyclobutene,[2] and 98 cm^{-1} in perfluorocyclobutene.[3]

[1] V. T. Aleksanyan and O. G. Garkusha, Izv. Akad. Nauk SSSR, Ser. Khim. 1976, 2227.

[2] Unpublished results: N. C. Craig, S. S. Borick, H. Kim, J. R. Seidel, and T. R. Tucker.

[3] P. Klaeboe, C. J. Nielsen, and D. L. Powell, Spectrochim. Acta, 43A, 893 (1987).

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RH9.

VIBRONIC STATES OF PuF$_6$ IN THE NEAR IR AND VISIBLE SPECTRAL REGIONS

S.J. David and K.C. Kim

The entire absorption spectrum of PuF$_6$ in the near ir and visible regions has been obtained by coupling a long path length absorption cell with a BOMEM DA3.002 Fourier transform spectrometer. This setup allows us to obtain spectra at very high sensitivity and high resolution.

An analysis of the vibronic energy levels and spectroscopic assignments of the observed transitions will be presented. The energy levels obtained from those spectroscopic measurements of the gas phase PuF$_6$ molecule are the most accurate values available. A comparison is shown of our assignments and results with available theoretical studies and the matrix-isolation results.

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RHI0.

INTEGRATED INTENSITIES OF CO_2 AND SF_6 VIBRATIONAL BANDS FROM 1800 TO 5000 CM^{-1} AS A FUNCTION OF DENSITY AND TEMPERATURE

Michael E. 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 FTS. Densities from 4×10^{-5} to 2×10^{-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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RHI1.

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 $T_{10}O_{12}$ (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 Badgen'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:

$$FR = 2.595 \times N4E / (N4E + NSI) + 5.587$$

The changes in the bending constant are very small.

FOURIER TRANSFORM INFRARED SPECTROSCOPY OF NITRIC OXIDE IN ELECTRIC AND MICROWAVE DISCHARGES

K.L. 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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*G. Herzberg, Molecular Spectra and Molecular Structure, D. Van Nostrand Co., Inc., Vol. I, p. 121, 1950.

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FOURIER TRANSFORM DETECTION OF THE ν_3 FUNDAMENTAL OF THE N_3 RADICAL

C. R. BRAZIER, P. F. BERNATH, J. B. BURKHOLDER, AND C. J. HOWARD

We have observed the ν_3 asymmetric stretching fundamental of the azide radical. N_3 was produced in a long pathlength absorption cell by the reaction of HN_3 with Cl atoms. The use of multipass mirrors gave an effective pathlength of about 100 m and absorption of upto 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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(8:52)

RA'.

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 (upto 9-7) due to the high temperature and the increase in the transition strength of the overtones with increasing v.

Molecular constants and RKR curves for the $X^1\Sigma^+$ states of LiBr and NaF will be presented.

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(9:08)

FA4.

Progress on NH_3:
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 NH_3: vibrational overtones and combination bands from 6000 cm^{-1} to 18000 cm^{-1} has lead to the assignment of several new bands. These include $v_2 + v_3 + v_4^2$ at about 6050 cm^{-1}, and $3v_3^0$ and $3v_3^2$ both near 10100 cm^{-1}. The hamiltonian being used to fit band origins in the N-H stretch overtone regions includes Darling-Dennison or local mode coupling which mixes v_1 and v_3, and the Fermi resonance between $2v_4$, 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.

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(9:19)

FA5.

INVESTIGATION OF HOT BAND TRANSITIONS OF NH_3 IN THE 10 μm REGION

R. D'CUNHA, K. SINGH AND V.B. KARTHA

Intensity measurements and N_2 pressure broadening studies have been carried out on several vibration rotation transitions in the $a2v_2 \leftarrow sv_2$ hot band of $^{14}NH_3$, 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 CO_2 laser will be presented and the role of hot bands in the interpretation of these signals will be discussed.

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             COLUMBUS DEPT OF PHYSICS K N RAO JUN 88

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FA6.
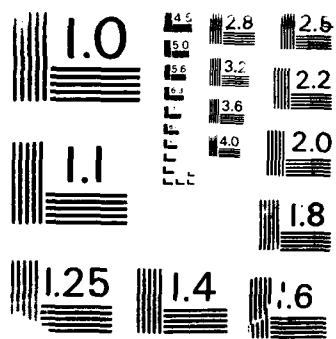
THE $s2\nu_2 \leftarrow a\nu_2$ HOT BAND IN $^{14}NH_3$ AND $^{15}NH_3$

R. D'CUNHA AND M.N. DEO

Numerous transitions have been identified and assigned in the $s2\nu_2 \leftarrow a\nu_2$ 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 $s2\nu_2$ levels with the corresponding ν_4 levels will be briefly discussed.

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FA7.

INTERPRETATION OF HIGH RESOLUTION FTS SPECTRA OF $^{14}NH_3$ AT 2-3 μm

N. Tu, S. Urban, G. Guelachvili, and K. Narahari Rao

The Fourier transform spectra of ammonia, $^{14}NH_3$, have been measured in the 2-3 μm region with 0.005 cm^{-1} resolution. The ν_1, ν_3, $2\nu_4$, $\nu_1 + \nu_2$, $\nu_2 + \nu_3$, and $\nu_2 + 2\nu_4$ bands have been assigned and analyzed. Among them, the $\nu_3 + 2\nu_4$ bands have been assigned for the first time. The band origins for the $\nu_3 + 2\nu_4$ symmetrical and antisymmetrical paralell bands are 4115.62 cm^{-1} and 4173.25 cm^{-1} respectively. These band origins differ from the calculated values (1). The band origins for the symmetrical and antisymmetrical perpendicular bands are also found at 4135.94 cm^{-1} and 4193.14 cm^{-1} respectively.

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(1)V. Spirko, J. Mol. Spectrosc. vol.101,30-47(1983).

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HIGH RESOLUTION SUPERSONIC BEAM INFRARED SPECTRA OF ACETYLENE TETRAMER

G. 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 v_3 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.

[1] G.W. Bryant, D.F. Eggers and R.O. Watts, *J. Chem. Soc.*, Faraday Trans. 2, **84**, 0000 (1988).
[2] D. Prichard, J.S. Muenter and B.J. Howard, *Chem. Phys. Letters* **135**, 9 (1987).

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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 C_2H_2 dimer have been recorded in the monomer v_5 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 $^qP_0$, $^qR_0$, $^qP_1$, $^qQ_1$, and $^qR_1$ 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 A from the B and C constants. This distance is too large for a slipped parallel geometry of C_{2h} symmetry but is consistent with a hydrogen-bonded T-shaped geometry of C_{2v} 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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FA10.   (10:37)

INFRARED DIODE LASER SPECTROSCOPY OF THE BF₃ VAN DER WAALS COMPLEXES WITH RARE GASES

YOSHIYASU MATSUMOTO, YASUHIRO OHSHIMA, MICHIO 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 ν_3 band (ν_0 =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, -1.767, and -2.577 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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FA11.   (10:53)

FAR-INFRARED SPECTRA OF HCl - 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[1] 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.

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[1]E.W. Boom and J. van der Elsken, J. Chem. Phys. 73, 15 (1980).

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FA12.   (10:59)

INFRARED SPECTRA OF HYDROGEN - RARE GAS VAN DER WAALS MOLECULES

A.R.W. MCKELLAR

Spectra of $H_2(D_2)$ - rare gas van der Waals molecules are being studied using long absorption paths (110-160 m) at low temperatures and a Bomem DA3.02 spectrometer. Among the interesting results are:

1.) New spectra of H_2-Ne, obtained at about 25 K, are much cleaner and better resolved than previously available results.

2.) Spectra of D_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 $S_0(0)$ (350 cm^{-1}) and $S_0(1)$ (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-N_2 and H_2-CO molecules will also be presented.

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FA13.   (11:15)

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 rf hyperfine spectrum.[3] The present results involve a refinement of the mid-infrared (2-4 μm) spectrum,[1,2] which corresponds to the fundamental hydrogen stretching band, and an extension to the far-infrared (15-30 μm) region, which corresponds to the H_2 pure rotational transitions. The experiments are performed with long absorption paths (>100 m) of H_2 or D_2 at low temperatures (77 or <20 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[4] 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 30 distinct rotational lines are resolved.

[1] A. Watanabe and H.L. Welsh, Phys. Rev. Lett. 13, 810 (1964).

[2] A.R.W. McKellar and H.L. Welsh, Can. J. Phys. 52, 1082 (1974).

[3] J. Verberne and J. Reuss, Chem. Phys. 50, 137 (1980).

[4] A.R.W. McKellar, Astrophys. J. Lett., March 1988.

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FA14. (11:31)

FAR-INFRARED SPECTRUM OF THE HCl DIMER

N. MOAZZEN-AHMADI, J.W.C. JOHNS, AND A.R.W. MCKELLAR

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 ($\approx$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 $H^{35}Cl$, and anticipate that this will simplify and strengthen the spectrum sufficiently that further analysis will be possible in the near future.

[1] N. Ohashi and A. Pine, J. Chem. Phys. 81, 73 (1984).

[2] K. von Puttkamer and M. Quack, Mol. Phys. 62, 1047 (1988).

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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 tunnelling 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 ($\kappa \cong -0.998$ 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.

[1] M. Kofranek, H. Lischka and A. Karpfen, Chem. Phys., submitted for publication.

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

FA16. (12:03)

The 5 μm INFRARED SPECTRUM OF NH_3 COLLISION-BROADENED BY H2

C. CHAPADOS AND G. BIRNBAUM.

Measurements on mixtures of ammonia and hydrogen in the 5 μm in 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 $36^{\circ}C$. The density dependance of these results and their significance will be discussed.

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194

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 ± 10 cm^{-1} which is the NC_2 out-of-plane wag.

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(8:54)

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 $^{12}CH_3OH$ up to J = 22 on a supercomputer and have measured and assigned a large number of excited torsional state transitions in $^{13}CH_3OH$. In this talk, some of our recent progress will be discussed.

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(9:11)

PRESSURE BROADENING OF MILLIMETER WAVE TRANSITIONS OF HNO_3, NO_2, CF_2Cl_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_2Cl_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_2Cl_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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(9:28)

THE MICROWAVE SPECTRUM OF DIFLUOROMETHANIMINE, F_2CNH

K. MOELLER, M. WINNEWISSER, G. PAWELKE and H. BÜRGER

The rotational spectrum of diflouromethanimine, F_2CNH, has been observed for the first time. In the region from 16 to 40 GHz 99 strong b-type transitions belonging to the branches $^bR_{1,1}$ and $^bQ_{1,-1}$ and 4 weak a-type transitions belonging to the $^aQ_{0,1}$ 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^r-axis representation. The preliminary spectroscopic constants are: A = 11464.021 MHz, B = 11151.888 MHz, C = 5643.143 MHz, Δ_J = 5.25 kHz, Δ_{JK} = 0.184 kHz, Δ_K = 9.555 kHz, δ_J = 2.175 kHz, and δ_K = 5.087 kHz. These results confirm the assumption that F_2CNH is a planar oblate asymmetric rotor molecule having C_s symmetry with asymmetry parameters κ = 0.8927 and b_o = -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_2CNH will be reported at the meeting.

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Address of G. Pawelke and H. Bürger: FB 9, Anorganische Chemie, Gesamthochschule Wuppertal, D-5600 Wuppertal 1, West Germany.

(9:45)

MICROWAVE SPECTRUM OF $^{13}CD_3OH$

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 $^{13}CD_3OH$ is currently of interest in supporting identifications of optically-pumped far-infrared laser lines in this species, particularly the strong and efficient 127 μm FIR line reported not long ago.[1]

In this work, the microwave absorption spectrum of $^{13}CD_3OH$ has been investigated, and the a-type R-branch transitions have been measured for J=1←0 and J=2←1 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=1←0 E_1, K=1←2 E_1 and K=3←2 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]M. Inguscio, K.M. Evenson, F.R. Petersen, F. Strumia and E.C.C. Vasconcellos, Int. J. Infrared and Millimeter Waves 5, 1289-1296 (1984).

Address of authors: Department of Physics, University of New Brunswick, Fredericton, N.B. Canada E3B 5A3.

FB7. (10:15)

THE SUBMILLIMETER-WAVE SPECTRUM OF THE $^{12}CH_3O$ AND THE $^{13}CH_3O$ RADICALS

TAKAMASA MOMOSE, YASUKI ENDO, EIZI HIROTA, AND TADAMASA SHIDA

The pure rotational spectrum of the isotopically substituted methoxy radical $^{13}CH_3O$ was observed in the millimeter and the submillimeter wave regions. The $^{12}CH_3O$ radical was also studied in the same wavelength regions and the molecular parameters of the previous work[2] 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 analyse the spectrum in the submillimeter-wave region.

With reference to the rotational constants of CD_3O, the r_s structure was determined. Parameters of the structure[3] are $r(CO)=1.3926Å$, $r(CH)=1.1178Å$, and $\angle HCO=113.9$.

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 recource to the information from the far-infrared LMR experiment as was done in our previous work[2].

1 T. Momose, Y. Endo, E. Hirota, and T. Shida, J. Chem. Phys., in print.
2 Y. Endo, S. Saito, and E. Hirota, J. Chem. Phys. 81, 122 (1984).

Address of Momose and Shida: Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan.
Address of Endo: Department of Pure and Applied Science, College of Arts and Science, The University of Tokyo.
Address of Hirota: Institute for Molecular Science, Okazaki 444, Japan.

FB8. (10:32)

MICROWAVE SPECTRUM AND STRUCTURE OF CYCLOBUTADIENE OZONIDE

P. LORENCAK AND R. L. KUCZKOWSKI

Six isotopic species of cyclobutadiene ozonide (2,3,7-trioxabicyclo[2.2.1] hept-5-ene) containing D, ^{18}O and ^{13}C enrichment were prepared by singlet oxygen addition to furan. Rotational and centrifugal distortion constants were determined for all six species and were sufficient to determine the complete structure of the molecule. Perhaps the most interesting structural feature is the non-planarity about the C=C bond, where tne hydrogen atoms are bent 8.9° towards the endo side.

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FB9.   (10:54)

MILLIMETER WAVE ABSORPTION AND FAR INFRARED LASER MAGNETIC RESONANCE SPECTROSCOPY OF FO_2*

M. BOGEY, C. DEMUYNCK, J. L. DESTOMBES, P. B. DAVIES AND T. J. SEARS

We have recorded many absorptions due to the FO_2 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 $6 \leq N \leq 15$ and $0 \leq K \leq 7$. 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[1] 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.

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Address of Davies: Physical Chemistry Laboratory, Lensfield Road, Cambridge, CB21EP England.
Address of Sears: Chemistry Dept. Brookhaven National Laboratory, Upton, NY, 11973.

FB10.   (11:01)

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 C_2F_3Cl. The spectrum has been reexamined using a FTMW 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 χ_{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 reports.

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Address of Gerry: Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6.

Address of Bittner, Hillig, and Kuczkowski: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

THE MICROWAVE SPECTRUM OF KR·PF$_3$

K. W. HILLIG II, M. S. LABARGE, E. BITTNER, R. BOHN, R. C. TAYLOR, AND
R. 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 r_{cm} between the krypton atom and the center of mass of the PF$_3$ molecule is 4.072 Å and the angle between the r_{cm} vector and the C_3 axis of the PF$_3$ is 68.25°. The P^4 centrifugal distortion constants, the dipole moment and the ^{83}Kr quadrupole coupling constants have also been determined. The results will be compared to those of Ar·PF$_3$.

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Address of Bohn: Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268.

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CONFORMATIONAL STUDY OF 1,2-AMINO ALCOHOLS BY VIBRATIONAL CIRCULAR DICHROISM

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 $v(NH_2)^{asym}$ and $v(NH_2)^{sym}$ 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.

Address of Ragunathan, Nafie and Freedman: Department of Chemistry, Syracuse University, Syracuse, New York 13244-1200.

CIRCULAR DICHROISM 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⁻¹ 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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FC3.   (9:04)

ON THE CIRCULAR DICHROISM MEASUREMENTS IN THE 800-600 cm⁻¹ RANGE

P. L. POLAVARAPU

Circular dichroism measurements in the 800-600 cm⁻¹ range were shown to be feasible about five years ago.[1] Some of these earlier results were 'misinterpreted' recently.[2] These differences will be clarified and new results will be presented.

[1]P. L. Polavarapu, Appl. Spectrosc. 38, 26 (1984).
[2]F. Devlin and P. J. Stephens, Appl. Spectrosc. 41, 1142 (1987).

Address of Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, TN 37235

FC4.   (9:16)

NEW DEVELOPMENTS IN RAMAN OPTICAL ACTIVITY

P. L. Polavarapu

Raman optical activity (ROA) is conventionally measured by modulating the incident laser polarisation between right and left circular polarisation 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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FC5.   (9:28)

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 our to date. α-D-glucose represents the largest system ever attempted for ab initio vibrational properties.

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FC6.   (9:40)

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 - α Pinene and R + Limonene will be presented.

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FC7.   (10:05)

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. El-Azhary and Timothy A. Keiderling

FT-IR and Raman spectra were measured for trans-1,2-dicyanocyclopropane and its trans-1,2-d_2 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.[1] 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.[2] showed a better agreement.

[1] V.J. Heintz and T.A. Keiderling, J. Am. Chem. Soc., 1981, 103, 2395.

[2] K.J. Jalkanen and P.J. Stephens, J. Am. Chem. Soc., 1987, 109, 7193.

Address of A.A. El-Azhary and T.A. Keiderling: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, Illinois 60680

VIBRATIONAL CIRCULAR DICHROISM OF 1,3-DIDEUTERIOALLENE, CALCULATIONAL RESULTS

A. ANNAMALAI, U. NARAYANAN, K. J. JALKANEN, M.-C. TISSOT, P. J. STEPHENS, T. A. KEIDERLING

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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Address of Jalkanen, Stephens: Department of Chemistry, University of Southern California, Los Angeles, CA 90089

FC10. (10:46)

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 (-)-α-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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FC11. (11:03)

VIBRATIONAL CIRCULAR DICHROISM 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 $CDCl_3$ and in D_2O 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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FC12. (11:20)

VIBRATIONAL CIRCULAR DICHROISM OF SMALL PEPTIDES AND PEPTIDE MODELS IN SOLUTIONS: EXPERIMENTAL DATA AND CALCULATIONS

G. 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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FC13.

VIBRATIONAL CIRCULAR DICHROISM OF OLIGO-NUCLEOTIDES: EXPERI-
MENTAL DATA AND CALCULATIONS

M. GULOTTA 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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1.   A.Annamalai and T.A.Keiderling, J.Amer.Chem.Soc., 1987,
     109. 3125

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