ARO 26430.2-PH-CF

AD-A224 349

45th

OHIO STATE UNIVERSITY
SYMPOSIUM ON
MOLECULAR SPECTROSCOPY
JUNE 11-15, 1990

DTIC
ELECTE
JUL 20 1990
S B D

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

99 07 20 112

INFORMATION

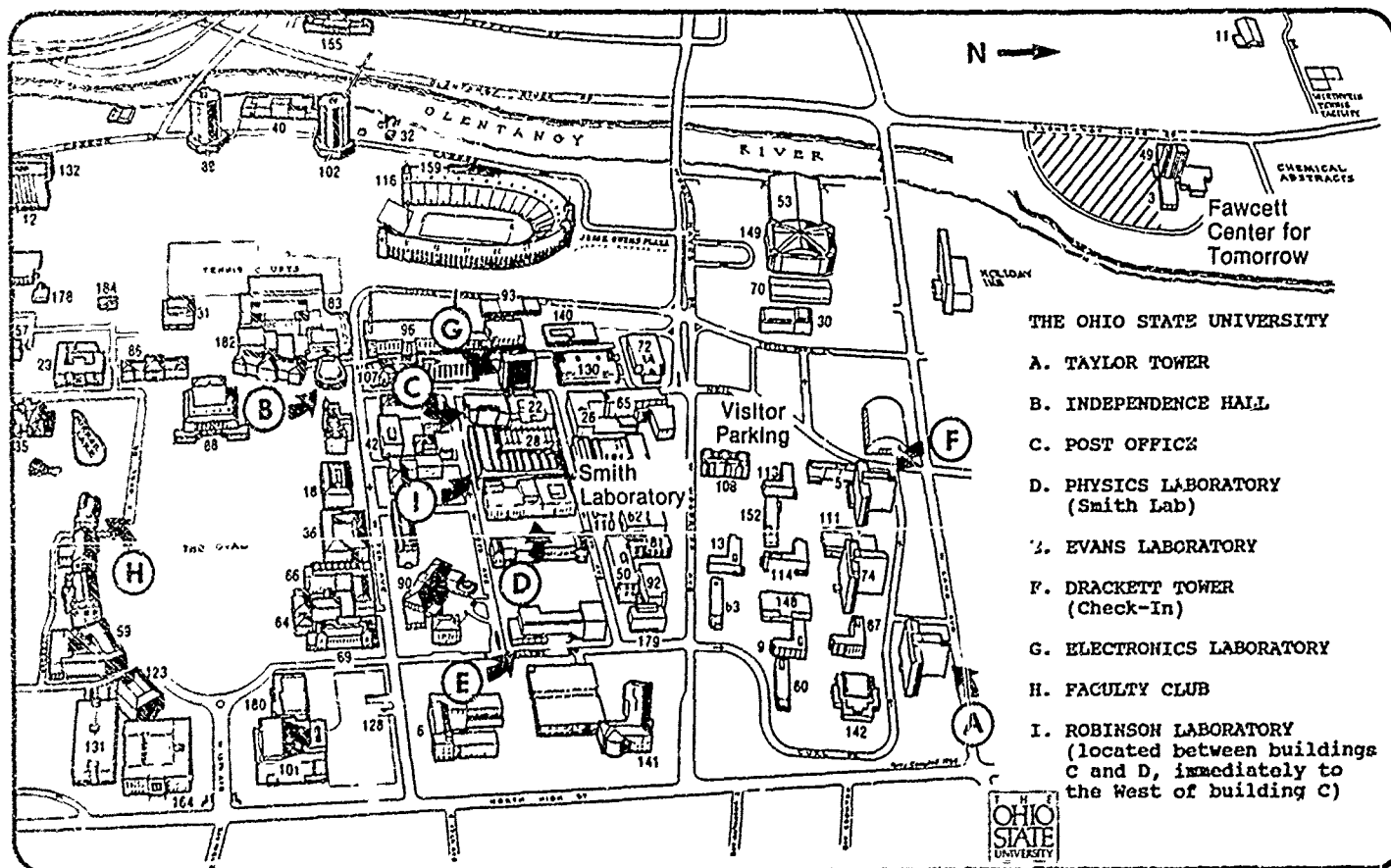ACCOMMODATIONS: The check-in for dormitory accommodations is located in Drackett Tower (F) on Curl Drive.

BANQUET: This will take place at the Ohio State University Faculty Club (H) on We'nesday, June 13, 1990, at 7:00 p.m. preceded by a reception starting at 6:00 p.m. Prof. Richard N. Zare, Stanford University will speak on "CHEMICAL REACTIONS: HOW CLOSE IS CLOSE ENOUGH?"

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

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

REGISTRATION: The Registration Desk will be located in Room 1036, Physics Laboratory. It will be kept open between 8:30 a.m. - 12 n and 1:00 - 4:30 p.m., Monday through Friday. The registration fee is $65.00 per participant and $55.00 if paid by May 10. The special rate of $25.00 per Graduate Student will be reduced to $20.00 if paid by May 10. Please send the completed registration form along with your check before this date.

SESSIONS: They will be held in: Independence Hall (B), Physics Lab (D), and Evans Chemical Lab (E). Letters in parentheses correspond to the campus map below:

THE OHIO STATE UNIVERSITY

A. TAYLOR TOWER

B. INDEPENDENCE HALL

C. POST OFFICE

D. PHYSICS LABORATORY
   (Smith Lab)

E. EVANS LABORATORY

F. DRACKETT TOWER
   (Check-In)

G. ELECTRONICS LABORATORY

H. FACULTY CLUB

I. ROBINSON LABORATORY
   (located between buildings
   C and D, immediately to
   the West of building C)

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 1990	3. REPORT TYPE AND DATES COVERED Final 6 Mar 90 – 5 Mar 91

4. TITLE AND SUBTITLE

Forty-Fifth Symposium on Molecular Spectroscopy

5. FUNDING NUMBERS

DAAL03-89-G-0020

6. AUTHOR(S)

K. Narahari Rao   (principal investigator)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Ohio State University
Columbus, OH 43210-0020

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

ARO 26430.2-PH-CF

11. SUPPLEMENTARY NOTES

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The 45th Ohio State University Symposium on Molecular Spectroscopy was held June 11-15, 1990. A book of abstracts has been compiled by the University.

14. SUBJECT TERMS

Molecular Spectroscopy, Spectroscopy, Symposium

15. NUMBER OF PAGES
203

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

→ Topics inclu[...]

MONDAY, JUNE 11, 1990 -- 8:45 A.M.

Auditorium, Independence Hall

Chair: K. NARAHARI RAO, Department of Physics, The Ohio State University,
         Columbus, Ohio and R. S. McDOWELL, Los Alamos National Laboratory,
         Los Alamos, New Mexico.

Plenary Session

MA1. CLUSTERS: SPECTROSCOPY BY DISSOCIATION................................35 min.

   JAMES M. LISY, School of Chemical Sciences, University of
   Illinois at Urbana-Champaign, Urbana, Illinois, 61801.

MA2. LARGE-AMPLITUDE MOTIONS IN WEAKLY BOUND COMPLEXES...............35 min.

   GERALD T. FRASER, Molecular Physics Division, National
   Institute of Standards and Technology, Gaithersburg,
   Maryland, 20899.

MA3. SLIT JET INFRARED SPECTROSCOPY: PROBING THE INTERNAL
   DYNAMICS OF WEAKLY BONDED MOLECULAR COMPLEXES..................35 min.

   CHRISTOPHER M. LOVEJOY, Quantum Physics Division, National
   Institute of Standards and Technology, Boulder, Colorado,
   80309-0440.

Intermission

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

MA4. LASER SPECTROSCOPY OF EXOTIC CHEMICAL SPECIES: TRANSIENT,
   WEAKLY BOUND, REACTIVE, AND SURFACE ADSORBED MOLECULES..........35 min.

   HAI-LUNG DAI, Department of Chemistry, University of
   Pennsylvania, Philadelphia, Pennsylvania, 19104-6323.

MEMO TO THOSE CHAIRING SESSIONS:

The program as given in this BOOK OF ABSTRACTS
incorporates all changes that came to our atten-
tion until May 1. Please follow the schedules
as given in this book while conducting sessions.

YOUR HELP IS APPRECIATED IMMENSELY

Rao

MONDAY, JUNE 11, 1990 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chair: R. E. BUMGARNER, Division of Geology and Planetary Sciences, Caltech, Pasadena, California.

ME1. SLOWING OF IVR WITH THE HEAVY ATOM EFFECT: TRIMETHYL SUBSTITUTED ACETYLENES.....15 min.(1:30)

K. K. LEHMANN, T. MENTEL, B. H. PATE, and G. SCOLES, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

ME2. THE FUNDAMENTAL AND FIRST OVERTONE OF THE $CF_3C\equiv CH$ ACETYLENIC STRETCH.............15 min.(1:47)

E. KERSTEL, K. K. LEHMANN, T. MENTEL, B. H. PATE, and G. SCOLES, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

ME3. VIBRATIONAL PREDISSOCIATION STUDIES OF $Cs(NH_3)_n^+$ CLUSTER IONS....................15 min.(2:04)

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

ME4. VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF $(CD_3OD)_2$ IN THE 10.6μ REGION.........15 min.(2:21)

JEFFREY P. LACOSSE and JAMES M. LISY, School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois, 61801.

ME5. VIBRATIONAL PREDISSOCIATION STUDIES OF $Cs(ACETONE)_N^+$ CLUSTER IONS................15 min.(2:38)

THOMAS J. SELEGUE and JAMES M. LISY, School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois, 61801.

ME6. EXPERIMENTS ON THE ON-SET OF MULTIPHOTON TRANSITIONS OF SF_6 WITH HIGH RESOLUTION..15 min.(2:55)

S. TE LINTEL HEKKERT, A. LINSKENS, and J. REUSS, Molecular and Laser Physics, Faculty of Sciences, University of Nijmegen, 6525 ED Nijmegen, The Netherlands.

Intermission

ME7. HIGH RESOLUTION VIBRATIONAL SPECTROSCOPY ON HOMOGENEOUS COMPLEXES OF BENZENE AND DEUTERATED BENZENES...15 min.(3:30)

B. F. HENSON, G. V. HARTLAND, V. A. VENTURO, R. A. HERTZ, and P. M. FELKER, Department of Chemistry and Biochemistry, University of California-Los Angeles, Los Angeles, California, 90024-1569.

ME8. FOURIER-TRANSFORM IONIZATION DETECTED STIMULATED RAMAN SPECTROSCOPY STUDIES OF HETEROGENEOUS COMPLEXES OF PHENOL AND BENZENE...............................15 min.(3:47)

G. V. HARTLAND, B. F. HENSON, V. A. VENTURO, R. A. HERTZ, and P. M. FELKER, Department of Chemistry and Biochemistry, University of California-Los Angeles, Los Angeles, California, 90024-1569.

ME9. ROTATIONAL ANALYSIS OF THE UV SPECTRUM OF BENZENE-DIATOMIC VAN DER WAALS COMPLEXES...15 min.(4:04)

A. M. SMITH, TH. WEBER, E. RIEDLE, H. J. NEUSSER, and E. W. SCHLAG, Institut für Physikalische und Theoretische Chemie, Technische Universität München, D-8046 Garching, West Germany.

ME10. ROTATIONALLY RESOLVED SPECTRA OF BENZENE-NOBLE GAS COMPLEXES....................15 min.(4:21)

TH. WEBER, A. M. SMITH, E. RIEDLE, H. J. NEUSSER, and E. W. SCHLAG, Institut für Physikalische und Theoretische Chemie, Technische Universität München, D-8046 Garching, West Germany.

ME11. ROTATIONAL COHERENCE SPECTROSCOPY APPLIED TO THE STRUCTURAL ANALYSIS OF JET-COOLED TRYPTOPHAN ANALOGS AND THEIR HYDROGEN-BONDED COMPLEXES WITH POLAR SOLVENTS...15 min.(4:38)

L. L. CONNELL, T. C. CORCORAN, P. W. JOIREMAN, P. M. FELKER, Department of Chemistry and Biochemistry, University of California-Los Angeles, Los Angeles, California, 90024-1569.

ME12. FTIR SPETROSCOPY OF CRYOGENIC AEROSOLS................Arrived Late..............15 min.(4:55)

T. A. DUNDER and R. E. MILLER, Department of Chemistry, University of
North Carolina, Chapel Hill, North Carolina, 27599.

ME13. STATE-TO-STATE PHOTODISSOCIATION OF BINARY COMPLEXES.......Arrived Late..........15 min. (5:12)

E. J. BOHAC, JR. and R. E. MILLER, Department of Chemistry, University
of North Carolina, Chapel Hill, North Carolina, 27599.

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.

Chair Before Intermission: NORMAN C. CRAIG, Department of Chemistry, Oberlin
College, Oberlin, Ohio.

Chair After Intermission: G. R. SUDHAKARAN, Department of Physics, State
University of New York, Oswego, New York.

MF1. A COMBINED ANALYSIS OF THE ν_1, ν_3, AND $2\nu_2$ VIBRATIONAL STATES OF THE NH_2 RADICAL
USING FOURIER TRANSFORM ABSORPTION AND EMISSION DATA.............................10 min.(1:30)

JAMES B. BURKHOLDER, CARLETON J. HOWARD, NOAA Aeronomy Laboratory,
R/E/AL2, 325 Broadway, Boulder, Colorado, 80303 and Cooperative Institute
for Research in Experimental Sciences, University of Colorado, Boulder,
Colorado, 80309; A.R.W. McKELLAR, and M. VERVLOET, Herzberg Institute of
Astrophysics, National Research Council of Canada, 100 Sussex Drive,
Ottawa, Ontario, K1A OR5, Canada.

MF2. BANDS OF HNO_2...10 min.(1:42)

J. M. GUILMOT and M. HERMAN, Laboratoire de Chimie Physique Moléculaire,
Université Libre de Bruxelles CP.160, 1050 Bruxelles, Belgium.

MF3. ANALYSIS OF THE ν_3 VIBRATION-TORSION-ROTATION BAND OF H_2O_2.......................15 min.(1:54)

J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research
Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada;
J.-M. FLAUD, and C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et
Atmospherique, Université Pierre et Marie Curie et CNRS, 75252 Paris,
France.

MF4. FIR LASER STARK SPECTROSCOPY OF CH_3OH AT 190 μm AND 195 μm.......................15 min.(2:11)

G. R. SUDHAKARAN, Department of Physics, St   University of New York at
Oswego, Oswego, New York, 13126; I. MUKHOPADHYAY, Department of Physics,
University of British Columbia, Vancouver, British Columbia, V6T 2A6,
Canada; J. C. SARKER, Department of Electrical Engineering, University
of Idaho, Moscow, Idaho, 83843; R. L. BHATTACHARJEE, Department of
Chemistry, University of Rochester, Rochester, New York, 14627; and
L. H. JOHNSTON, Department of Physics, University of Idaho, Moscow,
Idaho, 83843.

MF5. TUNABLE DIODE LASER SPECTROSCOPY OF CF_2Cl_2 IN THE 9 μm REGION....................15 min.(2:28)

S. GIORGIANNI, A. GAMBI, A. BALDACCI, A. DE LORENZI, and S. GHERSETTI,
Dipartimento di Chimica Fisica, Universita' di Venezia, D.D. 2137-
30123 Venezia, Italy.

Intermission

MF6. HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CH_2F_2: THE ν_4 BAND AT 528.7 CM^{-1}.......10 min.(3:00)

M. N. DEO, R. D'CUNHA, Spectroscopy Division, Bhabha Atomic Research
Centre, Bombay 400085, India; A. WEBER, and W. B. OLSON, Molecular
Physics Division, National Institute of Standards and Technology,
Gaithersburg, Maryland, 20899.

MF7. ANALYSIS OF THE 5_0^1, 6_0^1 AND 9_0^1 BANDS OF CH_2DF.................................15 min.(3:12)

W. LEWIS-BEVAN, W. D. STORK, Department of Chemistry and Biochemistry,
Southern Illinois University, Carbondale, Illinois, 62901-4409;
D. F. EGGERS, Department of Chemistry BG-10, University of Washington,
Seattle, Washington, 98195; and M.C.L. GERRY, Department of Chemistry,
University of British Columbia, Vancouver, British Columbia, V6T 1Y6
Canada.

MF8. THE HIGH RESOLUTION INFRARED SPECTRUM OF DBF_2: THE 4_0^1 BAND......................15 min.(3:29)

W. D. STORK and W. LEWIS-BEVAN, Department of Chemistry and Biochemistry,
Southern Illinois University, Carbondale, Illinois, 62901-4409.

MF9.   THE FUNDAMENTAL TORSION BAND IN ACETALDEHYDE.................................15 min.(3:46)

I. KLEINER. Division of Molecular Physics, National Institute for Standards
and Technology, Gaithersburg, Maryland, 20899; M. GODEFROID, M. HERMAN,
Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles,
1050 Bruxelles, Belgium; and A.R.W. McKELLAR, Herzberg Institute of
Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa,
Ontario, K1A OR6, Canada.

MF10.   FAR INFRARED SPECTROSCOPY OF MALONALDEHYDE.................................15 min.(4:03)

D. W. FIRTH, K. R. LEOPOLD, Department of Chemistry, University of
Minnesota, Minneapolis, Minnesota, 55455; and K. BEYER, Department of
Chemistry, MIT, Cambridge, Massachusetts, 02139.

MF11.   HIGH RESOLUTION FT-IR SPECTROSCOPY OF TRANS-1,2-DIFLUOROETHYLENE.................15 min.(4:20)

NORMAN C. CRAIG, DAVID W. BRANDON, Department of Chemistry, Oberlin
College, Oberlin, Ohio, 44074; and WALTER J. LAFFERTY, Molecular Physics
Division, National Institute of Standards and Technology, Gaithersburg,
Maryland, 20899.

MF12.   VIBRATIONAL SPECTRA OF TRANS-3,4-DICHLOROCYCLOBUTENE...........................15 min.(4:37)

NORMAN C. CRAIG, SUSAN E. HAWLEY, and CATHERINE L. PERRY, Department of
Chemistry, Oberlin College, Oberlin, Ohio, 44074.

MF13.   FAR INFRARED SPECTRA OF DCCCN..........Late Paper added to Abstracts Book.......10 min.(4:54)

B. COVELIERS, A. FAYT, Université Catholique de Louvain, Molecular
Spectroscopy Laboratory, B1348 Louvain-la-Neuve, Belgium; and
H. BUERGER, FB9 Anorgan. Chemie, Bergische University, Gaussstrasse 20,
D5600 Wuppertal 1, Republic of Germany.

46TH MOLECULAR SPECTROSCOPY SYMPOSIUM

JUNE 17-21, 1991

SO FAR, THE FOLLOWING INVITED SPEAKERS HAVE ACCEPTED
TO PRESENT PAPERS:

C. DEMUYNCK, LILLE, FRANCE
N. HANDY, UNIVERSITY OF CAMBRIDGE, UK
E. HERBST, DUKE UNIVERSITY, USA
H. PICKETT, JET PROPULSION LABORATORY, USA
D. H. SUTTER, WEST GERMANY

MONDAY, JUNE 11, 1990 — 1:30 P.M.

Room 1005, Physics Laboratory

Chair: T. C. STEIMLE, Department of Chemistry, Arizona State University,
           Tempe, Arizona.

MG1.   THE EXTENT OF CS_2 CONTINUUM-LIKE EMISSION EXCITED BY 266 - 340 nm RADIATION......15 min.(1:30)

       S. J. McNICHOL and S. J. SILVERS, Department of Chemistry, Virginia
       Commonwealth University, Richmond, Virginia, 23284-2006.

MG2.   MAGNETIC MOMENTS AND LIFETIMES OF INDIVIDUAL ROTATIONAL LEVELS OF V $^1B_2$ CS_2......15 min.(1:47)

       D. WARNAAR and S. J. SILVERS, Department of Chemistry, Virginia
       Commonwealth University, Richmond, Virginia, 23284-2006.

MG3.   OBSERVATION OF $\widetilde{B}$–$\widetilde{X}$ FLUORESCENCE EXCITATION SPECTRUM OF FORMYL RADICAL............15 min.(2:04)

       X. ZHAO, G. W. ADAMSON, and R. W. FIELD, Department of Chemistry and
       George R. Harrison Spectroscopy Laboratory, MIT, Cambridge, Massachusetts,
       02139.

MG4.   HIGH RESOLUTION VACUUM ULTRAVIOLET STUDIES OF A^1A'' HCN.........................15 min.(2:21)

       D. M. JONAS, X. ZHAO, S. SOLINA, R. W. FIELD, Department of Chemistry and
       George R. Harrison Spectroscopy Laboratory, MIT, Cambridge, Massachusetts,
       02139; and K. YAMANOUCHI, Department of Pure and Applied Sciences,
       University of Tokyo, Komaba, Megoro-ku, Tokyo 153, Japan.

MG5.   THE VIBRATIONAL STRUCTURE OF HCN BETWEEN 9000 and 19000 CM^{-1}....................10 min.(2:38)

       XUEMING YANG, C. A. ROGASKI, and A. M. WODTKE, Department of Chemistry,
       University of California, Santa Barbara, California, 93106.

MG6.   NEW ABSORPTION SPECTRA IN THE VACUUM UV FROM CYANAMIDE AND FLOURINE ATOMS........10 min.(2:50)

       PATRICK FLEMING and C. WELDON MATHEWS, Department of Chemistry, The Ohio
       State University, Columbus, Ohio, 43210.

MG7.   PYROLYSIS JET SPECTROSCOPY: THE $\widetilde{A}$ - $\widetilde{X}$ TRANSITION OF FORMYL CYANIDE (HCOCN)......10 min.(3:02)

       DENNIS J. CLOUTHIER, JAY RAE, Department of Chemistry, University of
       Kentucky, Lexington, Kentucky, 40506-0055; JERZY KAROLCZAK, Quantum
       Electronics Laboratory, Institute of Physics, A. Mickiewicz University,
       Grunwaldzka 6, 60-780 Poznan, Poland; RICHARD JUDGE, Department of
       Chemistry, University of Wisconsin-Parkside, Kenosha, Wisconsin, 53141-2000;
       DAVID MOULE, Department of Chemistry, Brock University, St. Catharines,
       Ontario, L2S 3A1, Canada; and JOHN D. GODDARD, Department of Chemistry
       and Biochemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada.

MG8.   PYROLYSIS JET SPECTROSCOPY: THE ROTATIONALLY RESOLVED ELECTRONIC SPECTRUM OF
       DICHLOROCARBENE...15 min.(3.14)

       DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky,
       Lexington, Kentucky, 40506-0055; and JERZY KAROLCZAK, Quantum Electronics
       Laboratory, Institute of Physics, A. Mickiewicz University, Grunwaldzka 6,
       60-780 Poznan, Poland.

Intermission

MG9.   A NEW TRIPLET BAND SYSTEM OF C_3..15 min.(3:45)

       H. SASADA, Department of Physics, Keio University, Yokohama, Japan 223;
       T. AMANO, Herzberg Institute of Astrophysics, National Research Council of
       Canada, 100 Sussex Dr., Ottawa, Ontario, K1A OR6, Canada; C. JARMAN, and
       P. F. BERNATH, Department of Chemistry, University of Arizona, Tucson,
       Arizona, 85721.

MG10.   VIBRONIC INTERACTIONS IN CO_2^+ AND THE PERTURBED $\tilde{B}(000)$ STATE.....................15 min.(4:02)

J. ROSTAS, Laboratoire de Photophysique Moléculaire du CNRS, Université de
Paris-Sud, 91405 Orsay, France; D. KLAPSTEIN, Department of Chemistry,
St. Francis Xavier University, Antigonish, Nova Scotia, B2G 1C0, Canada;
M. VERVLOET, and J.K.G. WATSON, Herzberg Institute of Astrophysics,
National Research Council of Canada, Ottawa, Ontario, K1A OR6, Canada.

MG11.   MOLECULAR BEAM VISIBLE-LASER SPECTROSCOPY OF $^{11}BO_2$...............................15 min.(4:19)

A. G. ADAM. M.C.L. GERRY, A. J. MERER, Department of Chemistry, University
of British Columbia, Vancouver, British Columbia, V6T 1Y6, Canada; and
I. OZIER, Department of Physics, University of British Columbia, Vancouver,
British Columbia, V6T 2A6, Canada.

MG12.   LASER SPECTROSCOPY OF THE RYDBERG STATES OF H_3................................15 min.(4:36)

C. M. BORDAS, H. HELM, D. L. HUESTIS, Molecular Physics Laboratory, SRI
International, Menlo Park, California, 94025; and L. J. LEMBO, TRW,
1 Space Park, Redondo Beach, California, 90278.

MG13.   OBSERVATION OF HIGHLY VIBRATIONALLY EXCITED $\tilde{X}$ $^1\Sigma^+$ HCP BY STIMULATED EMISSION
PUMPING SPECTROSCOPY..15 min.(4:53)

YIT-TSONG CHEN, DAVID M. WATT, ROBERT W. FIELD, Department of Chemistry,
MIT, Cambridge, Massachusetts, 02139; and KEVIN K. LEHMANN, Department
of Chemistry, Princeton University, Princeton, New Jersey, 08544.

MG14.   ANALYSIS OF THE 460nm BAND SYSTEM OF $NiCl_2$ PRODUCED IN A FREE JET EXPANSION......15 min.(5:10)

S. H. ASHWORTH, J. M. BROWN, Physical Chemistry Laboratory, Oxford OX1 3QZ,
England; and F. J. GRIEMAN, Seaver Chemistry Laboratory, Pomona College,
Claremont, California, 91711.

8

Room 1008, Evans Chemical Laboratory

Chair Before Intermission: P. GRONER, Department of Chemistry, University of
South Carolina, Columbia, South Carolina.

Chair After Intermission: KENNETH J. MILLER, Department of Chemistry, Rensselaer
Polytechnic Institute, Troy, New York.

MH1.   AN EMPIRICAL RULE RELATING FUNDAMENTAL TO HARMONIC FREQUENCIES...................15 min.(1:30)

K. J. MILLER and F. GANDA-KESUMA, Department of Chemistry, Rensselaer
Polytechnic Institute, Troy, New York, 12180.

MH2.   POTENTIAL ENERGY FUNCTIONS FOR STRETCHING, BENDING, AND TORSIONAL ENERGY AND
FUNDAMENTAL VIBRATIONAL LEVELS..15 min.(1:47)

K. J. MILLER and F. GANDA-KESUMA, Department of Chemistry, Rensselaer
Polytechnic Institute, Troy, New York, 12180.

MH3.   VIBRATIONAL OVERTONE SPECTRUM OF PYRROLIDINE, 3-PYRROLINE AND PYRROLE............15 min.(2:04)

D. L. SNAVELY, F. BLACKBURN, Department of Chemistry, Bowling Green
State University, Bowling Green, Ohio, 43403; and Y. RANASINGHE,
Department of Chemistry, Purdue University, West Lafayette, Indiana,
47907.

MH4.   OVERTONE AND COMBINATION SPECTRA OF TRIATOMIC MOLECULES IN THE VIBRON MODEL......10 min.(2:21)

S. OSS, Department of Physics, University of Trento, 38050 Povo,
(TN) Italy.

MH5.   CHARGE FLOW CONTRIBUTIONS TO INFRARED ABSORPTION AND VIBRATIONAL CIRCULAR
DICHROISM INTENSITIES OF 1-d-ETHANOL..15 min.(2:33)

F. MAURER, R. A. SHAW, R. DUTLER, A. RAUK, and H. WIESER, Department of
Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4, Canada.

Intermission

MH6.   UNIQUE EVALUATION OF MOLECULAR CONSTANTS.......................................15 min.(3:05)

P. THIRUGNANASAMBANDAM, Department of Nuclear Physics, University of
Madras, Madras-600025, India.

MH7.   REDUCED FORM OF THE ROTATION-INTERNAL ROTATION HAMILTONIAN......................15 min.(3:22)

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

MH8.   LOW FREQUENCY VIBRATIONAL SPECTRA, CONFORMATIONAL STABILITY, AND BARRIERS TO
INTERNAL ROTATION FOR 3-BROMOPROPENE AND 1-BROMO-2-FLUOROETHANE..................15 min.(3:39)

J. LIU, QUN TANG, T. S. LITTLE, and J. R. DURIG, Department of Chemistry,
University of South Carolina, Columbia, South Carolina, 29208.

MH9.   THE STRUCTURE OF METHYL CYANOFORMATE FROM MICROWAVE SPECTROSCOPY AND AB INITIO
CALCULATIONS...10 min.(3:56)

JIE LIN, P. GRONER, J. R. DURIG, Department of Chemistry, University of
South Carolina, Columbia, South Carolina, 29208; and B. VAN DER VEKEN,
Laboratorium voor Anorganische Scheikunde, Rijksuniversitair Centrum
Antwerpen, B-2020 Antwerpen, Belgium.

MH10.   VIBRATIONAL SPECTRA AND ASSIGNMENTS, CONFORMATIONAL STABILITY, STRUCTURE AND
AB INITIO CALCULATIONS OF 2-METHYLPROPANAL AND 2-METHYLPROPANAL-d_7..............15 min.(4:08)

W. E. BREWER, J. R. DURIG, Department of Chemistry, University of
South Carolina, Columbia, South Carolina, 29208; and G. A. GUIRGIS,
Mobay Chemical Corporation, Analytical Research Laboratory, Charleston,
South Carolina, 29411.

MH11. RAMAN TORSIONAL OVERTONE SPECTROSCOPY ON PROPANE AND DIMETHYLAMINE................15 min.(4:25)

R. ENGELN, J. REUSS, Molecular and Laser Physics, Faculty of Sciences,
University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands;
D. CONSALVO. Dipartimento di Chimica, Università la Sapienza,
P.le A. Moro 5, I-00185 Roma, Italy; J. VAN BLADEL, and A. VAN DER AVOIRD,
Theoretical Chemistry, Faculty of Sciences, University of Nijmegen,
Toernooiveld, 6525 ED Nijmegen, The Netherlands.

MH12. VIBRATIONAL CIRCULAR DICHROISM SPECTRA AND CONFORMATIONAL ANALYSIS OF
DIISOCYANANO-CYCLOPROPANE...........Late Paper added to Abstracts Book ....15 min.(4:42)

SRITANA C. YASUI, U. S. Food and Drug Administration, 1141 Central
Parkway, Cincinnati, Ohio, 45202; LIJIANG WANG, and T. A. KEIDERLING,
Department of Chemistry, University of Illinois at Chicago, Chicago,
Illinois, 60680.

MH13. MULTIPHOTON DISSOCIATION AND IONIZATION OF $Ni(CO)_4$ AND VARIOUS COBALT COMPLEXES
IN A JET-COOLED MOLECULAR BEAM: COMPARISON WITH MPI OF WF_6
.....................Late Paper added to Abstracts Book. ....15 min.(4:59)

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

TUESDAY, JUNE 12, 1990 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chair Before Intermission: W. LEO MEERTS, Department of Molecular and Laser Physics,
University of Nijmegen, Nijmegen, The Netherlands.

Chair After Intermission: PETER G. GREEN, Division of Geological and Planetary
Sciences, California Institute of Technolog,, Pasadena,
California.

TA1.   FAR INFRARED VIBRATIONAL SPECTROSCOPY OF ArHBr USING A CO_2 LASER DIFFERENCE
FREQUENCY SYSTEM...15 min.(8:30)

> D. W. FIRTH, M. A. DVORAK, S. W. REEVE, R. S. FORD, and K. R. LEOPOLD,
> Department of Chemistry, University of Minnesota, Minneapolis, Minnesota,
> 55455.

TA2.   HIGH RESOLUTION INFRARED SPECTROSCOPY OF THE $Ar-H_2O$ VAN DER WAALS COMPLEX –
VIBRATIONAL ENERGY TRANSFER IN WEAKLY BOUND COMPLEXES...........................15 min.(8:47)

> ROBERT LASCOLA, CHRISTOPHER M. LOVEJOY, and DAVID J. NESBITT, Joint
> Institute for Laboratory Astrophysics, University of Colorado, and
> National Institute of Standards and Technology, and the Department of
> Chemistry and Biochemistry, University of Colorado, Boulder,
> Colorado, 80309-0440.

TA3.   DETERMINATION OF THE INTERMOLECULAR POTENTIAL OF $Ar-H_2O$ FROM TUNABLE FAR
INFRARED LASER SPECTROSCOPY...15 min.(9:04)

> R. C. COHEN and R. J. SAYKALLY, Department of Chemistry, University of
> California and Materials and Chemical Sciences Division, Lawrence
> Berkeley Laboratory, Berkeley, California, 94720.

TA4.   MICROWAVE AND TUNABLE FAR-INFRARED LASER SPECTROSCOPY OF WATER CONTAINING
DIMERS..15 min.(9:21)

> R. E. BUMGARNER and GEOFFREY A. BLAKE, Division of Geological and
> Planetary Sciences 170-25, California Institute of Technology, Pasadena,
> California, 91125.

TA5.   FAR-INFRARED LASER SIDEBAND SPECTRA OF $Ar-D_2O$ AND Ar-HDO........................10 min.(9:38)

> S. SUZUKI, P. A. STOCKMAN, PETER G. GREEN, R. E. BUMGARNER, and
> GOEFFREY A. BLAKE, Division of Geological and Planetary Sciences 170-25,
> California Institute of Technology, Pasadena, California, 91125.

TA6.   FAR INFRARED VIBRATION-ROTATION-TUNNELING SPECTROSCOPY AND THE INTERMOLECULAR
POTENTIAL ENERGY SURFACE OF $Ar-NH_3$...15 min.(9:50)

> CHARLES A. SCHMUTTENMAER, RONALD C. COHEN, and R. J. SAYKALLY, Department
> of Chemistry, University of California, and Materials and Chemical
> Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California,
> 94720.

TA7.   THE STRUCTURAL DEPENDENCE OF HF VIBRATIONAL RED SHIFTS IN Ar_nHF CLUSTERS VIA
HIGH RESOLUTION INFRARED SPECTROSCOPY...15 min.(10:07)

> ANDREW McILROY, ROBERT LASCOLA, CHRISTOPHER M. LOVEJOY, and DAVID J.
> NESBITT, Joint Institute for Laboratory Astrophysics, University of
> Colorado, and National Institute of Standards and Technology, and the
> Department of Chemistry and Biochemistry, University of Colorado,
> Boulder, Colorado, 80309-0440.

Intermission

TA8.   INFRARED SPECTROSCOPY OF THE $CO_2-D(H)Br$ COMPLEXES: LOCATION OF THE HYDROGEN
ATOM...10 min.(10:40)

> Y. P. ZENG, S. W. SHARPE, C. WITTIG, and R. A. BEAUDET, Department of
> Chemistry, University of Southern California, Los Angeles, California,
> 90089-0482.

TA9.   SUBMILLIMETER SPECTROSCOPY OF $(H_2O)_2$ AND $(D_2O)_2$..................................15 min.(10:52)

E. ZWART, J. J. TER MEULEN, and <u>W. LEO MEERTS</u>, Department of Molecular
and Laser Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen,
The Netherlands.

TA10. FAR INFRARED VIBRATION-ROTATION-TUNNELING SPECTROSCOPY AND TUNNELING DYNAMICS
OF CH_4-H_2O...15 min.(11:09)

KERRY L. BUSAROW, RONALD C. COHEN, <u>CHARLES A. SCHMUTTENMAER</u>, Y. T. LEE,
and R. J. SAYKALLY, Department of Chemistry, University of California and
Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory,
Berkeley, California, 94720.

TA11. THE INFRARED SPECTRUM OF THE $HCCH-N_2O$ VAN DER WAALS COMPLEX......................15 min.(11:26)

T. A. HU, LING HONG SUN, and <u>J. S. MUENTER</u>, Department of Chemistry,
University of Rochester, Rochester, New York, 14627.

TA12. FAR INFRARED SPECTRA OF HYDROGEN DIMERS.......................................15 min.(11:43)

<u>A.R.W. McKELLAR</u>, Herzberg Institute of Astrophysics, National Research
Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

TA13. THE ROVIBRATIONAL SPECTRUM, STRUCTURE AND INTERMOLECULAR DYNAMICS OF CO-Ar.......15 min.(12:00)

<u>Y. P. ZENG</u>, S. W. SHARPE, C. WITTIG, and R. A. BEAUDET, Department of
Chemistry, University of Southern California, Los Angeles, California,
90089-0482.

TUESDAY, JUNE 12, 1990 -- 8:30 A.M.

Room 1009, Physics Laboratory

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

Chair After Intermission: K. K. LEHMANN, Department of Chemistry, Princeton
                             University, Princeton, New Jersey.

TB1.   FOURIER TRANSFORM EMISSION SPECTROSCOPY AT 13 μm: SiS..........................10 min.(8:30)

        C. I. FRUM, R. ENGLEMAN, and P. F. BERNATH, Department of Chemistry,
University of Arizona, Tucson, Arizona, 85721.

TB2.   FOURIER TRANSFORM SPECTROSCOPY OF THE VIBRATION-ROTATION BANDS OF THE IF
MOLECULE...10 min.(8:42)

        C. I. FRUM, R. ENGLEMAN, JR., and P. F. BERNATH, Department of Chemistry,
University of Arizona, Tucson, Arizona, 85721.

TB3.   FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE ν_3 MODE OF BeF_2...................10 min.(8:54)

        C. I. FRUM, R. ENGLEMAN, and P. F. BERNATH, Department of Chemistry,
University of Arizona, Tucson, Arizona, 85721.

TB4.   LASER SPECTROSCOPY OF GAS PHASE C_2D IN THE 2800 CM^{-1} REGION.....................15 min.(9:06)

        W-B. YAN and H. E. WARNER, Herzberg Institute of Astrophysics, National
Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6,
Canada.

TB5.   OVERTONE SPECTRA OF HCCF VIA FTIR, OPTOACOUSTIC AND MODR SPECTROSCOPIES..........15 min.(9:23)

        S. L. COY, Department of Chemistry, MIT, Cambridge, Massachusetts, 02139;
J. HOLLAND, I. M. MILLS, D. NEWNHAM, Department of Chemistry, University
of Reading, Reading RG6 2AD, United Kingdom; and K. K. LEHMANN, Department
of Chemistry, Princeton University, Princeton, New Jersey, 08544.

TB6.   CHARACTERIZATION AND CALIBRATION OF THE BRUKER IFS 120 HR....... ....10 min.(9:40)

        M. BIRK. D. B. PETERSON, and H. M. PICKETT, Jet Propulsion Laboratory
California Institute of Technology, Pasadena, California, 91109.

TB7.   WAVENUMBER STANDARDS IN THE 9-22 μm REGION.......................................10 min.(9:52)

        J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council
of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

Intermission

TB8.   THE INFRARED ABSORPTION SPECTRUM OF C_2H_2 AROUND 1300 CM^{-1}.......................10 min.(10:20)

        Y. KABBADJ, M. HERMAN, T. R. HUET, and J. VANDER AUWERA, Laboratoire de
Chimie Physique Moléculaire, Université Libre de Bruxelles, 1050 Bruxelles,
Belgium.

TB9.   INTERPRETATION OF THE HIGH RESOLUTION FOURIER TRANSFORM SPECTRUM OF C_2H_2
IN THE 2.4 μm REGION...10 min.(10:32)

        Y. A. SARMA, R. D'CUNHA, Spectroscopy Division, Bhabha Atomic Research
Centre, Trombay, Bombay 400085, India; G. GUELACHVILI, R. FARRENQ,
K. QING LI, Laboratoire d'Infrarouge, Université de Paris-Sud, Associé
au CNRS, 91405 Orsay, France; V. MALATHY DEVI, D. C. BENNER, Department
of Physics, College of William and Mary, Williamsburg, Virginia, 23185;
and K. NARAHARI RAO, Department of Physics, The Ohio State University,
Columbus, Ohio, 43210.

TB10. DECOUPLING IN THE LINE MIXING OF ACETYLENE INFRARED Q BRANCHES....................15 min.(10:44)

        A. S. PINE and J. P. LOONEY, Molecular Physics and Temperature and Pressure
Divisions, National Institute of Standards and Technology, Gaithersburg,
Maryland, 20899.

TB11. THE $\nu_3/\nu_2 + \nu_4 + \nu_5$ RESONANCE IN ACETYLENE.....................................15 min.(11:01)

W. J. LAFFERTY and A. S. PINE, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

TB12. THE ν_7 AND ν_6 BAND SYSTEMS OF CARBON SUBOXIDE...................................10 min.(11:18)

J. VANDER AUWERA and J.W.C. JOHNS, Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles CP.160, 1050 Bruxelles, Belgium.

TB13. HIGH RESOLUTION FTS SPECTRUM OF SEVERAL BANDS OF ClO_2.................... ......15 min.(11:30)

J. B. BURKHOLDER, C. J. HOWARD, Aeronomy Laboratory, National Oceanic Atmospheric Administration, Boulder, Colorado, 80303; J. ORTIGOSO, R. ESCRIBANO, Instituto de Estructura de al Materia, Consejo Superior de Investigaciones Cientificas, Serrano 119, 28006 Madrid, Spain; and W. J. LAFFERTY, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

TB14. AN EXPERIMENTAL AND THEORETICAL REVIEW OF PRESSURE BROADENING AND SHIFT IN THE ROTOVIBRATIONAL SPECTRUM OF AMMONIA..........Arrived late.................15 min.(11:47)

G. BALDACCHINI, ENEA, TIB-FIS, P.O. BOX 65, 00044 FRASCATI(ROME), ITALY; G. BUFFA, and O. TARRINI, Dipartimento di Fisica, Università di Pisa, 56100 Pisa, Italy.

TB15. FOURIER TRANSFORM SPECTROSCOPY OF CARBONYL SULFIDE FROM 1800 TO 3120 CM^{-1}
........................Late Paper added to Abstracts Book...................10 min.(12:02)

A. BELAFHAL, V. MASSON, A. FAYT, Université Catholique de Louvain, Molecular Spectroscopy Laboratory, B1348 Louvain-la-Neuve, Belgium; and G. GUELACHVILI, Laboratoire d'Infrarouge, Université de Paris-Sud, F91405 Orsay, France.

TUESDAY, JUNE 12, 1990 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chair: JANE RICE, Naval Research Laboratory, Washington, D.C.

TC1.   THE SUB-DOPPLER SPECTRUM OF TiO...10 min.(8:30)

J. E. SHIRLEY, L. M. RUSSON, K. Y. JUENG, and T. C. STEIMLE, Department
of Chemistry, Arizona State University, Tempe, Arizona, 85287-1604.

TC2.   MOLECULAR BEAM OPTICAL STARK MEASUREMENTS OF ScF AND YF........................15 min.(8:42)

J. E. SHIRLEY, C. T. SCURLOCK, and T. C. STEIMLE, Department of
Chemistry, Arizona State University, Tempe, Arizona, 85287-1604.

TC3.   MOLECULAR BEAM-OPTICAL STARK SPECTROSCOPY OF THE $A^2\Pi-X^2\Sigma^+$ BAND SYSTEM OF ScO.....15 min.(8:59)

J. E. SHIRLEY, C. T. SCURLOCK, and T. C. STEIMLE, Department of
Chemistry, Arizona State University, Tempe, Arizona, 85287-1604.

TC4.   VISIBLE LASER SPECTROSCOPIC STUDIES OF FeH.....................................10 min.(9:16)

D. A. FLETCHER, R. T. CARTER, J. M. BROWN, Physical Chemistry Laboratory,
Oxford University, Oxford, OX1 3QZ, England; and T. C. STEIMLE,
Department of Chemistry, Arizona State University, Tempe, Arizona,
85287-1604.

TC5.   THE EMISSION SPECTRUM OF $InCl^+$ REVISITED....................................15 min.(9:28)

W. J. BALFOUR, K. S. CHANDRASEKHAR, and M. D. SAKSENA, Department of
Chemistry, University of Victoria, Victoria, British Columbia, V8W 2Y2,
Canada.

TC6.   U.V. SPECTRA OF InO AND InO^+..15 min.(9:45)

W. J. BALFOUR and M. D. SAKSENA, Department of Chemistry, University of
Victoria, Victoria, British Columbia, V8W 2Y2, Canada.

INTERMISSION

TC7.   FLUORESCENCE-BASED LASER INTRACAVITY SPECTROSCOPY AND THE ELECTRONIC STRUCTURE
OF NiH...15 min.(10:20)

E. J. HILL and R. W. FIELD, Department of Chemistry, MIT, Cambridge,
Massachusetts, 02139.

TC8.   INTERPRETATION OF THE LOW-LYING STATES OF THE NiH RADICAL......................15 min.(10:37)

M. LI, TH. NELIS, and R. W. FIELD, Department of Chemistry, MIT,
Cambridge, Massachusetts, 02139.

TC9.   A NEW LOW-LYING STATE OF THE PtH MOLECULE......................................10 min.(10:54)

R. ENGLEMAN, JR. and P. F. BERNATH, Department of Chemistry,
University of Arizona, Tucson, Arizona, 85721.

TC10. THE GROUND STATE SPIN-ORBIT SPLITTING OF PtH...................................15 min.(11:06)

M. C. McCARTHY and R. W. FIELD, Department of Chemistry, MIT, Cambridge,
Massachusetts, 02139.

TC11. LASER SPECTROSCOPIC INVESTIGATION OF THE ORANGE BANDS OF SrO...................10 min.(11:23)

R.F.W. HERRMANN, W. E. ERNST, Department of Physics, Pennsylvania State
University, University Park, Pennsylvania, 16802; M. GRUNDLER, and
M. STEIN, Institut für Molekulphysik, Freie Universität Berlin,
D-1000 Berlin 33, West Germany.

TC12. ROTATIONAL ANALYSIS OF THE $C^2\Pi - X^2\Sigma^+(0,0)$ SYSTEM OF CaF..........................15 min.(11:35)

W. E. ERNST, Department of Physics, Pennsylvania State University, University Park, Penrsylvania, 16802; O. KNUPPEL, Institut für Molekulphysik, Freie Universität Berlin, D-1000 Berlin 33, West Germany; and J. KANDLER, VDI Technologiezentrum, Graf-Recke-Str., D-4000 Dusseldorf, West Germany.

TC13. THE FIRST OBSERVATION OF A GASEOUS TRIATOMIC CONTAINING A TRANSITION METAL ATOM: THE VISIBLE SPECTRUM OF H-Y-N...15 min.(11:52)

B. SIMARD, P. A. HACKETT, Laser Chemistry Group, National Research Council of Canada, 100 Sussex Dr., Ottawa, Ontari... -1A OR5, Canada; W. J. BALFOUR, Department of Chemistry, University of Victoria, Victoria, British Columbia, V8W 2Y2, Canada; and H. NIKI, Institute of Laser Engineering, Osaka University, Osaka, Japan.

Chair Before Intermission: E. A. COHEN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California.

Chair After Intermission: J. A. ROBERTS, Department of Physics, University of North Texas, Denton, Texas.

TD1. ROTATIONAL SPECTRA IN THE $n\nu_8$, n=1, 2, 3, ν_7 AND ν_4 VIBRATIONS OF THE $^{13}CH_3{}^{12}C^{15}N$,$^{13}CH_3{}^{13}C^{15}N$ MOLECULES FOR $1 \leq J \leq 5$ IN THE FREQUENCY RANGE 17-95 GHz.....15 min.(8:30)

        M. AL-SHARE, J. A. ROBERTS, Department of Physics, University of North Texas, Denton, Texas, 76203; and G. K. JOHRI, D.A.-V. College, Kanpur University, Kanpur - 208 001, India.

TD2. COLLISIONALLY COOLED SPECTROSCOPY: EXPERIMENTAL RESULTS AND APPROACHES TO A PARAMETRIZED THEORY..15 min.(8:47)

        D. R. WILLEY, Department of Physics, Allegheny College, Meadville, Pennsylvania, 16335; and F. C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

TD3. TEMPERATURE DEPENDENCE OF COLLISIONAL PROCESSES IN CH_3F.......................15 min.(9:04)

        H. O. EVERITT and F. C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.

TD4. PRESSURE BROADENING BETWEEN 80 K AND 600 K.....................................15 min.(9:21)

        T. M. GOYETTE, J. J. HOLTON, W. GUO, W. L. EBENSTEIN, 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.

TD5. THE PERTURBED MICROWAVE SPECTRUM OF CYCLOPROPYL BROMIDE.........................15 min.(9:38)

        H. LI, M.C.L. GERRY, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1Y6, Canada; and W. LEWIS-BEVAN, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois, 62901-4409

TD6. TWO-PHOTON MICROWAVE TRANSITIONS WITHIN A TWO-LEVEL SYSTEM......................10 min.(9:55)

        L. MARTINACHE, I. OZIER, and A. BAUDER, Laboratorium für Physikalische Chemie, Eidgenössische Technische, Hochschule, CH-8092 Zürich, Switzerland. Permanent address of Ozier-Department of Physics, University of British Columbia, Vancouver, British Columbia, V6T 2A6, Canada.

TD7. GROUP-THEORETICAL FORMALISM FOR THE LARGE-AMPLITUDE VIBRATION-ROTATION PROBLEM IN METHYLAMINE-d_1 AND PRELIMINARY ANALYSIS OF THE GROUND-STATE MICROWAVE SPECTRUM..15 min.(10:07)

        MOTOKI ODA, NOBUKIMI OHASHI, Department of Physics, Faculty of Science, Kanazawa University, Kanazawa, Ishikawa 920, Japan; KOJIRO TAKAGI, Department of Physics, Faculty of Science, Toyama University, Toyama 930, Japan; and JON T. HOUGEN, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

Intermission

TD8. THE ROTATIONAL SPECTRUM AND STRUCTURE OF Cl_2O_3................................15 min.(10:40)

        M. BIRK, R. R. FRIEDL, and E. A. COHEN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

TD9. MICROWAVE SPECTRUM OF NS IN THE HIGHLY EXCITED VIBRATIONAL STATES...............10 min.(10:57)

        TAKAYOSHI AMANO and TAKAKO AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

TD10. MICROWAVE SPECTRUM OF NCS...15 min.(11:09)

TAKAYOSHI AMANO and TAKAKO AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

TD11. FIRST EXPERIENCES WITH AN AUTOMATIC PULSED MOLECULAR BEAM MICROWAVE FOURIER TRANSFORM SPECTROMETER...15 min.(11:26)

W. STAHL, U. ANDRESEN, H. DREIZLER, and J. U. GRABOW, Institut für Physikalische Chemie, Universität Kiel, 2300 Kiel 1, Federal Republic of Germany.

TD12. MICROWAVE SPECTRA AND STRUCTURES OF THE NONLINEAR ONN-HCN, ONN^{15}-HCN, AND ONN-DCN COMPLEXES...   ....10 min.(11:43)

D. J. PAULEY, M. A. ROEHRIG, and S. G. KUKOLICH, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

TD13. MICROWAVE SPECTRUM OF CHLOROMETHYLTHIIRANE....Late Paper added to Abstracts Book. 10 min.(11:55)

C. F. SU, M. T. HO, R. L. COOK, Department of Physics and Astronomy, Mississippi State University, Mississippi State, Mississippi, 39762; and V. F. KALASINSKY, Armed Forces Institute of Pathology, Walter Reed Army Medical Center, Washington, DC, 20306.

TUESDAY, JUNE 12, 1990 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chair: C. LOVEJOY, National Institute of Standards and Technology, Boulder, Colorado.

TE1. QUANTUM MECHANICAL TREATMENT OF TWO INTERACTING RIGID ROTORS: APPLICATION TO $(HCl)_2$..15 min.(1:30)

MICHAEL D. SCHUDER and DAVID J. NESBITT, Joint Institute fo Laboratory Astrophysics, University of Colorado, and National Institute of Standards and Technology, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado. 80309-0440.

TE2. AN AB INITIO POTENTIAL ENERGY SURFACE AND RO-VIBRATIONAL CALCULATIONS FOR $(HCl)_2$..15 min.(1:47)

V. C. EPA, P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada; A. KARPFEN, H. LISCHKA, and M. KOFRANEK, Institut für Theoretische Chemie und Strahlenchemie, University of Vienna, A-1090 Vienna, Austria.

TE3. INVESTIGATION OF H_2HCl AND H_2DCl COMPLEXES: H_2 ORIENTATION EFFECTS IN THE VAN DER WAALS COMPLEX..15 min.(2:04)

MICHAEL D. SCHUDER and DAVID J. NESBITT, Joint Institute for Laboratory Astrophysics, University of Colorado, and National Institute of Standards and Technology, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309-0440.

TE4. THEORETICAL CALCULATIONS OF THE TRANS-BEND, CIS-BEND AND TORSIONAL ENERGY LEVELS OF THE HF, HCl AND HBr DIMERS..15 min.(2:21)

S. C. ALTHORPE, D. C. CLARY, Department of Theoretical Chemistry, Cambridge University, Cambridge, England; and P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

TE5. THE STRETCHING VIBRATIONAL STATES OF THE HF DIMER..20 min.(2:38)

P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada; P. JENSEN, Institute of Physical Chemistry, Justus-Liebig-Universitat, D-6300 Giessen, Germany; A. KARPFEN, H. LISCHKA, and M. KOFRANEK, Institut für Theortische Chemie und Strahlenchemie, Universität Wien, A-1090 Vienna, Austria.

TE6. P-TYPE DOUBLING IN THE INFRARED SPECTRUM OF NO-HF..15 min.(3:00)

WAFAA M. FAWZY, Department of Chemist , Brookhaven National Laboratory, Upton, New York, 11973; GERALD T. FRASER, JON T. HOUGEN, and ALAN S. PINE, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

Intermission

TE7. SiS, C_2H_2, AND HCN IN IRC+10216: ASTRONOMY AT 12-14 MICRONS WITH A POSTDISPERSED FTS..15 min.(3:30)

D. E. JENNINGS G. R. WIEDEMANN, Planetary Systems Branch, Code 693, Laboratory for Extraterrestrial Physics, NASA Goddard Space Flight Center, Greenbelt, Maryland, 20771; R. J. BOYLE, Department of Physics and Astronomy, Dickinson College, Carlisle, Pennsylvania, 17013; and J. J. KEADY, T-4, MS-B212, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545.

TE8. ELECTRONIC SPECTRA AND RELAXTION PATHWAYS OF THE Ne-CN AND Ar-CN VAN DER WAALS COMPLEXES..15 min.(3:47)

Y. LIN, S. K. KULKARNI, and M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, Georgia, 30322.

TE9.   ELECTRONIC SPECTRA FOR THE Ne OH AND Ne OD VAN DER WAALS COMPLEXES...............15 min.(4:04)

Y. LIN, S. K. KULKARNI, and M. C. HEAVEN, Department of Chemistry,
Emory University, Atlanta, Georgia, 30322.

TE10. THE CHARACTERIZATION OF He_2Cl_2: SPECTROSCOPY AND DYNAMICS......................15 min.(4:21)

W. D. SANDS, C. R. BIELER, and K. C. JANDA, Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

TE11. $KrCl_2$ AND $XeCl_2$: CHEMICAL COMPOUNDS OR VAN DER WAALS MOLECULES?............... .15 min.(4:38)

C. R. BIELER, K. E. SPENCE, and K. C. JANDA, Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

TE12. FLUORESCENCE DECAY AND NON-RADIATIVE RELAXATION DYNAMICS OF THE $A^2\Sigma^+$ STATES OF
OH-Ar AND OD-Ar..10 min.(4:55)

S. K. KULKARNI, Y. LIN, and M. C. HEAVEN, Department of Chemistry, Emory
University, Atlanta, Georgia, 30322.

TE13. VIBRATIONAL PREDISSOCIATION IN ACETYLENE AND HYDROGEN CYANIDE - HYDROGEN HALIDE
COMPLEXES................................Arrived Late........................10 min.(5:07)

P. A. BLOCK, D. C. DAYTON, and R. E. MILLER, Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina, 27599.

TUESDAY, JUNE 12, 1990 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chair Before Intermission: MICHAEL HOKE, OPI/Air Force Geophysics Laboratory,
Hanscom AFB, Bedford, Massachusetts.

Chair After ntermission: W. E. BLASS, Molecular Spectroscopy Laboratory,
Department of Physics and Astronomy, University of
Tennessee. Knoxville, Tennessee.

TF1. MEASUREMENTS OF NITROGEN-SHIFTING COEFFICIENTS OF WATER VAPOR LINES BETWEEN
5000 AND 10700 CM^{-1} .... 5 min.(1:30)

J.-P. CHEVILLARD, J.-Y. MANDIN, J.-M. FLAUD, and C. CAMY-PEYRET,
Laboratoire de Physique Moléculaire et Atmosphérique, Université
Pierre et Marie Curie et CNRS, 75252 Paris, France.

TF2. THE $\nu_2+3\nu_3$ BAND OF $^{16}O_3$ AT 2.7 μm: LINE POSITIONS AND INTENSITIES............... 5 min.(1:36)

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

TF3. PRESSURE BROADENING OF O_3 LINES IN THE 3 μm REGION............................10 min.(1:42)

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

TF4. TEMPERATURE DEPENDENCE OF N_2-BROADENING COEFFICIENTS IN THE ν_1 AND ν_3 BANDS
OF OZONE...15 min.(1:54)

M. N. SPENCER and C. CHACKERIAN, JR., NASA Ames Research Center, Mail
Stop 245/4, Moffett Field, California, 94035-1000.

TF5. MEASUREMENT OF COLLISION BROADENING BY HYDROGEN AND NITROGEN OF ACETYLENE
LINES IN THE 14 μm REGION USING A TUNABLE DIODE LASER SPECTROMETER...............10 min.(2:11)

J. F. BRANNON, JR., M. WEBER, and W. E. BLASS, Molecular Spectroscopy
Laboratory, Department of Physics and Astronomy, University of
Tennessee, Knoxville, Tennessee, 37996-1200.

TF6. MOLECULAR PARAMETER RETRIEVAL FROM SPECTRA IN THE PRESENCE OF COMPLEX
INTRAMOLECULAR ENERGY PIPELINES USING A SUPERCOMPUTER WITH A VECTOR PROCESSOR....15 min.(2:23)

W. E. BLASS, Molecular Spectroscopy Laboratory, Department of Physics
and Astronomy, University of Tennessee, Knoxville, Tennessee, 37996-1200.

TF7. DETERMINATION OF ATOMIC AND MOLECULAR SPECIES IN SPECTRA USING ARTIFICIAL
NEURAL NETWORKS..15 min.(2:40)

A. L. SUMNER, P. J. GRIGSBY, Foreign Technology Division/SQDEO,
Wright-Patterson Air Force Base, Ohio, 45433-6508; S. K. ROGERS,
M. KABRISKY, and D. NORMAN, Air Force Institute of Technology/ENG,
Wright-Patterson Air Force Base, Ohio, 45433-6583.

Intermission

TF8. BAND AND LINE STRENGTHS OF FIFTEEN MICRON CARBON DIOXIDE BANDS FROM GAS SAMPLES
AT HIGH TEMPERATURES..10 min.(3:10)

MICHAEL HOKE, OPI/GL(AFSC), Hanscom Air Force Base, Bedford,
Massachusetts, 01731; and MARK ESPLIN, Stewart Radiance Laboratory,
Utah State University, Bedford, Massachusetts, 01730.

TF9. LINE POSITIONS OF CO_2 IN THE 580 TO 940 CM^{-1} REGION AT ELEVATED TEMPERATURES.....10 min.(3:22)

MARK P. ESPLIN, Stewart Radiance Laboratory, Utah State University, Bedford, Massachusetts, 01730; and MICHAEL HOKE, OPI/Air Force Geophysics Laboratory, Hanscom Air Force Base, Bedford, Massachusetts, 01730.

TF10. CENTRIFUGAL CORRECTIONS TO ROTATIONAL INTENSITIES..............................15 min.(3:34)

H. M. PICKETT, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

TF11. HERMAN-WALLIS FACTORS FOR CARBON DIOXIDE CALCULATED BY DIRECT NUMERICAL DIAGONALIZATION(DND)...15 min.(3:51)

R. B. WATTSON, A. NEWBURGH, Visidyne, Inc., 10 Corporate Place, S. Bedford St., Burlington, Massachusetts, 01830; and L. S. ROTHMAN, Optical Physics Division, Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 01730-5000.

TF12. DIODE LASER SPECTRA OF SiS IN THE REGION FROM 700 TO 800 CM^{-1}. ROTATIONAL CONSTANTS AND FOREIGN-GAS BROADENING PARAMETERS......................15 min.(4:08)

D. C. REUTER and J. KURTZ, Planetary Systems Branch, Code 693, Laboratory for Extraterrestrial Physics, NASA Goddard Space Flight Center, Greenbelt, Maryland, 20771.

TF13. HALFWIDTH AND PRESSURE-INDUCED LINESHIFT COEFFICIENTS IN THE ν_3, $\nu_2+\nu_4$, $\nu_3+\nu_4$ AND $\nu_1+\nu_4$ BANDS OF $^{12}CH_4$..15 min.(4:25)

D. CHRIS BENNER, V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; CURTIS P. RINSLAND, and MARY ANN H. SMITH, Atmospheric Sciences Division, Mail Stop 401A, NASA Langley Research Center, Hampton, Virginia, 23665-5225.

TF14. PRELIMINARY RESULTS ON THE ANALYSIS OF THE PENTAD OF $^{13}CH_4$......................10 min.(4:42)

J. M. JOUVARD, B. LAVOREL, J. P. CHAMPION, Laboratoire de Spectronomie Moléculaire et Instrumentation Laser, Université de Bourgogne, U.A. CNRS N°777, 21100 Dijon, France; and L. R. BROWN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

TF15. BROADENING AND SHIFTS OF CH_4 LINES IN THE ν_4 BAND AT LOW TEMPERATURES............15 min.(4:54)

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

TF16. COLLISIONAL LINE BROADENING CALCULATIONS FOR HF-He.......Arrived Late............15 min.(5:11)

MARK THACHUK and FREDERICK R. W. McCOURT, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada.

TUESDAY, JUNE 12, 1990--1:30 P.M.

Room, Physics Laboratory

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

TG1.   QUADRUPOLE N_2 LINES AT 4.1 μm STUDIED WITH A DIODE LASER AND AN ABSORPTION PATH
        OF 5.016 km-UPDATE...15 min.(1:30)

PAUL P. BALOG, Balog Physical Systems, 789 S. Front Street, Columbus, Ohio,
43206; K. NARAHARI RAO, Department of Physics, The Ohio State University,
Columbus, Ohio, 43210; and MICHAEL E. MICKELSON, Department of Physics
and Astronomy, Denison University, Granville, Ohio, 43023.

TG2.   GENERAL EXPRESSION FOR THE INTEGRATED ABSORPTION COEFFICIENT OF ZERO-PHONON
        DOUBLE TRANSITION OF THE TYPE $(\Delta J)_{v_1 \leftarrow 0} + S_{v_2 \leftarrow 0}(0)$ IN SOLID PARAHYDROGEN...........10 min.(1:47)

T. K. BALASUBRAMANIAN, R. D'SOUZA, R. D'CUNHA, Spectroscopy Laboratory,
Bhabha Atomic Research Centre, Trombay, Bombay 400085, India; and
K. NARAHARI RAO, Department of Physics, The Ohio State University,
Columbus, Ohio, 43210.

TG3.   PREDICTED INTENSITY OF THE $S_0(0) + S_0(0) + S_0(0)$ TRIPLE TRANSITION IN THE
        INFRARED SPECTRUM OF SOLID ORTHODEUTERIUM...10 min.(1:59)

R. H. TIPPING, Q. MA, Department of Physics and Astronomy, University of
Alabama, Tuscaloosa, Alabama, 35487-0324; and J. D. POLL, Department of
Physics, University of Guelph, Guelph, Ontario, N1G 2W1, Canada.

TG4.   HIGH RESOLUTION INFRARED SPECTROSCOPY OF SOLID HYDROGEN: ANALYSIS OF THE
        FINE STRUCTURE OF THE $Q_1 \leftarrow_0(1)$ TRANSITION OF ORTHOHYDROGEN IMPURITY IN SOLID
        PARAHYDROGEN...15 min.(2:11)

MAN-CHOR CHAN, and TAKESHI OKA, Department of Chemistry and Department of
Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TG5.   HEXADECAPOLE-INDUCED $\Delta J=4$ INFRARED TRANSITIONS OF SOLID DEUTERIUM................15 min.(2:28)

MAN-CHOR CHAN and TAKESHI OKA, Department of Chemistry and Department of
Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TG6.   2-D IMAGES OF DENSITY DISTRIBUTIONS OF O_2 IN SPECIFIC v,J QUANTUM STATES
        OBTAINED VIA PREDISSOCIATIVE LASER INDUCED FLUORESCENCE
        ....Late Paper added to Abstracts Book............................. 8 min.(2:45)

GYUNG-SOO KIM, LYNNE M. HITCHCOCK, ERHARD W. ROTHE, Department of
Chemical Engineering, Wayne State University, Detroit, Michigan, 48202;
and GENE P. RECK, Department of Chemistry, Wayne State University, Detroit,
Michigan, 48202.

TUESDAY, JUNE 12, 1990 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chair: PAUL BALOG, Balog Physical Systems, 789 S. Front Street, Columbus, Ohio.

TG'1. VIBRATIONAL CIRCULAR DICHROISM STUDIES OF AZIDOMETHEMOGLOBIN AND
       AZIDOMETMYOGLOBIN...10 min.(3:00)

           T. B. FREEDMAN, N. RAGUNATHAN, L. A. NAFIE, Department of Chemistry,
           Syracuse University, Syracuse, New York, 13244-4100; P. J. LARKIN,
           S. A. ASHER, Department of Chemistry, University of Pittsburgh,
           Pittsburgh, Pennsylvania, 15260; B. SPRINGER, S. SLIGAR, Department
           of Biochemistry, University of Illinois, Urbana, Illinois, 61801;
           and R. W. NOBLE, Department of Medicine and Biochemistry, State
           University of New York, Buffalo, New York, 14215.

TG'2. VIBRATIONAL CIRCULAR DICHROISM STUDIES OF DEHYDROPHENYL ALANINE PEPTIDES.........15 min.(3:12)

           M. G. PATERLINI, T. B. FREEDMAN, Department of Chemistry, Syracuse
           University, Syracuse, New York, 13244-4100; C. PRATESI, and
           O. PIERONI, Instituto di Biofisica, 56100 Pisa, Italy

TG'3. THEORETICAL AND EXPERIMENTAL COMPARISON OF INCIDENT CIRCULAR POLARIZATION (ICP)
       AND SCATTERED CIRCULAR POLARIZATION (SCP) RAMAN OPTICAL ACTIVITY..................15 min.(3:29)

           L. HECHT, D. CHE, and L. A. NAFIE, Department of Chemistry, Syracuse
           University, Syracuse, New York, 13244-4100.

TG'4. INVESTIGATIONS OF THE THERMOLYSIS KINETICS OF DIDEUTERIOCYCLOPROPANE BY
       VIBRATIONAL CIRCULAR DICHROISM AND FTIR SPECTROSCOPIES............................10 min.(3:46)

           L. A. NAFIE, T. B. FREEDMAN, K. M. SPENCER, S. J. CIANCIOSI, and
           J. E. BALDWIN, Department of Chemistry, Syracuse University, Syracuse,
           New York, 13244-4100.

TG'5. ROTATIONALLY RESOLVED MAGNETIC VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF NO......15 min.(3:58)

           R. K. YOO, B. WANG, P. V. CROATTO, and T. A. KEIDERLING, Department of
           Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

TG'6. MOLECULAR ZEEMAN SPECTROSCOPY IN THE EXCITED STATE. ROTATIONALLY RESOLVED
       MAGNETIC VCD SPECTRA OF CH_4...15 min. (4:15)

           B. WANG, R. K. YOO, P. V. CROATTO, and T. A. KEIDERLING, Department of
           Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

TG'7. VIBRATIONAL CIRCULAR DICHROISM SPECTRA AND NORMAL MODE ANALYSES OF THF..........15 min. (4:32)

           A. A. EL-AZHARY, J. S. CHICKOS, and T. A. KEIDERLING, Department of
           Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

TG'8. THE VIBRATIONAL CIRCULAR DICHROISM SPECTRUM OF 2-METHYLTHIETANE..................15 min.(4:49)

           R. A. SHAW, N. IBRAHIM, and H. WIESER, Department of Chemistry,
           University of Calgary, Calgary, Alberta, T2N 1N4, Canada.

TG'9. THE VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF SELECTED METHYL SUBSTITUTED
       6,8-DIOXABICYCLO[3.2.1] OCTANES..15 min.(5:06)

           T. EGGIMANN, N. IBRAHIM, and H. WIESER, Department of Chemistry,
           University of Calgary, Calgary, Alberta, T2N 1N4, Canada.

TUESDAY, JUNE 12, 1990 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chair: PAUL BALOG, Balog Physical Systems, 789 S. Front Street, Columbus, Ohio.

TG'1. VIBRATIONAL CIRCULAR DICHROISM STUDIES OF AZIDOMETHEMOGLOBIN AND
       AZIDOMETMYOGLOBIN...10 min.(3:00)

           T. B. FREEDMAN, N. RAGUNATHAN, L. A. NAFIE, Department of Chemistry,
           Syracuse University, Syracuse, New York, 13244-4100; P. J. LARKIN,
           S. A. ASHER, Department of Chemistry, University of Pittsburgh,
           Pittsburgh, Pennsylvania, 15260; B. SPRINGER, S. SLIGAR, Department
           of Biochemistry, University of Illinois, Urbana, Illinois, 61801;
           and R. W. NOBLE, Department of Medicine and Biochemistry, State
           University of New York, Buffalo, New York, 14215.

TG'2. VIBRATIONAL CIRCULAR DICHROISM STUDIES OF DEHYDROPHENYL ALANINE PEPTIDES.........15 min.(3:12)

           M. G. PATERLINI, T. B. FREEDMAN, Department of Chemistry, Syracuse
           University, Syracuse, New York, 13244-4100; C. PRATESI, and
           O. PIERONI, Instituto di Biofisica, 56100 Pisa, Italy

TG'3. THEORETICAL AND EXPERIMENTAL COMPARISON OF INCIDENT CIRCULAR POLARIZATION (ICP)
       AND SCATTERED CIRCULAR POLARIZATION (SCP) RAMAN OPTICAL ACTIVITY.................15 min.(3:29)

           L. HECHT, D. CHE, and L. A. NAFIE, Department of Chemistry, Syracuse
           University, Syracuse, New York, 13244-4100.

TG'4. INVESTIGATIONS OF THE THERMOLYSIS KINETICS OF DIDEUTERIOCYCLOPROPANE BY
       VIBRATIONAL CIRCULAR DICHROISM AND FTIR SPECTROSCOPIES.........................10 min.(3:46)

           L. A. NAFIE, T. B. FREEDMAN, K. M. SPENCER, S. J. CIANCIOSI, and
           J. E. BALDWIN, Department of Chemistry, Syracuse University, Syracuse,
           New York, 13244-4100.

TG'5. ROTATIONALLY RESOLVED MAGNETIC VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF NO......15 min.(3:58)

           R. K. YOO, B. WANG. P. V. CROATTO, and T. A. KEIDERLING, Department of
           Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

TG'6. MOLECULAR ZEEMAN SPECTROSCOPY IN THE EXCITED STATE. ROTATIONALLY RESOLVED
       MAGNETIC VCD SPECTRA OF CH_4...15 min.(4:15)

           B. WANG, R. K. YOO, P. V. CROATTO, and T. A. KEIDERLING, Department of
           Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

TG'7. VIBRATIONAL CIRCULAR DICHROISM SPECTRA AND NORMAL MODE ANALYSES OF THF...........15 min.(4:32)

           A. A. EL-AZHARY, J. S. CHICKOS, and T. A. KEIDERLING, Department of
           Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

TG'8. THE VIBRATIONAL CIRCULAR DICHROISM SPECTRUM OF 2-METHYLTHIETANE..................15 min.(4:49)

           R. A. SHAW, N. IBRAHIM, and H. WIESER, Department of Chemistry,
           University of Calgary, Calgary, Alberta, T2N 1N4, Canada.

TG'9. THE VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF SELECTED METHYL SUBSTITUTED
       6,8-DIOXABICYCLO[3.2.1] OCTANES..15 min.(5:06)

           T. EGGIMANN, N. IBRAHIM, and H. WIESER, Department of Chemistry,
           University of Calgary, Calgary, Alberta, T2N 1N4, Canada.

TUESDAY, JUNE 12, 1990 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chair Before Intermission: A. MEENAKSHI, Department of Chemistry, State University of New York, Binghamton, New York.

Chair After Intermission: T. J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York.

TH1. A LIF STUDY OF RENNER-TELLER, SPIN ORBIT AND FERMI RESONANCE INTERACTIONS IN $X^2\Pi$ NCS..15 min.(1:30)

> F. J. NORTHRUP and T. J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973.

TH2. STIMULATED EMISSION PUMPING SPECTROSCOPY OF JET COOLED C_3.......................15 min.(1:47)

> F. J. NORTHRUP, T. J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973; and E. A. ROHLFING, Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551.

TH3. LASER INDUCED FLUORESCENCE OF RADICAL SPECIES PRODUCED IN A PULSED DISCHARGE AND COOLED BY SUPERSONIC EXPANSION...10 min.(2:04)

> S.-J. TSAY, T. A. MILLER, and V. E. BONDYBEY, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

TH4. THE SIMPLEST HETERONUCLEAR METAL CLUSTER:LiBe-DIMER.............................10 min.(2:16)

> K. PAK, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; R. SCHLACHTA, I. FISCHER, Institut für Physikalische und Theoretische Chemie der Technischen Universität München, D-8046 Garching, Federal Republic of Germany; P. ROSMUS, Fachbereich Chemie der Universität Frankfurt, D-6000 Frankfurt, Federal Republic of Germany; and V. E. BONDYBEY, Institut für Physikalische und Theoretische Chemie der Technischen Universität München, D-8046 Garching, Federal Republic of Germany and Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

TH5. HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF ArOH AND ArOD VAN DER WAALS COMPLEXES..15 min.(2:28)

> BOR-CHEN CHANG, DAVID W. CULLIN, JAMES M. WILLIAMSON, BRENT D. REHFUSS, LIAN YU, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

TH6. HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF AN INERT GAS-RADICAL VAN DER WAALS COMPLEX, NeOH..10 min.(2:45)

> BRENT D. REHFUSS, BOR-CHEN CHANG, DAVID W. CULLIN, JAMES M. WILLIAMSON, LIAN YU, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

TH7. ANTICROSSING RESONANCES IN THE FIR LMR SPECTRUM OF FO_2: A CLASSIC EXAMPLE.......15 min.(2:57)

> P. B. DAVIES, Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom; T. J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973; and F. TEMPS, MPI für Stroemungsforschung, 3400 Göttingen, West Germany.

*TH8 and TH9 have been interchanged with RD7 and RD9.

Intermission

*TH8. SPECTROSCOPIC CONSTANTS OF O_2^- ELECTRONIC STATES IN VACUO AND IN IONIC SOLIDS.....10 min.(3:25)

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

*TH9. LEAST-SQUARES ERROR PROPAGATION: NEGLECTED ASPECTS.............................10 min.(3:37)

> J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

TH10. NEW PATTERN RECOGNITION METHODS APPLIED TO SPECTRA IN TRANSITION FROM REGULARITY
TO CHAOS: C_2H_2 STIMULATED EMISSION PUMPING, AND NO_2 MODR.......................10 min.(3:49)

S. L. COY, R. J. SILBEY, R. W. FIELD, Department of Chemistry, MIT,
Cambridge, Massachusetts, 02139; and K. K. LEHMANN, Department of
Chemistry, Princeton University, Princeton, New Jersey, 08544.

TH11. RELAXATION IN $\tilde{A}$ $^1A_2 v_4=1$ D_2CO: EVIDENCE FOR COUPLING TO A LUMPY CONTINUUM FROM
SINGLE STATE DEPOPULATION RATES, AND A REVERSIBLE INTERSYSTEM CROSSING
INTERPRETATION OF FLUORESCENCE DECAY..15 min.(4:01)

S. HALLE, S. L. COY, R. W. FIELD, Department of Chemistry, MIT,
Cambridge, Massachusetts, 02139; and J. L. KINSEY, Rice University,
P.O. Box 1892, Houston, Texas, 77251.

TH12. MONOTONIC BEHAVIOUR OF DATA FOR MAIN-GROUP TRIATOMIC MOLECULES...................10 min.(4:18)

R. HEFFERLIN, B. D. HARTMAN, and A. M. HARPER, Department of Physics,
Southern College, Collegedale, Tennessee, 37315-0370.

TH13. PERIODIC BEHAVIOUR OF DATA FOR MAIN-GROUP TRIATOMIC MOLECULES....................10 min.(4:30)

R. HEFFERLIN, R. L. MARSA, R. J. CAVANAUGH, and K. A. LINDERMAN,
Department of Physics, Southern College, Collegedale, Tennessee,
37315-0370.

TH14. SiH_3 ELECTRONIC STATES OBSERVED BY 2+1 AND 3+1 RESONANCE ENHANCED MULTIPHOTON
IONIZATION SPECTROSCOPY...15 min.(4:42)

R. D. JOHNSON III and J. W. HUDGENS, Chemical Kinetics Division,
National Institute of Standards and Technology, Gaithersburg,
Maryland, 20899.

TH15. THE SUB-DOPPLER OPTICAL STARK SPECTRUM OF $A^2\Pi-X^2\Sigma^+$ BAND OF CaOH.................10 min.(4:59)

D. A. NACHMAN, J. E. SHIRLEY, T. C. STEIMLE, Department of Chemistry,
Arizona State University, Tempe, Arizona, 85287-1604; S. R. LANGHOFF,
and C. W. BAUSCHLICHER, NASA Ames Research Center, Moffett Field,
California, 94035.

TH16. PREDISSOCIATION LINE WIDTHS OF THE SCHUMANN-RUNGE BANDS OF $^{18}O_2$
AND $^{16}O^{18}O$...............................Arrived Late..........................10 min.(5:11)

S.S.-I. CHIU, A.S.-C. CHEUNG, Department of Chemistry, University of
Hong Kong, Hong Kong; K. YOSHINO, J. R. ESMOND, D. E. FREEMAN, and
W. H. PARKINSON, Harvard-Smithsonian Center for Astrophysics, Cambridge,
Massachusetts, 02138.

WEDNESDAY, JUNE 13, 1990 -- 8:45 A.M.

Auditorium, Independence Hall

Chair: ROBERT J. PERRY, Department of Physics, The Ohio State
         University, Columbus, Ohio.

Plenary Session

WA1. THE CO OVERTONE LASER, A MOST INTERESTING SOURCE FOR HIGH
      RESOLUTION SPECTROSCOPY OF OPEN SHELL SYSTEMS....................35 min.

      W. URBAN, Institut für Angewandte Physik der Universität
      Bonn, 5300 Bonn 1, West Germany.

WA2. ALGEBRAIC METHODS FOR MOLECULAR SPECTRA........................35 min.

      FRANCO IACHELLO, Center for Theoretical Physics, Yale
      University, New Haven, Connecticut, 06511.

Intermission

WA3. THE ACETYLENE MOLECULE * ....35 min.

      MICHEL HERMAN, Chimie Physique Moleculaire, Universite
      Libre de Bruxelles, Brussels, Belgium.

WA4. IMPROVED OZONE LINE PARAMETERS FROM MICROWAVE TO MID-INFRARED....20 min.

      J.-M. FLAUD[**], Laboratoire de Physique Moléculaire et
      Atmosphérique, Université Pierre et Marie Curie et CNRS,
      75252 Paris, France.

WA5. THE AB INITIO PREDICTIONS OF VIBRATION ROTATION SPECTRA:
      HCCF,HFCO, SiH_3^+ AND CH_2.....Contributed Paper added in Abstracts
      Book...15 min.

      W. H. GREEN and N. C. HANDY, Department of Chemistry, University
      of Cambridge, Cambridge CB2 1EW, United Kingdom.

   * This talk by M. HERMAN introduces the "ACETYLENE SEMINAR"
     which is continued in Sessions RA and FB.

  ** Research collaborators of the speaker will be identified
     in the abstracts book.

WEDNESDAY, JUNE 13, 1990 — 1:30 P.M.

Room 1005, Physics Laboratory

SPECIAL SEMINAR

"GEORGE PIMENTEL REMEMBERED"

Chair Before Intermission: BRUCE S. AULT, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio.

Chair After Intermission: MARILYN JACOX, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

WE1.   GEORGE PIMENTEL'S FIRST SPECTROSCOPY AND OTHER REMINISCENCES....................30 min.(1:30)

KENNETH S. PITZER, Department of Chemistry, University of California, Berkeley, Berkeley, California, 94720.

WE2.   GEORGE PIMENTEL---A FEW OTHER REFLECTIONS......................................10 min.(2:00)

MARILYN E. JACOX, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

WE3.   INFRARED-INDUCED CONFORMATIONAL ISOMERIZATION OF 1,2-ETHANEDIOL AND 1,2-ETHANEDIAMINE IN LOW-TEMPERATURE MATRICES..................................15 min.(2:10)

C. G. PARK, T. ISHIBASHI, M. NAKATA, and M. TASUMI, Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.

WE4.   NEW HORIZONS IN MATRIX ISOLATION SPECTROSCOPY. INFRARED SPECTRA OF SOME NITROGEN OXIDE IONS AND DIMER IONS...15 min.(2:27)

MARILYN E. JACOX, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899; and WARREN E. THOMPSON, National Science Foundation, Washington, D.C., 20550.

WE5.   TRANSITION-METAL DIATOMICS: GROUND STATE PROPERTIES OF MnNi, MnPd, and MnPt.....15 min.(2:44)

R. J. VAN ZEE, Y. M. HAMRICK, and W. WELTNER, JR., Department of Chemistry, University of Florida, Gainesville, Florida, 32611-2046.

Intermission

WE6.   MATRIX ISOLATION STUDIES OF WEAK HYDROGEN BONDING: ALKYNE AND ALKENE COMPLEXES..15 min.(3:15)

MEI-LEE H. JENG and BRUCE S. AULT, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.

WE7.   ULTRAVIOLET SPECTRA OF MATRIX-ISOLATED CYTOSINE AND SOME OF ITS DERIVATIVES, AND THE EFFECT OF FURTHER ULTRAVIOLET IRRADIATION...............................15 min.(3:32)

M. SZCZESNIAK and W. B. PERSON, Department of Chemistry, University of Florida, Gainesville, Florida, 32611-2046.

WE8.   FT SPECTROSCOPY OF THE ν_3 VIBRATION OF SiC_2 IN THE FAR IR......................10 min.(3:49)

J. D. PRESILLA and W.R.M. GRAHAM, Department of Physics, Texas Christian University, Fort Worth, Texas, 76129.

WE9.   FTIR STUDY OF TRICARBON HYDRIDE RADICALS (C_3H_n, $n \leq 5$) TRAPPED IN AN ARGON MATRIX AT 10 K...15 min.(4:01)

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

WE10. OBSERVATION OF C-H AND C≡C STRETCHING VIBRATIONS OF THE C_4H BUTADIYNYL RADICAL
TRAPPED IN AN ARGON MATRIX..15 min.(4:18)

L. N. SHEN and W.R.M. GRAHAM, Department of Physics, Texas
Christian University, Fort Worth, Texas, 76129.

WE11. INFRARED SPECTRUM OF SULFINIC ACID HSO_2H.......................................15 min.(4:35)

MATTHEW A. FENDER, FRANK T. PROCHASKA, Department of Chemistry and
Physics, Western Carolina University, Cullowhee, North Carolina, 28723;
and YASMIN M. SAYED, Department of Chemistry, University of Wyoming,
Laramie, Wyoming, 82070.

WE12. USING MONTE-CARLO SIMULATIONS OF MATRIX SHIFTS TO CHARACTERIZE TRAPPING SITES
IN RARE GAS MATRICES..........................Arrived Late.....................15 min.(4:52)

MARK R. DAVIES and ROBERT J. LE ROY, Guelph-Waterloo Centre for Graduate
Work in Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1,
Canada.

WE13. TROSCOPIC SEARCH FOR MATRIX-ISOLATED ACETYLNITRENE........Arrived Late.......10 min. (5:09)

ROBERT F. FERRANTE, Department of Chemistry, U.S. Naval Academy,
Annapolis, Maryland, 21402.

WEDNESDAY, JUNE 13, 1990 -- 2:15 P.M.

Room 1009, Physics Laboratory

Chair: WALTER J. LAFFERTY, Molecular Spectroscopy Division, National Institute
          of Standards and Technology, Gaithersburg, Maryland.

WF1.   RANDOM MATRIX STATISTICAL MEASURES AS APPLIED TO THE VIBRATION-ROTATION SPECTRA
        OF A FEW SIMPLE MOLECULES............ ....Invited Paper........................30 min.(2:15)

            LÁSZLÓ NEMES, Research Laboratory fo Inorganic Chemistry, Hungarian
            Academy of Sciences, Budapest, Hungary.

WF2.   OBSERVATION OF TRANSFERRF' 'IKES IN INFRARED-INFRARED FOUR-LEVEL DOUBLE
        RESONANCE IN $^{12}CH_3F$..15 min.(2:48)

            UHYON SHIN, QUAN SONG, and R. H. SCHWENDEMAN, Department of Chemistry,
            Michigan State University, East Lansing, Michigan, 48824-1322.

WF3.   VELOCITY DEPENDENCE OF COLLISIONALLY TRANSFERRED SPIKES OBSERVED BY INFRARED-
        INFRARED FOUR-LEVEL DOUBLE RESONANCE..15 min.(3:05)

            QUAN SONG and R. H. SCHWENDEMAN, Department of Chemistry, Michigan
            State University, East Lansing, Michigan, 48824-1322.

WF4.   TIME-RESOLVED MEASUREMENTS OF TRANSFERRED SPIKES IN INFRARED-INFRARED DOUBLE
        RESONANCE IN $^{13}CH_3F$..15 min.(3:22)

            UHYON SHIN and R. H. SCHWENDEMAN, Department of Chemistry, Michigan
            State University, East Lansing, Michigan, 48824-1322.

WF5.   INFRARED-INFRARED DOUBLE RESONANCE AND POLARIZATION LABELING SPECTROSCOPY OF
        METHYL FLUORIDE...15 min.(3:39)

            CYNTHIA M. FAUST, L. PETER GOLD, and ROBERT A. BERNHEIM, Department of
            Chemistry, Pennsylvania State University, University Park, Pennsylvania,
            16802.

WF6.   ROTATIONAL PARTITION FUNCTIONS FOR SYMMETRIC TOPS..............................15 min.(3:56)

            ROBIN S. McDOWELL, University of California, Los Alamos National
            Laboratory, Los Alamos, New Mexico, 87545.

WF7.   LOCAL MODE ROTATIONAL STRUCTURE IN THE (3000), (4000) AND (5000) STRETCHING
        OVERTONE BANDS OF SILANE: (1) EXPERIMENTS AND RESULTS........................10 min.(4:13)

            QING-SHI ZHU, BAO-SHU ZHANG, HAI-BO QIAN, YUE-REN MA, and HUI MA,
            Dalian Institute of Chemical Physics, P.O. Box 110, Dalian 116023, China.

WF8.   LOCAL MODE ROTATIONAL STRUCTURE IN THE (3000), (4000) AND (5000) STRETCHING
        OVERTONE BANDS OF SILANE: (2) ROTATIONAL ANALYSIS............................15 min.(4:25)

            QING-SHI ZHU, BAO-SHU ZHANG, HAI-BO QIAN, YUE-REN MA, and HUI MA,
            Dalian Institute of Chemical Physics, P.O. Box 110, Dalian 116023, China.

WF9.   INFRARED DIODE LASER AND FOURIER TRANSFORM SPECTROSCOPY OF THE NO_3 RADICAL
        ....Late Paper added to Abstracts Book.............10 min.(4:42)

            EIZI HIROTA, Institute for Molecular Science, Okazaki 444, Japan and
            Graduate University for Advanced Studies, Midori, Yokohama 227, Japan;
            KENTRAOU KAWAGUCHI, Institute for Molecular Science, Okazaki 444, Japan
            and Nobeyama Radio Observatory, Minamimaki, Minamisaku, Nagano 384-13,
            Japan, TAKASHI ISHIWATA, and IKUZO TANAKA, Department of Chemistry, Faculty
            of Science, Tokyo Institute of Technology, Meguro, Tokyo 152, Japan.

WF10.   HIGH RESOLUTION OVERTONE SPECTROSCOPY OF BENZENE USING IR-UV DOUBLE RESONANCE
        TECHNIQUE...............Late Paper added to Abstracts Book.....................10 min.(4:54)

            D-J. LIU, Chemistry Division, Argonne National Laboratory, Argonne, Illinois,
            60439; A. STOLOW, M. J. VRAKKING, E. F. CROMWELL, A. H. KUNG, and Y. T. LEE,
            Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory and
            Department of Chemistry, University of California at Berkeley, Berkeley,
            California, 94720.

30

Room 1005, Physics Laboratory

Chair: P. THIRUGNANASAMBANDAM, Department of Nuclear Physics, University of Madras, Madras, India.

WG1.   INFRARED SPECTROSCOPY AND STRUCTURE OF CH_4 ON NaCl(100).........................15 min.(2:15)

LAURA QUATTROCCI and GEORGE E. EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

WG2.   STRUCTURAL DETERMINATION FOR ACETYLENE PHYSISORBED ONTO NaCl(100).................15 min.(2:32)

S. KEITH DUNN and GEORGE EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

WG3.   INFRARED SPECTRA OF H_2O, D_2O, AND HDO ON ALKALI HALIDE FILMS....................15 min.(2:49)

L. GIANCARLO, C. A. BAUMAN, Department of Chemistry, University of Scranton, Scranton, Pennsylvania, 18510; and B. STONE, Department of Chemistry, San Jose State University, San Jose, California, 95192.

WG4.   SPECTRA OF GAS-PHASE CRYSTALLINE MICROPARTICLES................................15 min.(3:06)

J. P. DEVLIN and F. FLEYFEL, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, 74078.

WG5.   INFRARED SPECTROSCOPY OF LARGE WATER CLUSTERS.................................15 min.(3:23)

ROBERT DISSELKAMP and GEORGE E. EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

WG6.   PHOTOCHEMISTRY OF PHYSISORBED KETENE...15 min.(3:40)

OTTO BERG, GEORGE EWING, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405; and R. W. ANTHONY HUFF, Department of Chemistry, University of California, Berkeley, California, 94720.

WG7.   FT-IR SPECTRA OF EPITAXIALLY GROWN CLATHRATE HYDRATES..........................15 min.(3:57)

F. FLEYFEL and J. P. DEVLIN, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, 74078.

WG8.   SPECTROSCOPIC OBSERVATIONS ON DEFECT ACTIVITIES IN AMORPHOUS ICE.................15 min.(4:14)

M. FISHER and J. P. DEVLIN, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, 74078.

WG9.   OPTIMIZATION OF THE FOURIER DECONVOLUTION TECHNIQUE TO ENHANCE INFRARED SPECTRA
....Arrived Late............................10 min.(4:31)

J. MILETIC, Département de Physique, Université du Québec à Trois-Rivières, C.P. 500, Trois-Rivières, Québec, G9A 5H7, Canada; M. TRUDE, and C. CHAPADOS, Département de Chimie-Biologie, Université du Québec à Trois-Rivières, C.P. 500, Trois-Rivières, Québec, G9A 5H7, Canada.

WG10.   BAND SHAPE OF KETONE CARBONYLS IN SOLUTION.............Arrived Late..............15 min.(4:43)

G. PETIT and C. CHAPADOS, Département de Chimie-Biologie, Université du Québec à Trois-Rivières, C.P. 500, Trois-Rivières, Québec, G9A 5H7, Canada.

WG11.   TUNABLE FAR INFRARED LASER SPECTROSCOPY OF JET-COOLED CARBON CLUSTERS: THE ν_2
BENDING VIBRATION OF C_3..........LAST MINUTE ADDITION...........................10 min.(5:00)

C. A. SCHMUTTENMAER, R. C. COHEN, N. PUGLIANO, J. R. HEATH, A. L. COOKSY, K. L. BUSAROW, and R. J. SAYKALLY, Department of Chemistry, University of California, and Materials Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California, 94720.

WEDNESDAY, JUNE 13, 1990 — 2:15 P.M.

Room 1008, Evans Chemical Laboratory

Chair: W. C. ERMLER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey.

WH1. HIGH RESOLUTION $S_1 \leftarrow S_0$ FLUORESCENCE EXCITATION SPECTROSCOPY OF THE TAUTOMERS OF 2-HYDROXYPYRIDINE...15 min.(2:15)

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

WH2. ROTATIONALLY RESOLVED FLUORESCENCE EXCITATION SPECTRA OF 4-DIMETHYLAMINO-BENZONITRILE ALONG TWO LOW FREQUENCY COORDINATES...............................15 min.(2:32)

J. L. TOMER, A. HELD, J. F. PFANSTIEL, and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

WH3. OBSERVATION OF THE ARYLMETHYL RADICALS..10 min.(2:49)

CRISTINO P. DAMO, TAI-YUAN DAVID LIN, JAMES R. DUNLOP, and TERRY A. MILLER, Laser Spectrosocpy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

WH4. THE TORSIONAL ANALYSIS OF JET-COOLED ARYLMETHYL RADICALS........................15 min.(3:01)

TAI-YUAN DAVID LIN, CRISTINO P. DAMO, JAMES R. DUNLOP, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

WH5. JET COOLED EMISSION SPECTRA OF THE XYLENES AND XYLYL RADICALS....................10 min.(3:18)

J. I. SELCO, Department of Chemistry, University of Redlands, Redlands, California, 92373-0999; and P. G. CARRICK, Air Force Astronautics Laboratory/LSX, Edwards Air Force Base, California, 93523.

WH6. EVIDENCE FOR STATE DEPENDENT DECAY IN SYM-TRIAZINE..............................15 min.(3:30)

PAUL UIJT DE HAAG, W. LEO MEERTS, Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands; and JON T. HOUGEN, Molecular Spectroscopy Division, National Bureau of Standards and Technology, Gaithersburg, Maryland, 20899.

WH7. EXCITATION SPECTROSCOPY OF OZONE-HARTLEY SYSTEM.................................15 min.(3:47)

C. P. BEWICK, M. G. GARRIPOLI, H.-A. ECKEL, J. KREIL, and W. DEMTRÖDER, Fachbereich Physik, Universität Kaiserslautern, D-6750 Kaiserslautern, Federal Republic of Germany.

WH8. RESONANCE RAMAN SPECTROSCOPY OF FLAMES.............Arrived Late.................15 min.(4:04)

G. BARRALL, M. J. BURMEISTER, and P. B. KELLY, Department of Chemistry, University of California, Davis, California, 95616.

WH9. PREDISSOCIATION DYNAMICS OF THE METHYL RADICAL $\tilde{B}$ STATE........Arrived Late.......15 min.(4:21)

S. G. WESTRE and P. B. KELLY, Department of Chemistry, University of California, Davis, California, 95616.

WH10. INVESTIGATION OF THE HYPERFINE SPLITTING OF IODINE MOLECULAR LINES IN THE RED SPECTRAL REGION...............................Arrived Late....................10 min.(4:38)

S. RAKOWSKY and D. ZIMMERMANN, Institut für Strahlungs- und Kernphysik, Technische Universität Berlin, D-1000 Berlin 12, West Germany.

WH11. MOLECULAR BEAM RADIO FREQUENCY-OPTICALN DOUBLE-RESONANCE STUDY OF ^{87}SrF IN ITS $X^2\Sigma^+$ STATE.................................Arrived Late......................10 min.(4:50)

Y. AZUMA, W. J. CHILDS, G. L. GOODMAN, Physics Division, Argonne National Laboratory, Argonne, Illinois, 60439; and T. C. STEIMLE, Department of Chemistry, Arizona State University, Tempe, Arizona, 85287-1604.

WH12. LASERSPECTROSCOPIC INVESTIGATION OF THE VAN DER WAALS MOLECULE NaXe ....Arrived Late...........................10 min.(5:02)

P. BAUMANN and D. ZIMMERMANN, Institut für Strahlungs- und Kernphysik, Technische Universität Berlin, D-1000 Berlin 12, West Germany.

THURSDAY, JUNE 14, 1990 -- 8:30 A.M.

Room 1153, Physics Laboratory   ACETYLENE SEMINAR

Chair: M HERMAN, Universite Libre de Bruxelles, Brussels, Belgium.

RA1.   THE IR SPECTRUM OF ACETYLENE: APPLICATION TO MOLECULAR ASTRONOMY................25 min.(8:30)

J. J. HILLMAN, NASA/Goddard Space Flight Center, Laboratory for
Extraterrestrial Physics, Code 690, Greenbelt, Maryland, 20771.

RA2.   THE DISSOCIATION ENERGY OF ACETYLENE..20 min.(9:00)

PETER G. GREEN, Division of Geology and Planetary Sciences, California
Institute of Technology 170-25, Pasadena, California, 91125;
JAMES L. KINSEY, Weiss School of Natural Sciences, Rice University,
Houston, Texas, 77251; and ROBERT W. FIELD, Department of Chemistry,
MIT, Cambridge, Massachusetts, 02139.

RA3.   STARK AND ZEEMAN SPECTROSCOPY OF ACETYLENE LOCATING A TRIPLET ISOMERIZATION
BARRIER...15 min.(9:25)

P. G. GREEN, Division of Geological and Planetary Sciences, California
Institute of Technology 170-25, Pasadena, California, 91125; P. DUPRÉ,
M. LOMBARDI, R. JOST, Service National des Champs Intenses, CNRS,
38042 Grenoble, France; J. L. KINSEY, Weiss School of Natural Sciences,
Rice University, Houston, Texas, 77251; and R. W. FIELD, Department of
Chemistry, MIT, Cambridge, Massachusetts, 02139.

RA4.   STATISTICAL SPECTROSCOPY OF VIBRATIONALLY EXCITED ACETYLENE....................15 min.(9:42)

D. M. JONAS, R. J. SILBEY, R. W. FIELD, Department of Chemistry and
George R. Harrison Spectroscopy Laboratory, MIT, Cambridge, Massachusetts,
02139; and Y. CHEN, Department of Chemistry, University of Southern
California, 90089-0482.

RA5.   VIBRATIONALLY HIGHLY EXCITED ACETYLENE AS STUDIED BY DISPERSED FLUORESCENCE
AND STIMULATED EMISSION PUMPING SPECTROSCOPY..................................15 min.(9:59)

K. YAMANOUCHI, N. IKEDA, S. TSUCHIYA, Department of Pure and Applied
Sciences, University of Tokyo, Komaba, Megoro-ku, Tokyo 153, Japan;
D. M. JONAS, J. K. LUNDBERG, and R. W. FIELD, Department of Chemistry
and George R. Harrison Spectroscopy Laboratory, MIT, Cambridge,
Massachusetts, 02139.

Intermission

RA6.   AB INITIO STUDY OF VIBRATIONAL RESONANCES IN POLYATOMIC MOLECULES.............10 min.(10:30)

F. CULOT and J. LIEVIN, Laboratoire de Chimie Physique Moléculaire, CP.160,
Université Libre de Bruxelles, 1050, Brussels, Belgium.

RA7.   AB INITIO STUDY OF THE ^1A_g VALENCE STATES OF ACETYLENE.........................10 min.(10:42)

J. LIEVIN, Laboratoire de Chimie Physique Moléculaire, CP.160, Université
Libre de Bruxelles, 1050, Brussels, Belgium.

RA8.   THE RAMAN SCATTERING INTENSITY PARAMETERS OF ACETYLENE.........................15 min.(10:54)

K. M. GOUGH and W. F. MURPHY, Division of Chemistry, National Research
Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

RA9.   SOME RAMAN-ODR RESULTS ON ACETYLENE GAS..15 min.(11:11)

BRUCE CHADWICK, School of Chemistry, Macquarie University, Sydney 2109,
Australia.

RA10.   INTERMOLECULAR POTENTIAL FUNCTIONS FOR ACETYLENE...............................15 min.(11:28)

J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester,
New York, 14627.

RA11.   PHOTOELECTRON-INDUCED DISSOCIATIVE ATTACHMENT IN C_2H_2: D_0 (HCC-H)
...............Late Paper Added to Abstracts Book........................10 min.(11:45)

B. RUSCIC and J. BERKOWITZ, Argonne National Laboratory, Argonne, Illinois,
60439.

THURSDAY, JUNE 14, 1990 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chair: V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia.

RB1.   PERTURBATIONS IN THE ν_7 STATE OF CD_3CCH...15 min.(8:30)

R.J. KSHIRSAGAR, C. MEDHEKAR, V. A. JOB, V. B. KARTHA, Spectroscopy Division, Bhabha Atomic Research Centre, Bombay 400085, India; A. WEBER, and W. B. OLSON, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

RB2.   HIGH RESOLUTION FT SPECTROSCOPY OF THE $2\nu_9$ BAND OF CD_3CCH......................15 min.(8:47)

K. SINGH, G. RAJAPPAN, V. A. JOB, V. B. KARTHA, Spectroscopy Division, Bhabha Atomic Research Centre, Bombay 400085, India; A. WEBER, and W. B. OLSON, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

RB3.   IR SIDEBAND SPECTRA OF NF_3 AND PF_5..15 min.(9:04)

H. PRINZ, W. A. KREINER, Abt. Physikalische Chemie, University of Ulm, Ulm, West Germany; G. MAGL, N. ROHRINGER, and W. SCHUPITA, Institut fur Nachrichtentechnik, Technical University of Vienna, Vienna, Austria.

RB4.   VIBRATIONALLY INDUCED DIPOLE MOMENT OF TRIFLUOROSILANE..........................15 min.(9:21)

KENSUKE HARADA, KEIICHI TANAKA, and TAKEHIKO TANAKA, Department of Chemistry, Faculty of Science, Kyusyu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan.

RB5.   INFRARED DIODE LASER SPECTROSCOPY OF THE ν_3 FUNDAMENTAL AND $\nu_2+\nu_3 + \nu_2$ BANDS OF THE CD_3 RADICAL...15 min.(9:38)

WAFAA M. FAWZY, TREVOR J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973; and PAUL B. DAVIES, Department of Chemistry, University of Cambridge, Cambridge, CB21EP, United Kingdom.

RB6.   HIGH RESOLUTION FTIR AND DIODE LASER SPECTRA OF PROPYNE-D IN THE 9-11 μm REGION..15 min.(9:55)

S. B. KARTHA, V. A. JOB, V. B. KARTHA, Spectroscopy Division, Bhabha Atomic Research Centre, Bombay 400085, India; A. WEBER, and W. B. OLSON, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

Intermission

RB7.   ANALYSIS OF THE HIGH-RESOLUTION INFRARED SPECTRUM OF METHYL ISOCYANIDE...........15 min.(10:30)

MOHAMMAD ELSHAKRE, L. PETER GOLD, and ROBERT A. BERNHEIM, Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania, 16802.

RB8.   INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF ETHYL AT 19 μm...................15 min.(10:47)

T. J. SEARS, W. M. FAWZY, Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973; P. M. JOHNSON, Department of Chemistry, State University of New York-Stony Brook, Stony Brook, New York, 11790; and J. M. FRYE, Department of Chemistry, Howard University, Washington, D.C., 20059.

RB9.   INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF HOCO AND DOCO RADICALS...........15 min.(11:04)

WAFAA FAWZY and TREVOR J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973.

RB10. GAS COMPOSITION CONTROL FOR A PULSED NOZZLE FT MICROWAVE SPECTROMETER AND
APPLICATIONS..................Late Paper..15 min.(11:21)

TRYGGVI EMILSSON, T. C. GERMANN, and H. S. GUTOWSKY, Noyes Chemical
Laboratory, University of Illinois, Urbana, Illinois, 61801.

RB11. ROTATIONAL SPECTRUM OF Ar_2-HCN, A VERY FLOPPY T...........Late Paper.............15 min.(11:38)

T. D. KLOTS, C. r DIJKSTRA, and H. S. GUTOWSKY, Noyes Chemical Laboratory,
University of Illinois, Urbana, Illinois, 61801.

RB12. VIBRATIONS IN SMALL Be_n AND Mg_n CLUSTERS (n=3,4)
......................Late Paper added to Abstracts Book....................15 min.(11:55)

TIMOTHY J. LEE, ALISTAIR P. RENDELL, NASA Ames Research Center, MS 230-3,
Moffett Field, California, 94035; and PETER R. TAYLOR, ELORET Institute,
NASA Ames Research Center, MS 230-3, Moffett Field, California, 94035.

THURSDAY, JUNE 14, 1990 — 8:30 A.M.

Room 1005, Physics Laboratory

Chair: D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, Kentucky.

RC1. IMPROVED NONADIABATIC CALCULATION OF EXCITED SINGLET STATES OF THE HYDROGEN MOLECULE..10 min.(8:30)

        SHILIANG YU and KURT DRESSLER, Physical Chemistry Laboratory, ETH-Zentrum, CH-8092, Zurich, Switzerland.

RC2. ROVIBRATIONAL INTENSITIES OF THE ELECTRIC QUADRUPOLE AND MAGNETIC DIPOLE TRANSITIONS IN OXYGEN...................Invited Paper........................25 min.(8:42)

        T. K. BALASUBRAMANIAN, Bhabha Atomic Research Centre, Trombay, Bombay-400085, India.

RC3. VISIBLE-LASER SPECTROSCOPY OF NbN: NEW ELECTRONIC STATES AND HYPERFINE EFFECTS..15 min.(9:10)

        A. G. ADAM, G. HUANG, M.P.J. LYNE, A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1Y6, Canada; Y. AZUMA, Physics Division, Argonne National Laboratory, Argonne, Illinois, 60439; and V. I. SRDANOV, 926 W. Campus Lane, Goleta, California, 93117.

RC4. ROTATIONAL AND HYPERFINE ANALYSIS OF THE $B^4\Pi - X^4\Sigma^-$ (0,0) BAND OF NbO...........15 min.(9:27)

        A. G. ADAM, A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1Y6, Canada; Y. AZUMA, Department of Physics, Argonne National Laboratory, Argonne, Illinois, 60439; J. A. BARRY, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721; G. CHEVAL, J. L. FEMENIAS, Laboratoire d'Optique Atomique et Moléculaire, Faculte des Sciences et des Techniques, Université de Nice, Nice 06034, France; U. SASSENBERG, Department of Physics, University of Stockholm, Stockholm, S-113 46, Sweden; and J. O. SCHRODER, Drägerwerk Aktiengesellschaft, Moislinger Allee 53/55, P.O. Box 13 39, D-2400 Lübeck 1, Germany.

RC5. HYPERFINE STRUCTURE IN THE $B^3\Pi_{0^+u} \leftarrow X^1\Sigma_g^+$ TRANSITION OF $^{79}Br_2$...................15 min.(9:44)

        J. E. MAYHUGH, T. J. SLOTTERBACK, and K. C. JANDA, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

RC6. HYPERFINE STRUCTURE MEASUREMENTS IN THE $A^3\Pi(1) \leftarrow X^1\Sigma^+$ ELECTRONIC TRANSITION OF $I^{35}Cl$ NEAR THE DISSOCIATION LIMIT..15 min.(10:01)

        J. R. JOHNSON, Texas Instrument, Dallas, Texas; T. J. SLOTTERBACK, K. C. JANDA, D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; and C. M. WESTERN, Department of Chemistry, University of Bristol, Bristol, United Kingdom.

Intermission

RC7. NEW ELECTRONIC STATES OF NH...15 min.(10:30)

        R. D. JOHNSON III and J. W. HUDGENS, Chemical Kinetics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

RC8. EXAMINATION OF THE STRUCTURE, Λ-DOUBLING AND PERTURBATIONS IN THE $1^1\Pi_g$ STATE OF Li_2...15 min.(10:47)

        C. LINTON, F. MARTIN, and R. BACIS, Laboratoire de Spectrométrie Ionique et Moléculaire, Université Claude Bernard-Lyon I, 69622 Villeurbanne, France. LINTON on leave from Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada.

RC9. RYDBERG STATES OF CaF OBSERVED BY OPTICAL-OPTICAL DOUBLE RESONANCE...............15 min.(11:04)

        J. E. MURPHY, J. M. BERG, N. HARRIS, R. W. FIELD, Department of Chemistry, MIT, Cambridge, Massachusetts, 02139; and A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, V6T 1Y6, Canada.

RC10. RYDBERG STATES OF CaCl OBSERVED BY OPTICAL-OPTICAL DOUBLE RESONANCE..............15 min.(11:21)

NICOLE A. HARRIS, J. E. MURPHY, Z. J. JAKUBEK, and R. W. FIELD, Department of Chemistry, MIT, Cambridge, Massachusetts, 02139.

RC11. WHAT'S NEW ON YH..15 min.(11:38)

B. SIMARD, P. A. HACKETT, Laser Chemistry Group, National Research Council of Canada, 100 Sussex Dr., Ottawa, Ontario, K1A OR6, Canada; W. J. BALFOUR, Department of Chemistry, University of Victoria, Victoria, British Columbia, V8W 2Y2, Canada; and H. NIKI, Institute of Laser Engineering, Osaka University, Osaka, Japan.

RC12. STARK SPECTROSCOPY OF REFRACTORY MOLECULES: THE PERMANENT DIPOLE MOMENTS
OF YH AND HYN..15 min.(11:55)

B. SIMARD, P. A. HACKETT, Laser Chemistry Group, National Research Council of Canada, 100 Sussex Dr., Ottawa, Ontario, K1A OP6, Canada; W. J. BALFOUR, Department of Chemistry, University of Victoria, Victoria, British Columbia, V8W 2Y2, Canada; and H. NIKI, Institute of Laser Engineering, Osaka University, Osaka, Japan.

THURSDAY, JUNE 14, 1990 -- 8:30 A.M.

Room 1008, Evans Chemical Laboratory

Chair Before Intermission: KENNETH PITZER, Department of Chemistry, University of California-Berkeley, Berkeley, California.

Chair After Intermission: K. BALASUBRAMANIAN, Department of Chemistry, Arizona State University, Tempe, Arizona.

RD1. AB INITIO CALCULATIONS OF ELECTRONIC SPECTRA OF SEMICONDUCTOR CLUSTERS AND SURFACES...................... Invited Paper ....30 min.(8:30)

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

RD2. SPECTROSCOPIC PROPERTIES OF MOLECULES CONTAINING HEAVY ATOMS....Invited Paper....30 min.(9:05)

K. BALASUBRAMANIAN, Department of Chemistry, Arizona State University, Tempe, Arizona, 85287.

RD3. AB INITIO CALCULATIONS OF DIRHENIUM COMPLEXES USING RELATIVISTIC COMPLEXES USING RELATIVISTIC EFFECTIVE CORE POTENTIALS....................................15 min.(9:40)

JEAN-PHILIPPE BLAUDEAU, RICHARD ROSS, RUSSELL PITZER, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; PIERRE MOUGENOT, and MARC BENARD, Laboratoire de Chimie Quantique, E. R. 139 du CNRS, Institut Le Bel, Université Louis Pasteur, 67000 Strasbourg, France.

RD4. INVESTIGATION OF THE BULK/CLUSTER INTERFACE THROUGH AB INITIO STUDIES OF CLUSTERS OF UP TO 135 BERYLLIUM ATOMS...15 min.(9:57)

R. B. ROSS, W. C. ERMLER, C. W. KERN, and R. M. PITZER, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210. Permanent address of ERMLER- Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

Intermission

* The papers below have been assembled from the ones which arrived late. That partly explains the assortment.

RD5. ACCURATE DETERMINATION OF THE Na-Kr INTERACTION POTENTIAL FROM LASERSPECTROSCOPIC DATA..15 min.(10:30)

R. BRUHL and D. ZIMMERMANN, Institut fur Strahlungs- und Kernphysik, Technische Universitat Berlin, D-1000 Berlin 12, West Germany.

RD6. SUBSTITUENT EFFECTS IN TWO-AND THREE-COORDINATE BORON CATIONS....................15 min.(10:47)

W. F. SCHNEIDER, B. E. BURSTEN, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; C. K. NARULA, Department of Chemistry, Ford Motor Company, P.O. Box 2053, Dearborn, Michigan, 48121: and H. NOTH, Institute of Inorganic Chemistry, University of Munich, 8000 Munich 2, West Germany.

*RD7. A THEORETICAL STUDY OF C_2S AND C_3S..10 min.(11:04)

D. J. PEESO, D. W. EWING, and T. T. CURTIS, Department of Chemistry, John Carroll University, Cleveland, Ohio, 44118.

RD8. AB INITIO STUDIES OF THE DIURANIUM MOLECULE....................................15 min.(11:16)

M. PEPPER, B. E. BURSTEN, and R. M. PITZER, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

*RD9. ACCURATE PREDICTIONS OF ROTATIONAL CONSTANTS FOR LINEAR CARBON CHAIN MOLECULES...10 min.(11:33)

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

RD10. FLUORESCENT DECAY AND RADIATIVE LIFETIMES OF THE $A^1\Sigma_u^-$ STATE OF C_2N_2 ....Late Paper added to Abstracts Book...................10 min.(11:45)

S. BARTS, K. PINNEX, J. HALPERN, Laboratory of Extraterrestrial Chemistry, Department of Chemistry, Howard University, Washington, D.C., 20059; and P. MISRA, Laboratory of Extraterrestrial Chemistry, Department of Physics and Astronomy, Howard University, Washington, D.C., 20059.

* RD7 and RD9 have been interchanged with TH8 and TH9.

THURSDAY, JUNE 14, 1990 — 1:30 P.M.

Room 1153, Physics Laboratory

Chair: D. T. DURIG, Department of Chemistry, University of the South,
         Sewanee, Tennessee.

RE1.   LASER VAPORIZATION-FOURIER TRANSFORM MICROWAVE STUDY OF THE HYPERFINE STRUCTURE
       OF THE J = 3/2 ← 1/2 ROTATIONAL TRANSITION OF $X^4\Sigma^-$ NbO.........................15 min.(1:30)

         R. D. SUENRAM, G. T. FRASER, F. J. LOVAS, Molecular Physics Division,
         National Institute of Standards and Technology, Gaithersburg, Maryland,
         20899; and C. W. GILLIES, Department of Chemistry, Rensselaer Polytechnic
         Institute, Troy, New York. 12180.

RE2.   T   UCLEAR QUADRUPOLE COUPLING TENSOR FOR D_2O FROM LOW-J STARK-HYPERFINE
       SPL .RA: IMPLICATIONS FOR THE STRUCTURE DETERMINATION OF VAN DER WAALS
       COMPLEXES..15 min.(1:47)

         MARK D. MARSHALL, Department of Chemistry, Amherst College, Amherst,
         Massachusetts, 01002; RATAN BHATTACHARJEE, and JOHN S. MUENTER,
         Department of Chemistry, University of Rochester, Rochester, New York,
         14627.

RE3.   THE HYPERFINE SPECTRUM OF LiF...10 min.(2:04)

         J. CEDERBERG, D. OLSON, D. BARTZ, P. SOULEN, T. STEINBACH, H. TON,
         and K. URBERG, Department of Physics, St. Olaf College, Northfield,
         Minnesota, 55057.

RE4.   THE ROTATIONAL SPECTRUM OF THE T-SHAPED $HBr \cdot CO_2$ COMPLEX EXAMINED BY
       FT-MICROWAVE SPECTROSCOPY...15 min.(2:16)

         J. K. RICE, Chemistry Division, Code 6111, N-val Research Laboratory,
         Washington, D.C., 20375-5000; R. D. SUENRA , F. J. LOVAS, G. T. FRASER,
         and W. J. LAFFERTY, Molecular Physics Division, National Institute of
         Standards and Technology, Gaithersburg, Maryland, 20899.

RE5.   MICROWAVE AND CO_2-SIDEBAND-LASER OPTOTHERMAL SPECTROSCOPY OF $Ar-NH_3$..............15 min.(2:33)

         G. T. FRASER, A. S. PINE, Molecular Physics Division, National Institute
         of Standards and Technology, Gaithersburg, Maryland, 20899; W. A. KREINER,
         Abteilung für Physikalische Chemie, Universität Ulm, D-7900 Ulm, West
         Germany; D. D. NELSON, JR., Aerodyne Research, 45 Manning Road, Billerica,
         Massachusetts, 01821; and W. KLEMPERER, Department of Chemistry, Harvard
         University, Cambridge, Massachusetts, 02138.

RE6.   THE MICROWAVE SPECTRUM AND STRUCTURE OF THE $(CH_3)_2NH \cdot SO_2$ COMPLEX.................10 min.(2:50)

         J. J. OH, K. W. HILLIG II, and R. L. KUCZKOWSKI, Department of Chemistry,
         University of Michigan, Ann Arbor, Michigan, 48109.

RE7.   THE MICROWAVE SPECTRUM AND STRUCTURE OF THE $(CH_3)_2O \cdot SO_2$ COMPLEX..................10 min.(3:02)

         J. . . OH, K. W. HILLIG II, and R. L. KUCZKOWSKI, Department of Chemistry,
         University of Michigan, Ann Arbor, Michigan, 48109.

                                     INTERMISSION

RE8.   THE MICROWAVE ROTATION-INVERSION SPECTRUM AND STRUCTURE OF THE SO_2 DIMER.........15 min.(3:30)

         A. TALEB-BENDIAB, K. W. HILLIG II, and R. L. KUCZKOWSKI, Department of
         Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

RE9.   ROTATIONAL SPECTRA OF THE H_2O-HCCCCH AND HCCCCH-NH_3 COMPLEXES....................15 min.(3:47)

         K. MATSUMURA, Seinan Gakuin University, Nishijin, Sawaraku, Fukuoka 814,
         Japan; F. J. LOVAS, and R. D. SUENRAM, Molecular Physics Division,
         National Institute of Standards and Technology, Gaithersburg, Maryland,
         20899.

RE10. MICROWAVE SPECTRA AND MOLECULAR STRUCTURE OF THE KETENE-ACETYLENE COMPLEX........15 min.(4:04)

J. Z. GILLIES, Department of Chemistry, Union College, Schenectady, New York, 12308; C. W. GILLIES, B. PATRIARCA, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12180; F. J. LOVAS, and R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

RE11. THE STRUCTURE OF ArCH$_3$CN DETERMINED BY MICROWAVE SPECTROSCOPY...................15 min.(4:21)

R. S. FORD, K. R. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455; R. D. SUENRAM, F. J. LOVAS, and G. T. FRASER, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

RE12. MOLECULAR BEAM LINESHAPE ANALYSIS...15 min.(4:38)

D. OLSON, J. CEDERBERG, D. BARTZ, P. SOULEN, T. STEINBACH, H. TON, and K. URBERG, Department of Physics, St. Olaf College, Northfield, Minnesota, 55057.

RE13. THE ACETYLENE-SULFUR DIOXIDE VAN DER WAALS COMPLEX.............................15 min.(4:55)

A. M. ANDREWS, K. W. HILLIG II, R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109; N. W. HOWARD, Department of Chemistry, University of Exeter, Exeter EX4 4QD, Great Britain; and A. C. LEGON, Department of Chemistry, University College London, London, WCIH OAJ, Great Britain.

RE14. MICROWAVE SPECTRA OF THE NONLINEAR NNO-H^{35}Cl COMPLEX
........................Late Paper added to Abstracts Book....................10 min.(5:12)

M. A. ROEHRIG, D. J. PAULEY, J. C. SHEA, and S. G. KUKOLICH, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

RE15. ROTATIONAL ANALYSIS OF THE EXCITED STATES OF METHYL CYANIDE AND METHYL
CYANIDE-D$_3$......................Late Paper added to Abstracts Book.............10 min.(5:24)

J. COSLEOU, J. DEMAISON, D. BOUCHER, and G. WLODARCZAK, Laboratoire de Spectroscopie Hertzienne, UA CNRS 249, Universite de Lille 1, 59655 Villeneuve d'Ascq, France.

40

THURSDAY, JUNE 14, 1990 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chair Before Intermission: L. H. COUDERT, Laboratoire de Physique Moléculaire et
Atmospherique, Université Pierre et Marie Curie, Paris, France.

Chair After Intermission: T. AMANO, Herzberg Institute of Astrophysics, National Research
Council of Canada, Ottawa, Ontario, Canada.

RF1. THE OBSERVATION OF THE ν_1 AND $\nu_1+\nu_7-\nu_7$ BANDS OF HNCCN$^+$...........................15 min.(1:30)

H. E. WARNER and T. AMANO, Herzberg Institute of Astrophysics, National
Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6,
Canada

RF2. INFRARED-MICROWAVE DOUBLE RESONANCE SPECTROSCOPY OF COLLISION-INDUCED TRANSITIONS
BETWEEN ROTATIONAL ENERGY LEVELS IN THE ISOELECTRONIC SPECIES HN$_2^+$ AND HCN.......15 min.(1:47)

C. J. PURSELL, D. P. WELIKY, T. OKA, Department of Chemistry and Department
of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois,
60637; and K. TAKAGI, Department of Physics, Toyama University, Gofuku,
Toyama 930, Japan.

RF3. OBSERVATION OF ℓ-TYPE DOUBLING TRANSITIONS IN HN$_2^+$ USING INFRARED-MICROWAVE
DOUBLE RESONANCE SPECTROSCOPY...15 min.(2:04)

D. P. WELIKY, C. J. PURSELL, T. OKA, Department of Chemistry and Department
of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois,
60637; and K. TAKAGI, Department of Physics, Toyama University, Gofuku,
Toyama 930, Japan.

RF4. MICROWAVE SPECTRUM OF SO$^+$...10 min.(2:21)

TAKAYOSHI AMANO, TAKAKO AMANO, and H. E. WARNER, Herzberg Institute of
Astrophysics, National Research Council of Canada, 100 Sussex Drive,
Ottawa, Ontario, K1A OR6, Canada.

RF5. INFRARED DIODE LASER SPECTROSCOPY OF SiF AND SiF$^+$...............................15 min.(2:33)

KEIICHI TANAKA, YASUNOBU AKIYAMA, MASAHIRO TAMURA, and TAKEHIKO TANAKA,
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki,
Higashiku, Fukuoka 812, Japan.

RF6. INFRARED DIODE LASER AND MILLIMETERWAVE SPECTRA OF THE GeF$^+$ ION..................15 min.(2:50)

KEIICHI TANAKA, YASUNOBU AKIYAMA, TAKEHIKO TANAKA, Department of Chemistry,
Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812,
Japan; CHIKASHI YAMADA, and EIZI HIROTA, Institute for Molecular Science,
Okazaki 444, Japan.

Intermission

RF7. INFRARED STUDIES OF THE ν_1 BAND OF HCCD$^+$......................................15 min.(3:20)

M. ROSSLEIN, M.-F. JAGOD, C. GABRYS, and T. OKA, Department of Chemistry
and Department of Astronomy and Astrophysics, University of Chicago,
Chicago, Illinois, 60637-1403.

RF8. QUADRATIC HERMAN-WALLIS CORRECTION FACTORS FOR SYMMETRIC-TOP MOLECULES.
APPLICATION TO THE H$_3^+$ ION...15 min.(3:37)

J.K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council
of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A OR6, Canada.

RF9. INFRARED EMISSION SPECTRA OF H$_3^+$ AND ITS ISOTOPES................................15 min.(3:54)

W. A. MAJEWSKI, A.R.W. McKELLAR, and J.K.G. WATSON, Herzberg Institute of
Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa,
Ontario, K1A OR6, Canada.

RF10. OBSERVATION OF THE 4 μm FUNDAMENTAL ν_2 BAND OF H_3^+ IN JUPITER....................15 min.(4:11)

TAKESHI OKA, Department of Chemistry and Department of Astronomy and
Astrophysics, University of Chicago, Chicago, Illinois, 60637; and
T. R. GEBALLE, Joint Astronomy Center, Hilo, Hawaii.

RF11. THE TUNNELING ROTATIONAL ENERGY LEVELS OF H_5^+....................................15 min.(4:28)

L. H. COUDERT, Laboratoire de Physique Moléculaire et Atmospherique,
Université Pierre et Marie Curie et CNRS, 75252 Paris, France.

RF12. ROTATIONAL SPECTRUM AND INTERNAL ROTATION OF THE METHANE-HCL COMPLEX
.........................Late Paper added to Abstracts Book..................10 min.(4:45)

YASUHIRO OHSHIMA and YASUKI ENDO, Department of Pure and Applied Sciences,
The College of Arts and Sciences, University of Tokyo, Meguro-ku, Tokyo 153,
Japan.

RF13. PULSED LASER-MICROWAVE DOUBLE RESONANCE STUDY OF SO_2 $\tilde{C}-\tilde{X}$ BAND
.........................Late Paper added to Abstracts Book..................10 min.(4:57)

Y. ENDO and Y. OHSHIMA, Department of Pure and Applied Sciences, College of
Arts and Sciences, University of Tokyo, Meguro-ku, Tokyo 153, Japan.

THURSDAY, JUNE 13, 1990 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chair: R. H. JUDGE, Department of Chemistry, University of Wisconsin-Parkside, Kenosha, Wisconsin.

RG1.   DEVELOPMENT OF FT SPECTROMETER FOR HIGH-RESOLUTION EMISSION SPECTRA OF UNSTABLE SPECIES...15 min.(1:30)

> SANG K. LEE, M. H. SUH, T. A. MILLER, and V. E. BONDYBEY, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

RG2.   SPECTRA OF COLD FLUOROBENZENE IONS WITH AN FT SPECTROMETER.......................15 min.(1:47)

> M. H. SUH, S. K.LEE, T. A. MILLER, and V. E. BONDYBEY, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

RG3.   INTERNAL ROTATION, LOW FREQUENCY VIBRATIONS AND THEIR INTERACTIONS IN p-FLUOROTOLUENE AND ITS $-d_3$ DERIVATIVE..15 min.(2:04)

> Z. Q. ZHAO and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

RG4.   SINGLE VIBRONIC LEVEL FLUORESCENCE SPECTRA FROM THE S_1 ($^1B_{2u}$) STATE OF DEUTERATED p-DIFLUOROBENZENE [p-DFB(d_4)] VAPOR...................................15 min.(2:21)

> F. TODD and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

RG5.   ROTATIONALLY RESOLVED FLUORESCENCE EXCITATION SPECTRA OF 1-NAPHTHALDEHYDE........15 min.(2:38)

> S. JAGANNATHAN, B. B. CHAMPAGNE, A. HELD, J. L. TOMER, and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

RG6.   HIGH RESOLUTION FLUORESCENCE EXCITATION SPECTRA OF THE 1- AND 2- AMINONAPHTHALENES...15 min.(2:55)

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

Intermission

RG7.   PHOTOACOUSTIC ABSORPTION SPECTRUM OF THE 1436 CM^{-1} BAND OF THE $^3B_{3u}$-^1A_g SYSTEM OF s-TETRAZINE...10 min.(3:30)

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

RG8.   OBSERVATION OF LARGE VIBRATIONAL ℓ-TYPE RESONANCES IN THE S_1 STATE OF BENZENE....15 min.(3:42)

> E. RIEDLE, Institut für Physikalische Chemie, TU München, D-8046 Garching, West Germany; and J. PLIVA, Department of Physics, Pennsylvania State University, University Park, Pennsylvania, 16802.

RG9.   EFFECTIVE ROTATION AND FINE-STRUCTURE HAMILTONIANS OF SYMMETRIC TOP MOLECULES IN DEGENERATE VIBRONIC STATES..15 min.(3:59)

> XIANMING LIU and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

RG10.   TRANS-STILBENE AND ITS ARGON VAN DER WAALS COMPLEXES: ROTATIONALLY RESOLVED FLUORESCENCE EXCITATION SPECTRA OF THE ONE-PHOTON $S_1 \leftarrow S_0$ OPTICAL TRANSITION.....15 min.(4:16)

> B. B. CHAMPAGNE, J. F. PFANSTIEL, D. F. PLUSQUELLIC, and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

RG11.   INFRARED EMISSION SPECTRA OF POLYCYCLIC AROMATIC HYDROCARBONS....................15 min.(4:33)

> JOE KURTZ, Code 691, Goddard Space Flight Center, Greenbelt, Maryland, 20771.

RG12. PHOTO-EXCITATION AND PHOTOLUMINESCENCE STUDY OF COORDINATION COMPLEXES OF LEAD
DIIODIDE WITH PYRIDINE...................Arrived Late...........................15 min.(4:50)

L. C. YU and A. H. FRANCIS, Department of Chemistry, University of
Michigan, Ann Arbor, Michigan, 48109.

RG13. THE STRUCTURE AND PHOTOPHYSICS OF CLUSTERS OF IMMISCIBLE LIQUIDS:
C_6H_6-$(H_2O)n$..................Late Paper added to Abstracts Book...............15 min.(5:07)

ALBERT J. GOTCH, AARON W. GARRETT, RALPH E. BANDY, and TIMOTHY S. ZWIER,
Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907.

THE OHIO STATE UNIVERSITY

MOLECULAR SPECTROSCOPY SYMPOSIA -- 1992 AND BEYOND

The College of Mathematical and Physical Sciences through its Dean,
and the Physics and Chemistry Departments through their respective Chairs,
have expressed their strong support for the continuation of this annual
conference. Please note on your calendars the dates for the 47th through the
50th of these symposia and make them a success by participating actively in
all of them.

47th Symposium	June 15-19, 1992
48th Symposium	June 14-19, 1993
49th Symposium	June 13-17, 1994
50th Symposium	June 12-16, 1995

The organization of these future meetings will be coordinated by a local
Executive Committee with the support of Advisory Committees with substantial
international representation. Further details will be forthcoming.

THURSDAY, JUNE 14, 1990 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chair Before Intermission: ERNEST A. DORKO, Weapons Laboratory, Kirtland Air Force Base, New Mexico.

Chair After Intermission: DAVID S. PERRY, Department of Chemistry, University of Akron, Akron, Ohio.

RH1. PICOSECOND TRANSIENT RAMAN INVESTIGATION OF THE ROLE OF VIBRATIONAL ENERGY IN THE ULTRAFAST PHOTODISSOCIATION OF CHROMIUM HEXACARBONYL IN SOLUTION.............15 min.(1:30)

SOO-CHANG YU, XIAOBING XU, R. L. LINGLE, JR., and J. B. HOPKINS, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70803.

RH2. ACETIC ACID DECOMPOSITION DYNAMICS FOLLOWING $^1(n,\pi^*)$EXCITATION...................15 min.(1:47)

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

RH3. ROTATIONALLY-MEDIATED IVR IN JET-COOLED TRANS-ETHANOL AT 2990 CM^{-1}...............15 min.(2:04)

JUNGSUG GO, 1-402 Dongjin-Mansion, Sansu-2-Dong, Kwangju-jikhalsi, South Korea 501-092; G. A. BETHARDY, and DAVID S. PERRY, Department of Chemistry, University of Akron, Akron, Ohio, 44325-3601.

RH4. PULSED LASER HEATING AND SPECTROSCOPIC STUDIES OF ORGANIC AMORPHOUS/GLASSY SYSTEMS I. EXPERIMENTS WITH ANTHRACENE......................................15 min.(2:21)

DANIEL J. GRAHAM and DWAYNE L. LABRAKE, Department of Chemistry, Loyola University of Chicago, Chicago, Illinois, 60626.

RH5. PULSED LASER HEATING AND SPECTROSCOPIC STUDIES OF ORGANIC AMORPHOUS/GLASSY SYSTEMS II. EXPERIMENTS WITH BENZOPHENONE....................................15 min.(2:38)

DANIEL J. GRAHAM and DWAYNE L. LABRAKE, Department of Chemistry, Loyola University of Chicago, Chicago, Illinois, 60626.

RH6. PICOSECOND RAMAN INVESTIGATION OF ELECTRONIC CURVE CROSSING IN SOLUTION..........15 min.(2:55)

HUIPING ZHU, XIAOBING XU, SOO-CHANG YU, ROBERT LINGLE, JR., and J. B. HOPKINS, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70803.

RH7. A "KEYHOLE" MODEL OF IVR TO ACCOUNT FOR THE CONTRASTING EIGENSTATE-RESOLVED INFRARED SPECTRA OF 1-BUTYNE AND ETHANOL.....................................10 min.(3:12)

DAVID S. PERRY, Department of Chemistry, University of Akron, Akron, Ohio, 44325-3601.

Intermission

RH8. DIRECT OBSERVATION OF TIME DEPENDENT IVR IN THE EXCITED ELECTRONIC STATE $^1B_2$ OF ALKYLANILINE MOLECULES..15 min.(3:35)

XINBEI SONG, CHARLES W. WILKERSON, JOHN P. LUCIA, STEVE W. PAULS, and JAMES P. REILLY Department of Chemistry, University of Indiana, Bloomington, Indiana, 47405.

RH9. DETERMINATION OF RATE CONSTANTS FOR $^1DO2$ ELECTRONIC QUENCHING IN A FLOW TUBE REACTOR...15 min.(3:52)

ROBERT R. CRANNAGE, DANIEL E. JOHNSON, and ERNEST A. DORKO, WL/ARDJ, Weapons Laboratory, Kirtland Air Force Base, New Mexico, 87117-6008.

RH10. VISIBLE/ULTRAVIOLET SPECTROSCOPY OF VIBRATION-VIBRATION (V-V) PUMPED CARBON
MONOXIDE EXCITED BY A Q-SWITCHED CO LASER....................................15 min.(4:09)

J. W. RICH, V. SUBRAMANIAM, K. MEISTER, D. STRAUB, Department of
Mechanical Engineering, The Ohio State University, Columbus, Ohio,
43210; J. P. MARTIN, and M. Y. PERRIN, Laboratoire E.M2.C.,
UPR 288 CNRS at Ecole Centrale Paris, 92295 Chatenay-Malabry, France.

RH11. SPECTROSCOPIC STUDIES OF ELECTRONIC ENERGY TRANSFER BETWEEN TRIPLET STATE N_2
AND ARGON..15 min.(4:26)

DANIEL J. GRAHAM and SCOTT M. HURST, Department of Chemistry, Loyola
University of Chicago, Chicago, Illinois, 60626.

RH12. DIRECT MEASUREMENT OF GEMINATE RECOMBINATION AND VIBRATIONAL RELAXATION IN I_2
USING PICOSECOND RAMAN SPECTROSCOPY...15 min.(4:43)

XIAOBING XU, SOO-CHANG YU, ROBERT LINGLE, JR., and J. B. HOPKINS,
Department of Chemistry, Louisiana State University, Baton Rouge,
Louisiana, 70803.

RH13. INFRARED-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF HIGH VIBRATIONAL OVERTONES
OF H_2O_2..15 min.(5:00)

X. LUO and T. R. RIZZO, Department of Chemistry, University of Rochester,
Rochester, New York, 14627.

FRIDAY, JUNE 15, 1990 — 8:30 A.M.

Room 1153, Physics Laboratory

Chair: A. M. SMITH, Institut für Physikalische und Theoretische Chemie, Technische Universität Munchen, Garching. West Germany.

FA1. SLIT JET INFRARED STUDIES OF HCl-DCl AND DCl-HCl ISOTOPOMERS.....................15 min.(8:30)

MICHAEL D. SCHUDER, CHRISTOPHER M. LOVEJOY, DAVID J. NESBITT, Joint Institute for Laboratory Astrophysics, University of Colorado, and National Institute of Standards and Technology, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309-0440; and DAVID D. NELSON, Aerodyne Research Inc., 45 Manning Road, The Research Center at Manning Park, Billerica, Massachusetts, 01821-4918.

FA2. HIGH RESOLUTION INFRARED SPECTRUM OF $(HCl)_2$ - HCl STRETCH FUNDAMENTAL AND COMBINATION BAND ANALYSIS..15 min.(8:47)

MICHAEL D. SCHUDER, CHRISTOPHER M. LOVEJOY, ROBERT LASCOLA, and DAVID J. NESBITT, Joint Institute for Laboratory Astrophysics, University of Colorado, and National Institute of Standards and Technology, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309-0440.

FA3. MICROWAVE AND TUNABLE FAR-INFRARED LASER SPECTROSCOPY OF N_2-H_2O.................15 min.(9:04)

R. E. BUMGARNER, JANET BOWEN, PETER G. GREEN, and GEOFFREY A. BLAKE, Division of Geological and Planetary Sciences 170-25, California Institute of Technology, Pasadena, California, 91125.

FA4. TUNABLE FAR-INFRARED LASER SPECTROSCOPY OF WATER-CO...........................15 min.(9:21)

R. E. BUMGARNER, P. G. GREEN, and G. A. BLAKE, Division of Geological and Planetary Sciences 170-25, California Institute of Technology, Pasadena, California, 91125.

FA5. RESONANCE RAMAN SCATTERING OF CH_3I IN A SUPERSONIC JET.........................15 min.(9:38)

Y. P. ZHANG, P. G. WANG, and L. D. ZIEGLER, Department of Chemistry, Northeastern University, Boston, Massachusetts, 02115.

FA6. DYNAMICS OF METHYL IODIDE B-STATE PHOTODISSOCIATION PROBED WITH RESONANCE RAMAN SCATTERING...15 min.(9:55)

P. G. WANG and L. D. ZIEGLER, Department of Chemistry, Northeastern University, Boston, Massachusetts, 02115.

FA7. TUNABLE FAR INFRARED LASER SPECTROSCOPY OF ULTRACOLD FREE RADICALS...............15 min.(10:12)

R. C. COHEN, C. A. SCHMUTTENMAER, K. L. BUSAROW, Y. T. LEE, and R. J. SAYKALLY, Department of Chemistry, University of California and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California, 94720.

Intermission

FA8. MEASUREMENT OF THE HYPERFINE STRUCTURE OF $(DCCD)_2$ DIMER........................15 min.(10:45)

L. H. COUDERT, Laboratoire de Physique Moléculaire et Atmospherique, Université Pierre et Marie Curie et CNRS, 75252 Paris, France; RATAN BHATTACHARJEE, and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

FA9. AN EFFICIENT APPROXIMATE METHOD FOR CALCULATING PRESSURE SHIFTING COEFFICIENTS
....Arrived Late.................................10 min.(11:02)

CLAUDIO CHUAQUI and ROBERT J. LE ROY, Guelph-Waterloo Centre for Graduate
Work in Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1,
Canada.

FA10. PREDICTING THE IR SPECTRA OF ATOM-MOLECULE VAN DER WAALS COMPLEXES:
HELIUM-ACETYLENE...................Arrived Late.................................10 min.(11:14)

TOM SLEE and ROBERT J. LE ROY, Guelph-Waterloo Centre for Graduate Work
in Chemistry, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada.

FA11. SOLUTE FREQUENCY SHIFTS AS A PROBE OF STRUCTURE AND DYNAMICS IN HETEROGENEOUS
VAN DER WAALS CLUSTERS............Arrived Late.................................10 min.(11:26)

DARRYL J. CHARTRAND, MARY ANN KMETIC, and ROBERT J. LE ROY, Guelph-Waterloo
Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo,
Ontario, N2L 3G1, Canada.

FA12. LINE STRENGTHS AND LINE MIXING IN THE 791 CM^{-1} Q BRANCH OF CO_2...Arrived Late....10 min.(11:38)

L. STROW and S. HANNON, Department of Physics, University of Maryland,
Baltimore, Maryland, 21228.

FA13. TEMPERATURE DEPENDENCE OF SELF-BROADENED LINE MIXING IN A CO_2 Q BRANCH
......................................Arrived Late.................................10 min.(11:50)

L. STROW and L. ZHENG, Department of Physics, University of Maryland,
Baltimore, Maryland, 21228.

FA14. LINE MIXING IN A CO_2 Q BRANCH BROADENED BY Ar AND He...........Arrived Late......10 min.(12:02)

L. STROW, Department of Physics, University of Maryland, Baltimore,
Maryland, 21228; and S. GREEN, NASA Goddard Space Flight Center,
Institute for Space Studies, New York, New York, 10025.

FRIDAY, JUNE 15, 1990 -- 8:30 A.M.

Room 1009, Physics Laboratory   <u>ACETYLENE SEMINAR</u>

Chair: W. F. MURPHY, Division of Chemistry, National Research Council of Canada,
          Ottawa, Ontario, Canada.

FB1.   VISIBLE OVERTONE SPECTROSCOPY OF ACETYLENE: WHERE DOES ITS OVERTONE INTENSITY
       COME FROM?..........................Invited Paper..........................20 min.(8:30)

          <u>K. K. LEHMANN</u>, Department of Chemistry, Princeton University, Princeton,
          New Jersey, 08544.

FB2.   LASER INDUCED FLUORESCENCE AND ZEEMAN QUANTUM BEAT SPECTROSCOPY OF
       ELECTRONICALLY EXCITED ACETYLENE AND ITS D-SUBSTITUENTS IN SUPERSONIC JETS.......15 min.(8:55)

          N. OCHI, N. IKEDA, and <u>S. TSUCHIYA</u>, Department of Pure and Applied
          Sciences, University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan.

FB3.   WHAT DO HIGH TEMPERATURE KINETIC MEASUREMENTS OF ACETYLENE PYROLYSIS TELL US
       ABOUT THE HEAT OF FORMATION OF C_2H?...10 min.(9:12)

          <u>R. D. KERN</u>, K. XIE, Department of Chemistry, University of New Orleans,
          New Orleans, Louisiana, 70148; and J. H. KIEFER, Department of Chemical
          Engineering, University of Illinois at Chicago, Chicago, Illinois, 60680.

FB4.   PREDISSOCIATION MECHANISM OF ACETYLENE $\tilde{X}^1A_u$ STATE................................15 min.(9:24)

          <u>M. FUJII</u>, A. HAIJIMA, and M. ITO, Department of Chemistry, Faculty of
          Science, Tohoku University, Sendai 980, Japan.

FB5.   PHOTODISSOCIATION OF ACETYLENE IN THE 201-216 nm REGION: DETERMINATION OF
       D_0(HCC-H)...15 min.(9:41)

          <u>D. P. BALDWIN</u>, D. W. CHANDLER, Combustion Research Facility, Sandia
          National Laboratories, Division 8353, Livermore, California, 94551;
          and M. A. BUNTINE, Department of Chemistry, Stanford University,
          Stanford, California, 94305.

FB6.   THE $\tilde{A} - \tilde{X}$ BAND SYSTEM IN C_2HD...10 min.(9:58)

          <u>J. VANDER AUWERA</u>, T. R. HUET, M. A. TANSAMANI, and M. HERMAN, Laboratoire
          de Chimie Physique Moléculaire, Université Libre de Bruxelles CP.160,
          1050 Bruxelles, Belgium.

<center>Intermission</center>

FB7.   CORRELATION FUNCTION AND SEMICLASSICAL SPECTRAL METHOD DIAGNOSIS FOR THE
       ONSET OF CLASSICAL CHAOS IN ACETYLENE...15 min.(10:25)

          <u>YOUNG JUNE CHO</u>, HAROLD H. HARRIS, Department of Chemistry, University of
          Missouri-St. Louis, Missouri, 63121; FREDERICK G. HAIBACH,
          and JOHN E. ADAMS, Department of Chemistry, University of Missouri-
          Columbia, Columbia, Missouri, 65211.

FB8.   PHOTODISSOCIATION PROCESSES OF ACETYLENE VIA TWO-PHOTON RESONANT STATES
       .... Late Paper added to Abstracts Book....................15 min.(10:42)

          M.-S. LIN, CHAO-PING HSU, ING-FANG LEE, and <u>YEN-CHU HSU</u>, Institute of
          Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, Republic
          of China, and Department of Chemistry, National Taiwan University, Taipei,
          Taiwan, Republic of China.

FB9. VUV PHOTOEXCITATION OF ACETYLENE
.............Invited Paper..........Late Paper added to Abstracts Book......15 min.(10:59)

C. Y. ROBERT WU and D. L. JUDGE, Department of Physics and Space Sciences Center, University of Southern California, Los Angeles, California, 90089-1341.

FB10. APPLICATIONS OF NEGATIVE ION SPECTROSCOPY TO DETERMINATIONS OF ELECTRON AFFINITIES AND BOND DISSOCIATION ENERGIES........Invited Paper....
.....................Late Paper added to Abstracts Book.................20 min.(11:16)

W. C. LINEBERGER and K. M. ERVIN, Department of Chemistry and Biochemistry, University of Colorado, and Joint Institute for Laboratory Astrophysics, Boulder, Colorado, 80309-0440.

FB11. ANOMALOUS BEHAVIOUR OF THE ANTICROSSING DENSITY AS A FUNCTION OF EXCITATION ENERGY IN THE C_2H_2 MOLECULE.............Late Paper added to Abstracts Book.....15 min.(11:38)

P. DUPRE, M. LOMBARDI. R. JOST, Service National des Champs Intenses, CNRS, 38042 Grenoble, France; P. G. GREEN, Mail Stop 170-25, California Institute of Technology, Pasadena, California, 91125; and R. W. FIELD, Department of Chemistry, MIT, Cambridge, Massachusetts, 02139.

FB12. DOUBLE RESONANCE SPECTROSCOPY OF ACETYLENE: VIBRATIONAL STATE MIXING AND A-STATE VIBRATIONAL FREQUENCIES........ Invited Paper..........
.....................Late Paper added to Abstracts Book.................15 min.(11:55)

A. L. UTZ, J. D. TOBIASON, and F. F. CRIM, Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, 53706.

50

Room 1005, Physics Laboratory

Chair: JODYE SELCO, Department of Chemistry, University of Redlands,
Redlands, California.

FC1.   HIGH RESOLUTION ELECTRONIC SPECTRA OF JET-COOLED CYCLOPENTADIENYL RADICAL:
OBSERVATION OF JAHN-TELLER INDUCED TRANSITIONS..................................15 min.(8:30)

JAMES M. WILLIAMSON, LIAN YU, and TERRY A. MILLER, Laser Spectroscopy
Facility, Department of Chemistry, The Ohio State University, Columbus,
Ohio, 43210.

FC2.   ROTATIONAL-TORSIONAL ANALYSIS OF ELECTRONIC SPECTRA OF JET-COOLED METHYL
CYCLOPENTADIENYL RADICAL ($CH_3-C_5H_4$ AND $CD_3-C_5H_4$).................................15 min.(8:47)

LIAN YU, JAMES M. WILLIAMSON, DAVID W. CULLIN, and TERRY A. MILLER,
Laser Spectroscopy Facility, Department of Chemistry, The Ohio State
University, Columbus, Ohio, 43210.

FC3.   OBSERVATION OF THE SPLITTING OF THE VIBRONIC DEGENERACY UPON ASYMMETRIC
DEUTERATION OF CYCLOPENTADIENYL RADICALS..15 min.(9:04)

LIAN YU, DAVID W. CULLIN, JAMES M. WILLIAMSON, and TERRY A. MILLER,
Laser Spectroscopy Facility, Department of Chemistry, The Ohio State
University, Columbus, Ohio, 43210.

FC4.   ROTATIONAL ENERGY DISBRIBUTIONS IN p-DIFLUOROBENZENE (pDFB) PRODUCED BY
VIBRATIONAL PREDISSOCIATION OF pDFB-Ar VAN DER WAALS COMPLEXES..................10 min.(9:21)

H. J. ELSTON, C. S. PARMENTER, Department of Chemistry, Indiana
University, Bloomington, Indiana, 47405; K. W. BUTZ, Department of
Chemistry, Griffith University, Nathan, QLD 4111, Australia; and
M.-C. SU, Department of Chemistry, Butler University, Indianapolis,
Indiana, 46208.

FC5.   VIBRATIONAL PREDISSOCIATION OF THE p-DIFLUOROBENZENE-N_2 VAN DER WAALS COMPLEX....15 min.(9:33)

B. D. GILBERT, C. S. PARMENTER, Department of Chemistry, Indiana
University, Bloomington, Indiana, 47405; K. W. BUTZ, Department of
Chemistry, Griffith University, Nathan, QLD 4111, Australia; and
M.-C. SU, Department of Chemistry, Butler University, Indianapolis,
Indiana, 46208.

FC6.   SELENOFORMALDEHYDE: A ROTATIONAL ANALYSIS OF THE $\tilde{A}^1A_2 - \tilde{X}^1A_1$ 735 nm BAND
SYSTEM OF $H_2C^{78}Se$, $H_2C^{80}Se$ AND $D_2C^{80}Se$ FROM HIGH RESOLUTION LASER
FLUORESCENCE EXCITATION SPECTRA..10 min.(9:50)

DENNIS J. CLOUTHIER, DUK-LAI JOO, Department of Chemistry, University
of Kentucky, Lexington, Kentucky, 40506-0055; R. H. JUDGE, Department
of Chemistry, University of Wisconsin-Parkside, Kenosha, Wisconsin,
53141-2000; and D. C. MOULE, Department of Chemistry, Brock University,
St. Catharines, Ontario L2S 3A1, Canada.

Intermission

FC7.   RESONANCE ENHANCED MULTIPHOTON IONIZATION SPECTRA OF CF_2Cl AND $CFCl_2$ RADICALS....15 min.(10:20)

JEFFREY W. HUDGENS, RUSSELL D. JOHNSON III, Chemical Kinetics Division,
Center for Chemical Technology, National Institute of Standards and
Technology, Gaithersburg, Maryland, 20899; and BILIN P. TSAI, Department
of Chemistry, University of Minnesota at Duluth, Duluth, Minnesota, 55812.

FC8.   THE METHYL TORSION MODES OF S_0 THIOACETONE FROM BULB AND SUPERSONIC JET LASER
EXCITATION SPECTROSCOPY...15 min.(10:37)

Y. G. SMEYERS, M. SENENT, Instituto de Material Science, c/Serrano,
119, 28006 Madrid, Spain; D. C. MOULE, Department of Chemistry, Brock
University, St. Catharines, Ontario L2S 3A1, Canada; R. H. JUDGE,
Department of Chemistry, University of Wisconsin-Parkside, Kenosha,
Wisconsin, 53141; D. J. CLOUTHIER, and J. KAROLCZAK, Department of
Chemistry, University of Kentucky, Lexington, Kentucky, 40506-0055.

FC9. ROTATIONALLY RESOLVED LASER INDUCED FLUORESCENCE SPECTROSCOPY OF JET-COOLED
SUBSTITUTED CYCLOPENTADIENYL RADICALS..15 min.(10:54)

DAVID W. CULLIN, LIAN YU, JAMES M. WILLIAMSON, and TERRY A. MILLER,
Laser Spectroscopy Facility, Department of Chemistry, The Ohio State
University, Columbus, Ohio, 43210.

FC10. A REINVESTIGATION OF THE JET-COOLED PHENYL NITRENE SPECTRUM.....................15 min.(11:11)

DAVID W. CULLIN, LIAN YU, JAMES M. WILLIAMSON, and TERRY A. MILLER,
Laser Spectroscopy Facility, Department of Chemistry, The Ohio State
University, Columbus, Ohio, 43210.

FC11. THE ELECTRONIC SPECTRUM OF THE CCl_3 RADICAL...................................15 min.(11:28)

JEFFREY W. HUDGENS, RUSSELL D. JOHNSON III, Chemical Kinetics Division,
Center for Chemical Technology, National Institute of Standards and
Technology, Gaithersburg, Maryland, 20899; BILIN P. TSAI, Department of
Chemistry, University of Minnesota at Duluth, Duluth, Minnesota, 55812;
and S. KAFAFI, Department of Environmental Chemistry and Biology, Johns
Hopkins University School of Hygiene and Public Health, Baltimore,
Maryland, 21205.

FC12. MICROWAVE-UV DOUBLE RESONANCE SPECTROSCOPY OF ND_3..............................15 min.(11:45)

S. A. HENCK, M. A. MASON, and K. K. LEHMANN, Department of Chemistry,
Princeton University, Princeton, New Jersey, 08544.

FC13. VIBRATIONAL STRUCTURE AND DYNAMICS OF p-CRESOL DIMER FROM THE EXCITATION SPECTRUM
.........................Late Paper added to Abstracts Book...................10 min.(12:02)

SHUXIN YAN and LEE H. SPANGLER, Department of Chemistry,
University, Bozeman, Montana, 59717.

FC14. SPECTRAL EVIDENCE FOR THROUGH THE RING COUPLING OF THE NITROGEN INVERSION
AND METHYL TORSION IN p-METHYLANILINE.....Late Paper added to Abstracts Book.....10 min.(12:12)

SHUXIN YAN, STEVEN G. MAYER, and LEE H. SPANGLER, Department of Chemistry,
Montana State University, Bozeman, Montana, 59717.

MA1. CLUSTERS: SPECTROSCOPY BY DISSOCIATION.........................35 min.

> JAMES M. LISY, School of Chemical Sciences, University of
> Illinois at Urbana-Champaign, Urbana, Illinois, 61801.

MA2. LARGE-AMPLITUDE MOTIONS IN WEAKLY BOUND COMPLEXES.................35 min.

> GERALD T. FRASER, Molecular Physics Division, National
> Institute of Standards and Technology, Gaithersburg,
> Maryland, 20899.

MA3. SLIT JET INFRARED SPECTROSCOPY: PROBING THE INTERNAL
DYNAMICS OF WEAKLY BONDED MOLECULAR COMPLEXES....................35 min.

> CHRISTOPHER M. LOVEJOY, Quantum Physics Division, National
> Institute of Standards and Technology, Boulder, Colorado,
> 80309-0440.

Intermission

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

MA4. LASER SPECTROSCOPY OF EXOTIC CHEMICAL SPECIES: TRANSIENT,
WEAKLY BOUND, REACTIVE, AND SURFACE ADSORBED MOLECULES...........35 min.

> HAI-LUNG DAI, Department of Chemistry, University of
> Pennsylvania, Philadelphia, Pennsylvania, 19104-6323.

MA4 (11:10)

LASER SPECTROSCOPY OF EXOTIC CHEMICAL SPECIES: TRANSIENT, WEAKLY BOUND, REACTIVE, AND SURFACE ADSORBED MOLECULES

HAI-LUNG DAI

Using laser spectroscopic techniques such as Stimulated Emission Spectroscopy and Stark Level Crossing Spectroscopy, in combination with molecular beam techniques, we can now study vibrational levels from 0 to 10^4 cm^{-1} with sub-Doppler resolution and single rotational level selectivity, for molecules with concentrations as low as 10^{-4} Torr. Low frequency intermolecular vibrational levels in a weakly bound complex can be directly observed for the elucidation of intermolecular forces. Short-lived radicals can be studied at high vibrational excitation. The reaction of a molecule with vibrational energy higher than dissociation barrier can be examined with single quantum state resolution. Furthermore, application of nonlinear optical techniques such as second harmonic generation allows us to probe the spectroscopy, structure, and energy transfer dynamics of the surface layer of atoms and molecules adsorbed on surfaces.

Address: Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

ME1 (1:30)

SLOWING OF IVR WITH THE HEAVY ATOM EFFECT: TRIMETHYL SUBSTITUTED ACETYLENES

K.K. Lehmann, T. Mentel, B.H. Pate, and G. Scoles

Spectra of $(CH_3)_3X-C\equiv C-H$ are being studied in the region of the acetylenic stretching fundamental using the technique of optothermal detection of the absorption spectrum of a collimated molecular beam, using an F-center laser for excitation. Species with $X = C$ and Si have already been studied. The t-butyl compound shows Lorentzian lineshapes with a full width of ~ 700 MHz, indicating that excitation in the C-H oscillator decays exponentially with a time constant of 500 psec. Substitution of Si for the C substantially raises the density of states. The spectrum, however, shows narrower lines that are partially structured. This structure is at least partially due to unresolved K and internal rotation splittings We presently attribute the reduced rate in intramolecular relaxation to the heavier mass of Si which reduces kinetic coupling of modes that involve Si motion. In order to test this conjecture we plan to take the spectrum of the X=Sn compound in the near future.

Address of Lehmann, Mentel, Pate and Scoles: Department of Chemistry, Princeton University, Princeton, NJ 08544

ME2 (1:47)

THE FUNDAMENTAL AND FIRST OVERTONE OF THE $CF_3C\equiv CH$ ACETYLENIC STRETCH

E. Kerstel, K.K. Lehmann, T. Mentel, B.H. Pate, G. Scoles

We have taken spectra of $CF_3C\equiv CH$ in the 3 and 1.5 micron region using a optothermal detection of the absorption of a collimated molecular beam using color center lasers for excitation. We achieve resolution of 10 MHz in the fundamental and 20 MHz in the overtone region. Because of the much greater laser intensity at 1.5 microns we obtain comparable sensitivities in each region. The fundamental spectrum shows a single bright state perturbed primarily by an anharmonic resonance with one dark state. The dark state, however, appears itself to be perturbed by a much stronger Coriolis resonance for the K=2 states. Numerous smaller perturbations have not yet been assigned. Unperturbed subbands have been fit with a standard deviation of about 1 MHz.

The overtone region shows a highly perturbed spectrum with sharp structure riding on a broader pedestal. The sharp structure is instrument limited at 20 MHz while the pedestal has a FWHM of about 600 MHz.

Address of Kerstel, Lehmann, Mentel, Pate and Scoles: Department of Chemistry, Princeton University, Princeton, NJ 08544

ME3 (2:04)

VIBRATIONAL PREDISSOCATION STUDIES OF $Cs(NH_3)_N^+$ CLUSTER IONS

Jeffrey A. Draves, and James M. Lisy

The combination of a thermionic emitter and a cw nozzle in a molecular beam apparatus has made possible the production of large, solvated alkali ion clusters. We have produced clusters of the form $M(SOL)^+_N$ where M is Na, K, Rb, or Cs and SOL can be methanol, ammonia, ethanol, water, ethylene etc. in the size range of N=1 to 50.

Recently we have produced clusters of $Cs(NH_3)_N^+$ for N=1 to 45. Vibrational predissociation spectra of mass selected $Cs(NH_3)_N^+$ have been observed in the 9.6 μ and 10.6 μ regions for the clusters of size N > 9. The Evaporative Ensemble/RRK analysis of these clusters indicates that the initial energy content for clusters of size N<10 is insufficient to cause dissociation on the time scale of our experiment. The dissociaiton dynamics and solvent shell structures will be discussed.

Address of Draves and Lisy: School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Mathews Ave., Urbana, IL 61801.

ME4 (2:21)

VIBRATIONAL PREDISSOCIATION SPECTROSCOPY
OF $(CD_3OD)_2$ IN THE 10.6μ REGION

Jeffrey P. LaCosse and James M. Lisy

Vibrational predissociation spectra of the d_4 isotopomer of methanol dimer has been recorded in the 10.6μ region. Using the beam depletion method, we have observed a vibrational transition at 974.6 cm^{-1} for $(CD_3OD)_2$ with a Lorentzian linewidth of 2.7 cm^{-1}. This transition is red shifted from the corresponding monomer by ~ 9 cm^{-1}, which was also observed for the corresponding proton or deuteron acceptor peaks for $(CH_3OH)_2$ and $(CH_3OD)_2$. Spectra of the $(CD_3OD)(CH_3OD)$ dimer will also be discussed.

Address of LaCosse and Lisy: School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Mathews Ave., Urbana, IL 61801.

ME5 (2:38)

VIBRATIONAL PREDISSOCATION STUDIES OF $Cs(ACTEONE)_N{}^+$ CLUSTER IONS
Thomas J. Selegue, and James M. Lisy

We recently reported the production of solvated alkali ions in the gas phase. Using our thermionic emitter as a source of alkali ions coupled with a continuous supersonic beam expansion, we have produced acetone solvated cesium ions of the form $Cs((CH_3)_2CO)_N{}^+$ ($N=1$ to 14) and $Cs((CD_3)_2CO)_M{}^+$ ($M=1$ to 11).

Using the molecular beam depletion method, we are able to monitor vibrational predissociation of mass selected clusters in the CO_2 laser region as a function of cluster size. We have observed substantial red shifts in absorptions of the larger $Cs((CD_3)_2CO)_M{}^+$ clusters in the 9.6 micron region relative to absorptions in pure gaseous $(CD_3)_2CO$.

Variation in the spectra as a function of cluster size will be discussed.

Address of Selegue and Lisy: School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Mathews Ave., Urbana, IL 61801.

ME6 (2:55)

EXPERIMENTS ON THE ON-SET OF MULTIPHOTON TRANSITIONS OF SF_6 WITH HIGH RESOLUTION

S. TE LINTEL HEKKERT, A. LINSKENS and J. REUSS

A molecular beam is crossed by a cw CO_2 laser tunable over 600 MHz. Excitation is observed by opto-thermal detection. One and two-photon transitions are observed. Conditions are varied such that rapid adiabatic passage phenomena (leading to inverted population) change to conventional power-broadened spectra. For still higher laser power five-photon transitions are found to limit this excitation process energetically. This limitation is attributed to the narrow-banded rapid-adiabatic-passage process occurring.

Address of te Lintel Hekkert, Linskens and Reuss: Molecular and Laser Physics, Faculty of Sciences, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Intermission

ME7 (3:30)

HIGH RESOLUTION VIBRATIONAL SPECTROSCOPY ON HOMOGENEOUS COMPLEXES OF BENZENE AND DEUTERATED BENZENES

B. F. HENSON, G. V. HARTLAND, V. A. VENTURO, R. A. HERTZ, AND P. M. FELKER

This work presents preliminary data on the application of Fourier Transform Ionization Detected Stimulated Raman Spectroscopy (FTIDSRS) to the ground state vibrational structure of benzene and deuterated benzene homogeneous complexes.

The benzene totally symmetric vibrational mode at 993 cm^{-1} is used to probe, at high resolution, vibrational shifts and splittings as a function of complexation for the benzene dimer, trimer and mixed complexes of d$_1$ and d$_6$ benzene. The pure dimer complex exhibits three lines in this region, with some indication that strikingly different temporal dynamics may obtain for two of the three features.

The pump-probe nature of the IDSRS scheme has been utilized to set lower limits on the lifetimes of these complexes.[1] In these experiments the complexes are not probed until approximately 10 nsec. after vibrational excitation via the stimulated Raman step. Thus, only those complexes whose lifetime exceeds this 10 nsec. delay can give rise to signal. We have used this fact to asses a 10 nsec. lower bound on the lifetime of the pure benzene dimer and trimer, a limit that is in sharp contrast to other measurements made on different fundamental bands in this energy region.[2]

[1] B. F. Henson, G.V. Hartland, V. A. Venturo, and P. M. Felker, J. Chem. Phys. **91**, 2751, (1989)

[2] R. D. Johnson, S. Burdenski, M. A. Hoffbauer, C. F. Giese, and W. R. Gentry, J. Chem. Phys. **84**, 2624, (1986)

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

ME8 (3:47)

FOURIER - TRANSFORM IONIZATION DETECTED STIMULATED RAMAN SPECTROSCOPY STUDIES OF HETEROGENEOUS COMPLEXES OF PHENOL AND BENZENE

G. V. HARTLAND, B. F. HENSON, V. A. VENTURO, R. A. HERTZ, AND P. M. FELKER.

Fourier transform ionization detected stimulated Raman spectroscopy (FT-IDSRS) is a powerful technique for obtaining high resolution Raman spectra of species in molecular beams. We have used this technique to study a wide variety of complexes of phenol (i.e. phenol-Ar, -N$_2$, -CH$_4$, -H$_2$O, -NH$_3$, -benzene) and benzene (i.e. benzene-Ar, -N$_2$, -CH$_4$, -CO$_2$).

One of the principle advantages of FT-IDSRS over conventional frequency domain techniques is that absolute line positions can be routinely measured with high precision. This feature of FT-IDSRS has been used to obtain accurate values for the shifts of the fundamental vibrational frequencies of phenol and benzene that occur upon complexation. In this talk we will present a short explanation of FT-IDSRS and a summary of the experimental results that we have obtained so far. The observed shifts of the vibrational frequencies are related to the strength and type of intermolecular interaction in the complex.

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

ME9 (4:04)

Rotational Analysis of the UV Spectrum of Benzene-Diatomic van der Waals Complexes

A.M. Smith, Th. Weber, E. Riedle, H.J. Neusser, and E.W. Schlag

$C_6H_6 \cdot X_2$ dimers represent the simplest aromatic complexes for which the anisotropy of the solute molecule may be important. In principle, the rotational dynamics of such a complex may be that of a rigid asymmetric top or a rigid symmetric top, with or without free or hindered internal rotation. The most unambigous means of distiniguishing these possiblities is through a rotationally resolved spectra. We have obtained rotationally resolved spectra of the 6_0^1 and $6_0^1 1_0^1$ bands of the $S_1 \leftarrow S_0$ transition of $C_6H_6 \cdot N_2$. The cluster is formed in a pulsed supersonic expansion, rovibronically excited by an extremely narrow bandwidth ($\Delta\nu = 100$ MHz) pulsed-amplified and doubled cw ring dye laser, ionized by a second (delayed) pulsed doubled dye laser, and mass-selectively detected by time-of-flight means. The rotationally resolved spectrum is obtained by scanning the high resolution laser over the vibronic bands.

For $C_6H_6 \cdot N_2$, 70% of the observed rotational structure is unambiguously modelled as a rigid symmetric top with first order Coriolis coupling as for the corresponding vibronic bands of the monomer. This clearly limits the possible structures to T-shaped, with or without internal rotation, or a parallel arrangement with nearly free internal rotation. The remaining set of interwoven lines (30% of total) can be most plausibly explained as an additional set of $\Delta m=0$ transitions [a] arising from nearly free internal rotation about the benzene C_6 axis, corroborating the parallel arranged structure supported by both chemical intuition and theoretical calculations. Given this structure and the fitted B rotational constants, we can derive the distance of the N_2 rotor from the benzene ring and establish that this distance substantially *decreases* in the excited electronic state, as expected by the benzene ring expansion and increased polarizability accompanying electronic excitation.

[a] m is the free internal rotation quantum number

Address: Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstraße 4, D-8046 Garching, West Germany

ME10 (4:21)

Rotationally Resolved Spectra of Benzene-Noble Gas Complexes

Th. Weber, A.M. Smith, E. Riedle and H.J. Neusser

Extremely narrow bandwidth pulsed tunable UV laser ($\Delta\nu = 100$ MHz) excitation combined with the sensitive technique of mass selected two-photon ionization was used to obtain rotationally resolved UV spectra of benzene-X clusters, where X= Ar [a], Ne, or Kr. The 6_0^1 and $6_0^1 1_0^1$ vibronic bands in the $S_1 \leftarrow S_0$ transition of each of $C_6H_6 \cdot Ar$, $C_6D_6 \cdot Ar$, $C_6H_6 \cdot {}^{20}Ne$, $C_6H_6 \cdot {}^{22}Ne$, $C_6H_6 \cdot {}^{84}Kr$, and $C_6H_6 \cdot {}^{86}Kr$ were measured with a resolution of 130 MHz.

An accurate set of rotational constants has been obtained for each band. In all cases, the rotational spectrum is unambiguously modelled as a symmetric rotor with first order Coriolis coupling, as for the corresponding bands for the monomer. From the precise rotational constants, we can conclude that: a) The structure of benzene itself, in both S_0 and S_1, remains unchanged. b) The noble gas atoms are located on the C_6 symmetry axis and their distance from the benzene ring is determined for both electronic states. c) For all of the noble gas solute atoms, the van der Waals bond length *decreases* upon electronic excitation, as anticipated by the increased polarizability and expansion of the benzene ring. d) Even at several times the van der Waals binding energy in benzene vibrational energy, no dissociation within 10 ns is evident.

[a] Th. Weber, A. von Bargen, E. Riedle, and H.J. Neusser, J. Chem. Phys. 92, 90 (1990)

Address: Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstraße 4, D-8046 Garching, West Germany

ME11 (4:38)

Rotational Coherence Spectroscopy Applied to the Structural Analysis of Jet-Cooled Tryptophan Analogs and their Hydrogen-Bonded Complexes with Polar Solvents

L. L. Connell, T. C. Corcoran, P. W. Joireman, P. M. Felker
Department of Chemistry and Biochemistry
University of California, Los Angeles, CA 90024-1569

Rotational Coherence Spectroscopy[1] , a time-resolved high resolution rotational spectroscopy, is performed to determine the structures of various jet-cooled tryptophan analogs and their hydrogen-bonded complexes with methanol and water. The time-resolved fluorescence depletion technique of J. D. McDonald[2] is used to do Rotational Coherence Spectroscopy(TRFD-RCS). Results from TRFD-RCS yield excited stated rotational constants of these large jet-cooled speicies. Once accurate excited state rotational constants have been obtained and results from molecular mechanics calculations evaluated, the structure of the tryptophan analogs and their complexes can be determined.

[1] (a) P. M. Felker,A. H. Zewail, J. Chem. Phys. 86, 2460-2482 91987); (b) J. S. Baskin, P. M. Felker, and A. H. Zewail, J. Chem. Phys. 86, 2483-2499 (1987).

[2] (a) M. J. Cote, J. F. Kauffman, P. G. Smith, and J. D. McDonald, J. Chem. Phys. 90, 2865-2873 (1989); J. F. Kauffman, M. J. Cote, P. G. Smith, and J. D. McDonald, J. Chem. Phys. 90, 2874-2891 (1989).

ME12 (4:55)

FTIR SPECTROSCOPY OF CRYOGENIC AEROSOLS

T.A. Dunder and R.E. Miller

Cryogenic aerosols are generated via homogeneous nucleation in a flowing mixture of condensible and non-condensible gases at low temperature[1]. FTIR spectra of the resulting cryo-cloud display features due to the interaction of scattering and absorption processes. Mie scattering calculations used in conjunction with the FTIR results indicate the spectra are highly sensitive to the particle size distribution. Compelling spectroscopic evidence indicates that C_2H_2 aerosol, formed in cold He at 95K, is in the high temperature cubic phase despite a solid-solid phase transition to the orthorhombic phase observed at 133K in the bulk solid.

Mixed aerosols, composed primarily of Xe, provide the opportunity to observe diffusion in micro-particles and afford a gas-phase analogy to matrix isolation. Moreover, competition between homogeneous and heterogeneous nucleation is readily studied in these mixed systems.

[1]T.A. Dunder and R.E. Miller, Molecular Spectroscopy Symposium, Columbus, 1989.

Address of Authors: Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27599.

ME13 (5:12)

STATE-TO-STATE PHOTODISSOCIATION OF BINARY COMPLEXES

E.J. Bohac, Jr. and R.E. Miller

The photodissociation dynamics of binary van der Waals complexes is studied using a variation of the opto-thermal detection technique. The angular distributions of the photo-fragments for many of these complexes show structure which yields information about the dissociation channels. For cases where fragment channel density is too high to permit assignment of the angular distribution, a second laser is used to probe the fragment molecules and record a state specific angular distribution. Combining the information from the probe laser with the photo-fragment angular distribution shows that these molecules dissociate in a highly non-statistical manner. These experiments give insights into the relative importance of V-T, V-V, and V-R energy transfer in these complexes. The data from these experiments is used to give relative state-to-state cross sections and accurate values for the zero-point dissociation energy, D_0, of these complexes.

Address of Bohac and Miller: Department of Chemistry, University of North Carolina, CB 3290, Chapel Hill, North Carolina, 27599

MF1 (1:30)

A COMBINED ANALYSIS OF THE ν_1, ν_3, AND $2\nu_2$ VIBRATIONAL STATES OF THE NH_2 RADICAL USING FOURIER TRANSFORM ABSORPTION AND EMISSION DATA

JAMES B. BURKHOLDER, CARLETON J. HOWARD, A.R.W. MCKELLAR, AND M. VERVLOET

The ν_3 ($\approx$3301 cm^{-1}) and ν_1 ($\approx$3219 cm^{-1}) fundamental bands of NH_2 have been measured at high resolution in Boulder using a Bomem Fourier transform infrared spectrometer and a fast-flow multiple-traversal absorption cell. Extensive information in the form of combination differences has been obtained for the nearby $2\nu_2$ ($\approx$2961 cm^{-1}) state from emission spectra in the visible and near-infrared regions that were recorded in Ottawa, also using a Bomem spectrometer. The absorption and emission data were combined to perform the first simultaneous least-squares fit of the interacting $(\nu_1\nu_2\nu_3)$ = (001), (100), and (020) vibrational states of NH_2. The analysis shows that extensive Coriolis mixing of (001) and (100) occurs for some rotational levels starting with $N \geq 4$, and that significant Fermi-type mixing of (100) and (020) occurs for certain levels with $N \geq 6$. The molecular parameters and calculated energy levels obtained here give an accurate characterization of the rotational energy levels for (100) and (020) up to N = 9 and K_a = 8, and for (001) up to N = 7, K_a = 4.

Address of Burkholder and Howard: NOAA Aeronomy Laboratory, R/E/AL2, 325 Broadway, Boulder, Colorado 80303; and Cooperative Institute for Research in Experimental Sciences, University of Colorado, Boulder, Colorado 80309.
Address of McKellar and Vervloet: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

MF2 (1:42)

BANDS OF HNO_2

J.M. Guilmot and M. Herman

Fourier Transform infrared spectra of HNO_2 have been recorded with a Bruker IFS 120HR, at an instrumental resolution better than 0.003 cm^{-1}. The pressure conditions of the various parent gases (NO_2, NO and H_2O) are optimized during the experiments. The analysis of the ν_1 band in trans-HNO_2 (1) will be reported. A very specific interaction pattern perturbing the ν_1=1 level will be discussed. Preliminary results of the analysis of other bands in several wavelength regions will be also reported.

(1) J.M. Guilmot, M. Carleer, M. Godefroid and M. Herman, submitted for publication.

Address : Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles CP.160, 50 av. F.D. Roosevelt, 1050 Bruxelles, Belgium.

MF3 (1:54)

ANALYSIS OF THE ν_3 VIBRATION-TORSION-ROTATION BAND OF H_2O_2.

J. W. C. Johns, J.-M. Flaud and C. Camy-Peyret.

The spectrum of H_2O_2 has been recorded in the region from 750 to 1000 cm^{-1} at a resolution of about 0.003 cm^{-1}. The two lowest torsional levels associated with ν_3, the O-O stretch, have been located near 870 cm^{-1}. These bands occur amongst hot bands associated with ν_6 (centered near 1600 cm^{-1}) and bands involving highly excited torsion-rotation levels and are therefore not easily recognized. Nevertheless sub-bands with $K_a'-K_a''$ = 6-5, 5-4, 4-3, 3-2, 2-1, 1-0, 0-1, 1-2, 2-3, 3-4 and 4-5 have been located for the two lowest (301 and 303) torsional levels of ν_3. The splitting between these two levels is about 12 cm^{-1} which is close to that observed in the ground state. The analysis, which involves interactions with ground state torsion-rotation levels, will be discussed.

Address of Camy-Peyret and Flaud: Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 4 place Jussieu, Tour 13, 75252 Paris, France.
Address of Johns: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

MF4 (2:11)

FIR LASER STARK SPECTROSCOPY OF CH3OH AT 190 μm and 195 μm.

G.R. SUDHAKARAN, I. MUKHOPADHYAY, J. C. SARKER,
R.L. BHATTACHARJEE, AND L.H. JOHNSTON

The FIR laser Stark spectrum of methanol has been investigated at λ = 190 μm and 195 μm of the DCN laser. The spectrum has been taken up to 60,000 volts/cm in both parallel and perpendicular polarizations. The low field structure observed with the 190 μm line is assigned as the J_k = 173 $\leftarrow$ 162 E2, v_t = o torsional state. A relatively strong transition observed with the 195 μm and also the 195' μm line is tentatively identified as the J_k = 114 $\leftarrow$ 103 E1, v_t = o torsional state.

Address of Sudhakaran: Department of Physics, SUNY at Oswego, Oswego, NY 13126

Address of Mukhopadhyay: Department of Physics, University of British Columbia, Vancouver, British Columbia, V6T 2A6 Canada

Address of Sarker: Department of Electrical Engineering, University of Idaho, Moscow, Idaho 83843

Address of Bhattacharjee: Department of Chemistry, University of Rochester, Rochester, NY 14627

Address of Johnston: Department of Physics, Univers'~' .f Idaho, Moscow, Idaho 83843

MF5 (2:28)

TUNABLE DIODE LASER SPECTROSCOPY OF CF_2Cl_2 IN THE 9 μm REGION

S. Giorgianni, A. Gambi, A. Baldacci, A. De Lorenzi and S. Ghersetti

The gas phase infrared spectrum of natural CF_2Cl_2 has been recorded in the range 1094-1109 cm^{-1} at a resolution of about 0.002 cm^{-1} using a tunable diode laser spectrometer. Besides the strong v_1 fundamental ($\sim$1101 cm^{-1}) and related hot-bands, at least two other bands, i.e. v_2+v_7 and v_2+v_9, are expected to absorb in this region. The low temperature spectrum ($\sim$200K), providing a significant depletion of the hot-band contributions, still shows the rotational structure extremely crowded and difficult to assign due to the presence of different overlapping chlorine isotopic lines.

At present, only the structure of the v_1 band of $CF_2{}^{35}Cl_2$ (B-type) has been interpreted: about 600 transitions of the allowed subbranches $^eP(1,-1)$, $^oP(-1,-1)$, $^eR(1,1)$ and $^oR(-1,1)$ covering J' values up to 46 and K_a' values up to 8 have been identified. From single subband analyses there is evidence that many rotational levels are influenced by perturbation. Although the main interaction may be due to a first order a-Coriolis resonance with v_8 ($\zeta^a_{1,8}$ = 0.77) lying about 60 cm^{-1} above v_1, second order a-Coriolis perturbation with v_8 as well as first order c-Coriolis resonance with v_2+v_7 are reasonably to be expected.

The assigned transitions were fitted to a set of effective upper state parameters in terms of fixed ground state constants, using the Watson's A-reduced Hamiltonian in the I^r representation. It is worthy noting that the symmetry (C_s) of $CF_2{}^{35}Cl^{37}Cl$ species predicts for the corresponding v_1 vibration a hybrid band consisting of both a-type and b-type transitions; the situation is so complex that a serious attempt at analyzing the involved structure was unsuccessful.

Spectra, details of the interpretation and results obtained from the analysis will be discussed.

Address: Dipartimento di Chimica Fisica, Universita' di Venezia, D.D. 2137 - 30123 Venezia (Italy)

Intermission (2:45)

MF6 (3:00)

HIGH RESOLUTION SPECTROSCOPIC STUDIES OF CH_2F_2: THE ν_4 BAND AT 528.7 cm^{-1}

M. N. DEO, R. D'CUNHA, A. WEBER, AND W. B. OLSON

The analysis of the FTIR spectra of methylene fluoride in the region of the lowest CF_2 bending fundamental has been completed. The spectra have been recorded with the NIST BOMEM DA3.002 spectrometer at an apodized resolution of 0.004 cm^{-1}. Detailed assignments up to $J_{max} = 55$ and $K_{max} = 25$, have been carried out for the ν_4, B type fundamental band centered at 528.7 cm^{-1}. Watson's A type reduced Hamiltonian in the I^r representation has been used in a combined weighted least squares fit of the FTIR, microwave[1] and far IR data[2] to obtain upper state molecular parameters. The experimental data are fitted well within the limits of their experimental accuracy. The details of the analysis will be discussed.

---

[1] E. Hirota, J. Mol. Spectrosc. 69, 409-420 (1978).
[2] M. Carlotti, G. D. Nivellini, F. Tullini, and B. Carli, J. Mol. Spectrosc. 132, 158-165 (1988).

Address of Deo and D'Cunha: Spectroscopy Division, Bhabha Atomic Research Centre, Bombay 400085, India.

Address of Weber and Olson: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899.

MF7 (3:12)

ANALYSIS OF THE 5_0^1, 6_0^1 AND 9_0^1 BANDS OF CH_2DF

W. Lewis-Bevan, D.F. Eggers, W.D. Stork and M.C.L. Gerry.

In a previous paper,[1] Eggers et al. outlined the initial assignment and analysis of the two stronger fundamentals of CH_2DF in the 9-11 μm region, ν_5 and ν_6. In this paper we report the progress of the analysis of the two strong fundamentals and the inclusion of the weak fundamental. The data were recorded using both a high resolution BOMEM DA3.002 FT-IR instrument and a tunable diode laser. The diode laser was used to improve the resolution, sensitivity, and signal to noise of the very weak ^rQ-branches of the ν_9 fundamental, first observed in the FT-IR spectrum.

The analysis has been extended to include the very weak ν_9 fundamental. The strongest band, ν_5, has its band origin near 1055.5 cm^{-1}. This is a hybrid ab-type band, but only A-type transitions have been assigned. The ν_6 band is slightly weaker and is centered near 938.3 cm^{-1}. In this band, strong A-type and somewhat weaker B-type transitions have been assigned. Finally, some very weak ^rQ-branches (C-type) have been assigned in the ν_9 band of the molecule. The diode laser data were recorded in the region of $^rQ_3$ through $^rQ_5$, while very weak FT-IR data exist up to $^rQ_7$. The approximate band origin of the ν_9 band is 1132 cm^{-1}. There are strong interactions between the $K_a = 10$ and $K_a = 8$ levels of 6^1 and 5^1 states respectively. The interaction between the 5^1 and 9^1 states is interesting since no evidence of ^rR-branch transitions has been detected so far. Molecular constants will be reported for the ground state and all three excited vibrational states of the molecule.

---

[1] D.F. Eggers, W. Lewis-Bevan, M.C.L. Gerry, M.S. Tobin and T.W. Daley, Paper TB1 at the Forty-Third Symposium on Molecular Spectroscopy, June 13-17, 1988.

Address of Lewis-Bevan and Stork: Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901-4409.
Address of Eggers: Department of Chemistry BG-10, University of Washington, Seattle WA 98195.
Address of Gerry: Department of Chemistry, University of British Columbia, Vancouver, B.C. V6T 1Y6, Canada.

MF8 (3:29)

THE HIGH RESOLUTION INFRARED SPECTRUM OF DBF_2: THE 4_0^1 BAND

W.D. Stork and W. Lewis-Bevan

A previous study on the normal species, HBF_2,[1] indirectly estimated the position of the unseen in-plane bending fundamental, v_6 via a small Coriolis perturbation. In an attempt to observe this fundamental directly, the deuterated analogue, DBF_2 was prepared *in situ* and its infrared absorption spectrum was recorded between 700 and 920 cm^{-1} using a high resolution Bomem DA3.002 FT-IR instrument. The strongest band in this region is the out-of-plane bending fundamental, v_4. This type-C band is heavily perturbed by a second, as yet, unidentified vibrational state.

The results of the assignment and analysis of the v_4 band of DBF_2 will be discussed, including the evaluation of a new set of ground state rotational constants for both $D^{11}BF_2$ and $D^{10}BF_2$. The nature of the perturbing vibration will also be discussed.

[1] M.C.L. Gerry, W. Lewis-Bevan, D.J. MacLennan, A.J. Merer, and N.P.C. Westwood, J. Mol. Spectrosc. 98, 143-166 (1986).

Address of Stork and Lewis-Bevan: Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901-4409.

MF9 (3:46)

THE FUNDAMENTAL TORSION BAND IN ACETALDEHYDE.

I.KLEINER, M.GODEFROID, M.HERMAN, A.R.W.MC KELLAR

High resolution and low temperature experimental conditions allowed us to proceed to the rotational analysis of the v_{15} fundamental band of acetaldehyde, observed around 150 cm^{-1}. Some 1000 lines of A and E types have been assigned to the main band and some 90 A-type lines have been identified in the first overtone of the torsion mode. The simultaneous fit of a very severely selected set of the FIR data (214 lines), with the restriction $J \leq 10$ and $K \leq 9$, together with microwave information published in the literature, using the non rigid internal axis method allowed us to produce accurate parameters about internal rotation in acetaldehyde. In particular, the Fourier coefficients V_3 and V_6 of the barrier for internal rotation as well as the rotationless origins of the v_{15} fundamental band and its first overtone were determined with improved accuracy, compared to the data previously available in the literature. The rms deviation of the microwave data are unacceptably large especially for the excited torsional state $v_t = 1$. Possible reasons for this will be discussed.

Present Address of Kleiner : Division of Molecular Physics, National Institute for Standards and Technology, Gaithersburg, MD 20899, U.S.A.
Address of Godefroid and Herman : Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CP 160, 50 ave. F.D.Roosevelt, 1050 Bruxelles, Belgium.
Address of Mc Kellar : Herzberg Institute of Astrophysics, National Research Council, Ottawa K1A0R6, Canada.

MF10 (4:03)

FAR INFRARED SPECTROSCOPY OF MALONALDEHYDE

D.W. Firth, K. Beyer, and K.R. Leopold

A tunable far infrared difference frequency spectrometer has been used to examine the fully protonated form of malonaldehyde in the region near the ground state tunneling spectrum (21 cm^{-1}). We find an extremely dense and complex spectrum in which the strongest features have been assigned as pure rotational lines involving high values of J and K_{-1}. These transitions, which have been observed within the rotational manifolds of both the lower and upper halves of the tunneling doublet, have been fit simultaneously with existing microwave data[1] for this species. The resulting set of spectroscopic constants significantly extends the range of rotational states that may be accurately calculated and should therefore be valuable in assigning the rotation-tunneling spectrum. The origins of the high spectral density will be discussed.

(1) P.Turner, S.L. Baughcum, S.L. Coy, and S. Smith, J. Amer. Chem. Soc., 106, 2265 (1984)

Address of Firth and Leopold: Department of Chemistry, University of Minnesota, Minneapolis, MN 55455
Address of Beyer: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

MF11 (4:20)

HIGH RESOLUTION FT–IR SPECTROSCOPY OF *TRANS*-1,2-DIFLUOROETHYLENE

NORMAN C. CRAIG, DAVID W. BRANDON AND WALTER J. LAFFERTY

Contrary to qualitative notions, the cis isomer of 1,2-difluoroethylene has a lower electronic energy than the trans isomer[1] Consequently, calculating the energy difference and the subtle structural differences has attracted the attention of ab initio theorists.[2] A complete, microwave-derived structure for the cis isomer is available,[3] but only a partial, electron diffraction-derived structure exists for the non-polar trans isomer.[4]

With the goal of obtaining a full structure of the trans isomer, we have begun an investigation of the high resolution FT-IR spectra of trans-1,2-difluoroethylene and its $-d_1$ and $-d_2$ modifications on a Bomem DA3 FT-IR spectrometer at a resolution of 0.004 cm^{-1}. This isomer is a near-symmetric prolate rotor with $\kappa = -0.9898$. Since this molecule has C_{2h} symmetry, bands are either pure type-C or hybrid type-A/B in shape. The dominant type-A component of the $v_{10}(b_u)$ fundamental centered at 1274 cm^{-1} and the type-C $v_6(a_u)$ fundamental centered at 874 cm^{-1} have been analyzed in detail. Part of the type-B component of the hybrid band of the $v_6 + v_8$ (A_u) combination tone centered at 1656 cm^{-1} has also been analyzed. Eleven rotational parameters have been fit to 1107 ground state combination differences, derived from the three bands, with $\sigma = 0.00060$ cm^{-1}. These ground state rotational parameters include A = 1.8934058(25), B = 0.1345413(11), C = 0.1255427(10) cm^{-1}. The significance of these results for the structure of the trans isomer will be discussed.

For the type-A band, which is unperturbed, nine upper state rotational constants were fit to 1052 transitions with $\sigma = 0.00060$ cm^{-1}. For this upper state, A = 1.8926002(29), B = 0.13464887(17), C = 0.12546217(19) cm^{-1}. The type-B and type-C bands are perturbed. A partial analysis of the latter will be discussed

[1] N. C. Craig and E. A. Entemann, J. Am. Chem. Soc. 83, 3047 (1961), N. C. Craig and J. Overend, J. Chem. Phys. 51, 1127 (1969).

[2] S. Saebo and H. Sellers, J. Phys. Chem. 92, 4266 (1988).

[3] V. W. Laurie and D. T. Pence, J. Chem. Phys. 38, 2693 (1963).

[4] J. L. Carlos, R. R. Karl, and S. H. Bauer, J. Chem. Soc., Faraday Trans. 2, 177 (1974); E. J. M. van Schaick, F. C. Mijlhoff, G. Renes, and H. J. Geise, J. Mol. Struct. 21, 17 (1974).

Address of Craig and Brandon: Department of Chemistry, Oberlin College, Oberlin, OH 44074
Address of Lafferty. Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

MF12 (4:37)

VIBRATIONAL SPECTRA OF *TRANS*-3,4-DICHLOROCYCLOBUTENE

NORMAN C. CRAIG, SUSAN E. HAWLEY AND CATHERINE L. PERRY

In 1974 Suzuki and Nibler observed the vibrational spectra of cis-3,4-dichlorocyclobutene and proposed an assignment of the fundamentals of this molecule.[1] At the time the trans isomer was unknown. In the meantime, Hoberg and Frölich obtained the trans isomer by aluminum-chloride-promoted isomerization of the cis isomer.[2]

As part of a continuing study of the vibrational spectra of halogen-substituted cyclobutenes and related cations, we have prepared the trans isomer and investigated its infrared and Raman spectra. This molecule has C_2 symmetry, and the I_b principal moment-of-inertia axis coincides with the two-fold symmetry axis. We propose the following assignment of fundamentals. For the 13 modes of a symmetry (type-B bands in the infrared, polarized Raman bands): 3107, 2984, 1555, 1284, 1248, 1126, 1010, 955, 920, 822, 452, 226, 132 cm^{-1}. For the 11 modes of b symmetry (hybrid type-B/C infrared bands, depolarized Raman bands): 3087, 2998, 1291, 1220, 956, 889, 782,---, 606, 329, 252 cm^{-1}. Most of these assignments correlate with those of the cis isomer. An important exception is the frequency of 132 cm^{-1} for the ring puckering mode in the trans isomer. The assignment of 380 cm^{-1} for ring puckering in the cis isomer[1] does not fit the pattern that has emerged for other halogen-substituted cyclobutenes.[3] A reassignment to 145 cm^{-1} is proposed.

[1] E. M. Suzuki and J. W. Nibler, Spectrochim. Acta, 30A, 15 (1974).

[2] H. Hoberg and C Frölich, Synthesis, 1981, 830.

3 N. C. Craig, S. S. Borick and T. R. Tucker, 44th Symposium on Molecular Spectroscopy, The Ohio State University, June 12-16, 1989, p. 120.

Address: Department of Chemistry, Oberlin College, Oberlin, OH 44074

MF13 (4:54)

FAR INFRARED SPECTRA OF DCCCN

B. COVELIERS, A. FAYT, AND H. BUERGER

The absorption spectrum of deutereted cyanoacethylene between 180 and 370 cm^{-1} has been recorded in Wuppertal with a resolution of 0.02 cm^{-1}. The following transitions and their associated hot bands have been observed : $v_7 \leftarrow G.S.$ $v_5^1 \leftarrow v_7^1$, $v_6^1 \leftarrow v_7^1$ and $v_4 \leftarrow v_6^1$. From these spectra we have obtained with an accuracy in the range of 0.01 cm^{-1} the vibrational energies of most states of DCCCN below 1100 cm^{-1}. These results combined with the Stark transitions $\Delta v_5 = 2$[1] and the microwave analysis[2] yields the determination of any x_{ij} and g_{ij} anharmonicity parameters with i,j = 4 to 7. The observation of the crossing of v_4 with $4v_7^2$ at J = 47 and with $4v_7^0$ at J = 57 confirms the anharmonic interactions scheme of Plummer et al.[2]

[1] B. Coveliers, W.K. Ahmed, A. Fayt and A.G. Maki, submitted to the J. Mol. Spectrosc.

[2] G.M. Plummer, D. Mauer, and K.M.T. Yamada, J. Mol. Spectrosc., 130, 407-418 (1988).

Address of Coveliers and Fayt . Université Catholique de Louvain, Molecular Spectroscopy Laboratory — 2 chemin du cyclotron — B1348 Louvain-la-Neuve, Belgium.
Address of Buerger : FB9 Anorgan. Chemie — Bergische Univ. — Gesamthochschule Wuppertal — Gaussstrasse 20 — D5600 Wuppertal 1, B.R.D.

MG1 (1:30)

THE EXTENT OF CS_2 CONTINUUM-LIKE EMISSION EXCITED BY 266 - 340 nm RADIATION

S. J. McNICHOL AND S. J. SILVERS

We have previously shown that CS_2 continuum-like emission persists under collision free conditions both in a bulb and in a supersonic jet.[1] Here we explore the range of excitation wavelengths over which this emission is excited, the ratio of continuum to discrete emission in this range and the lifetimes associated with the continuum emission.

Continuum emission is excited by 340 nm radiation; it is weak compared to discrete emission when the excitation is in band regions. As the excitation moves to shorter wavelengths, continuum emission becomes more intense relative to discrete. It is excited at all wavelengths, even between bands. When individual rotational lines of V system bands are excited, continuum as well as discrete emission is always observed. It becomes predominant when the excitation wavelength is less than 300 nm and at 280 nm it alone is present; discrete emission is no longer present. The lifetime associated with continuum emission is long compared to that of the discrete. It lengthens significantly to over 20 μsec as the excitation shifts to shorter wavelengths.

---

[1]Y. S. Lee, D. Giblin, S. J. McNichol and S. J. Silvers, Chem. Phys. Letters **161**, 116 (1989).

Address of authors: Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284-20006

MG2 (1:47)

MAGNETIC MOMENTS AND LIFETIMES OF INDIVIDUAL ROTATIONAL LEVELS OF V $^1B_2$ CS_2

D. WARNAAR AND S. J. SILVERS

Lifetimes and magnetic moments of individual rotational levels of the V $^1B_2$ state of CS_2 are reported. Rotational states from a number of vibrational leves are studied. The measurements are carried out in a supersonic jet and Zeeman quantum beat techniques are used to measure magnetic moments. Results on some of these levels have previously been reported by Ochi et. al.[1] These authors, however, did not take account of the biexponential nature of the fluorescence decays. The shorter lifetime component corresponds to discrete emission while the longer one corresponds to continuum emission. Only the short component shows quantum beats. For each rotational level the g-value, discrete lifetime and continuum lifetime are reported. Values for rotational states in vibrational levels previously unanalyzed are reported.

The g-values range from 0.002 to 0.04. Such values are very large for a singlet state and are probably due to perturbation by a nearby triplet state(or states). An interaction model is proposed and the extent of mixing is estimated.

---

[1]N. Ochi, H. Watanabe, S. Tsuchiya and S. Koda, Chem. Phys. **113**, 271 (1987).

Address of authors: Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284-2006

MG3 (2:04)

OBSERVATION OF $\tilde{B}$-$\tilde{X}$ FLUORESCENCE EXCITATION SPECTRUM OF FORMYL RADICAL

X. Zhao, G.W. Adamson, and R.W. Field

Several vibrational bands belonging to the $\tilde{B}$-$\tilde{X}$ electronic system) of formyl radical (HCO) have been observed in fluorescence excitation in the 38,750-38,340 cm^{-1} region. The formyl radical was formed by photodissociation of acetaldehyde at 308nm. Surprisingly, the lifetime for the lowest few $\tilde{B}$-state vibrational levels is 10-50ns. In contrast, the lifetimes of the first few $\tilde{A}$-state vibrational levels are approximately 30ps.[1] We have recorded high resolution spectra (FWHM 0.1 cm^{-1}) of the origin band and assigned the rotational tran.. ions as belonging to a type-A and type B hybrid band. The proof that these sub-bands are from HCO comes from ground state combination differences and term value plots. Analysis of the high resolution spectra has also allowed us to determine the upper state rotational constants (A'=15.8 ±0.5 cm^{-1}, B'=1.193 ±0.02 cm^{-1}, C'=1.106 ±0.02 cm^{-1}) and band origin (38,695.48 cm^{-1}) for the $\tilde{B}$-$\tilde{X}$ 0^0_0 band.

We are currently recording SEP spectra which will verify our rotational assignments, as well as fluorescence excitation spectra of DCO, to more accurately determine the geometry of the $\tilde{B}$-state.

Address of Zhao, Adamson, and Field: Department of Chemistry and George R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139

[1]R. Vasudev and R.N. Zare, J. Chem. Phys. **53**, 5267 (1982).

MG4 (2:21)

HIGH RESOLUTION VACUUM ULTRAVIOLET STUDIES OF A^1A'' HCN

D. M. Jonas, X. Zhao, S. Solina, K. Yamanouchi, and R. W. Field

The $\tilde{A}$-$\tilde{X}$ fluorescence excitation spectrum of HCN has been recorded using 4-wave mixing in Sr vapor as a tunable vacuum ultraviolet source. The excitation spectra are notable for the high signal to noise ratio, resolution of nearly all previously blended lines(FWHM ~ $0.3 cm^{-1}$) and absolute wavenumber accuracy($0.03 cm^{-1}$). Measured lifetimes for the first three bending levels of the $\tilde{A}$ state $[\tau(000)^1=13\pm7ns, \tau(010)^1=130\pm24ns, \tau(020)^1<2ns]$ qualitatively confirm the unusual trend in predissociation lifetimes reported by Hsu et al. [1] Stern-Volmer fluorescence quenching studies reported here yield a best fit quenching constant for the $\tilde{A}(000)^1$ level of $K_q=73\mu s/Torr$, which is of the same order of magnitude as the previously reported quenching constant for the $A(010)^1$ level. Stark effect measurements of the $\tilde{A}$-state electric dipole moment now in progress will also be reported.

[1]Y. C. Hsu, M. A. Smith, and S.C. Wallace, Chem. Phys. Lett. **111**, 219(1984)

Address of Jonas, Zhao, Solina, and Field: Department of Chemistry and George R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Address of Yamanouchi: Department of Pure and Applied Sciences, The University of Tokyo, Komaba, Megoro-ku, Tokyo 153, Japan.

MG5 (2:38)

The Vibrational Structure of HCN between 9 000 and 19 000 cm^{-1}, Xueming Yang, C.A. Rogaski, A.M. Wodtke, Department of Chemistry, University of California, Santa Barbara, California, 93106

Stimulated emission pumping spectra of HCN in its ground electronic state have been measured using a pulsed tunable Argon fluoride laser with a frequency doubled pulsed dye laser. Sixty seven vibrational states between 8 900 and 18 900 cm^{-1} have been observed. Eighty percent of the states can be described within a traditional normal mode picture. A full set of anharmonic vibrational constants was derived unifying the SEP data reported here with previous infrared data. Twenty percent of the states could not be explained by the normal mode picture and a systematic analysis was performed to show that only a few of the unexplained states might be a linear superposition of zero[th] order normal mode HCN states. Since most of the unexplained states cannot be constructed out of normal mode HCN states, it is suggested that "isomerizing" delocalized vibrational states are playing a role in the observed vibrational structure.

Direct comparison is possible with ab initio vibrational structure calculations[1] on the only available three dimensional potential energy surface[2]. The experimental results sho ı clearly that the true potential has a much higher barrier to isomerization.

The present state of experimental characterization of the HCN/HNC system should be good enough to derive a quantitatively accurate potential energy surface for this prototypical isomerization reaction.

[1]J.A. Bentley, J.-P. Brunet, R.E. Wyatt, R.A. Friesner, C. Leforestier, Chem. Phys. Lett., *161*, 393 (1989)

[2]J.N. Murrell, S. Carter, L.O. Halonen, J, Mol. Spectrosc., *93*, 307 (1982)

MG6 (2:50)

VACUUM ULTRAVIOLET SPECTRUM OBSERVED IN THE REACTION OF FLUORINE ATOMS AND CYANAMIDE

PATRICK E. FLEMING AND C. WELDON MATHEWS

Fluorine atoms, produced in a microwave discharge in fluorine-containing precursors, are reacted with H_2NCN and the products of the reaction are probed by absorption spectroscopy. A system of sharply defined bands have been observed in the region extending from 1870 Å to 2175 Å. At the present, the observations have been made photographically in the first order of a 6.65-meter grating vacuum spectrograph. The bands are degraded to lower energies and show spacings of approximately 375 cm^{-1}.

Address of Fleming and Mathews: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

MG7 (3:02)

PYROLYSIS JET SPECTROSCOPY: THE Ã - X̃ TRANSITION OF FORMYL CYANIDE (HCOCN).

Dennis J. Clouthier, Jerzy Karolczak, Jay Rae, Richard Judge, David Moule and John D. Goddard

High resolution, rotationally resolved LIF spectra of HCOCN and DCOCN have been observed. This transient species was produced by pyrolysis of allyloxyacetonitrile in the throat of a continuous supersonic jet expansion. Combining LIF jet and spectrographic absorption data have enabled the rotational analysis of the 0^0_0 band of HCOCN. A complete vibrational assignment of the spectra of both isotopic species has been made with the aid of ab initio predictions of the excited state frequencies. Some of the ground state frequencies have been obtained from resolved emission spectra and hot bands in the LIF spectra.

Address of Clouthier and Rae: Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.
Address of Karolczak: Quantum Electronics Laboratory, Institute of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland.
Address of Judge: Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141-2000.
Address of Moule: Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1.
Address of Goddard: Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

MG8 (3:14)

PYROLYSIS JET SPECTROSCOPY: THE ROTATIONALLY RESOLVED ELECTRONIC SPECTRUM OF DICHLOROCARBENE

Dennis J. Clouthier and Jerzy Karolczak

Rotationally cold spectra of the 600 nm band system of CCl_2 have been observed by LIF. The transient species was produced by pyrolysis of trichloromethyltrimethylsilane in the throat of a continuous supersonic jet expansion. The pyrolysis products are probed downstream of the nozzle with a cw scanning ring dye laser, producing high resolution, rotationally resolved spectra. Deatils of the vibrational and rotational analysis, isotope effects and derived geometries will be presented.

Address of Clouthier: Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.
Address of Karolczak: Quantum Electronics Laboratory, Institute of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland.

Intermission (3:31)

MG9 (3:45)

A NEW TRIPLET BAND SYSTEM OF C_3.

H. SASADA, T. AMANO, C. JARMAN, AND P. F. BERNATH

A new triplet band system has been discovered near 6500 cm^{-1} in absorption using distributed-feedback (DFB) diode lasers as radiation sources. The band system is also observed in emission from a microwave discharge of CH_4 in He using a Fourier-transform spectrometer. C_3 was generated in a hollow cathode discharge in C_2H_2, or C_2H_4, or C_2H_6 with He buffer. The band has exhibited a characteristic triplet pattern with a slight but significant staggering in the rotational line spacing. Numerous perturbations have been found in the upper state. According to ab initio calculations, the lowest triplet state, $\tilde{a}\,^3\Pi_u$, is located at about 2 eV above the ground state, $\tilde{X}\,^1\Sigma_g^+$, and Weltner and coworkers idenftified a weak emission band of C_3 in Ar or Ne matrices at around 590 nm to be from this triplet state to the ground state. The next triplet state is located about 0.77 eV above this lowest lying triplet state according to an ab initio calculation. The band found in this work has been assigned to be the transition between these triplet states, $\tilde{b}\,^3\Pi_g - \tilde{a}\,^3\Pi_u$. The vibrational assignments were not made uniquely, but it is very likely that the band is the $v = 0 - 0$ band A least-squares analysis has been carried out to determine the spectroscopic constants with an effective Hamiltonian derived by Brown and Merer.

Address of Sasada: Department of Physics, Keio University, Yokohama, Japan 223.
Address of Amano: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.
Address of Jarman and Bernath Department of Chemistry, University of Arizona, Tucson, Arizona 85721.

MG10 (4:02)

VIBRONIC INTERACTIONS IN CO_2^+ AND THE PERTURBED $\tilde{B}(000)$ STATE

J. ROSTAS, D. KLAPSTEIN, M. VERVLOET, AND J. K. G. WATSON.

It has been known for many years[1] that the (000) level of the $\tilde{B}^2\Sigma_u^+$ state of the CO_2^+ ion is severely perturbed at low values of J. Emission[2] and laser excitation spectra[3] with low rotational temperatures have given low-J rotational term values for the e and f components of the $\tilde{B}(000)$ state and of two perturbing states. The present work is concerned with rotational analyses of new emission spectra at rotational temperatures of about 40 K and 200 K from the perturbed $\tilde{B}(000)$ state to high levels (up to 10000 cm^{-1}) of the ground state. These bands, whose intensity is due to the perturbing states, are shown to be parallel bands to $^2\Sigma_g^+$ and $^2\Sigma_g^-$ vibronic levels with odd values of the vibrational quantum numbers v_2 and v_3 in the ground $\tilde{X}^2\Pi_g$ electronic state The states perturbing the $\tilde{B}(000)$ state, which must therefore be one $^2\Sigma_u^+$ state and one $^2\Sigma_u^-$ state, are assigned to the vibronic levels $\tilde{A}(231)\mu^2\Sigma_u^+$ and $\tilde{A}(151)\kappa^2\Sigma_u^-$ of the $\tilde{A}^2\Pi_u$ electronic state. Improved vibronic parameters for the $\tilde{X}^2\Pi_g$ and $\tilde{A}^2\Pi_u$ electronic states are obtained.

1. D. Gauyacq, M. Horani, S. Leach, and J. Rostas, Can. J. Phys. 53, 2040-2059 (1975).
2. J. Rostas and R. P. Tuckett, J. Mol. Spectrosc. 96, 77-86 (1982).
3. M. A. Johnson, R. N. Zare, J. Rostas, and S. Leach, J. Chem. Phys. 80, 2407-2428 (1984).

Address of Rostas Laboratoire de Photophysique Moléculaire du CNRS, Bâtiment 213, Université de Paris-Sud, 91405 Orsay, France.
Address of Klapstein Department of Chemistry, St. Francis Xavier University, Antigonish, Nova Scotia, Canada B2G 1C0.
Address of Vervloet and Watson Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

MG11 (4:19)

MOLECULAR BEAM VISIBLE-LASER SPECTROSCOPY OF $^{11}BO_2$

A.G. ADAM, M.C.L. GERRY, A.J. MERER AND I. OZIER

The hyperfine structures of various lines in the (0,0) band of the $\tilde{A}^2\Pi_u$ - $\tilde{X}^2\Pi_g$ system of $^{11}BO_2$, near 5450 Å, have been recorded at very high resolution using molecular beam laser techniques.

The results supplement the earlier R-branch measurements of Curl et al[1], which were taken using intermodulated fluorescence. In particular they show previously-unsuspected perturbations in the upper state hyperfine patterns at many of the places where the rotational lines have recently been found to be slightly shifted[2]. Ground state parameters have been extracted from the combination differences, but no simple model can be devised to fit the upper state, which turns out to be randomly perturbed as a result of extensive vibronic coupling with high vibrational levels of the ground state.

---

[1]R.S. Lowe, H. Gerhardt, W. Dillenschneider, R.F. Curl, Jr. and F.K. Tittel, J. Chem. Phys. 70, 42 (1979).
[2]A.G. Adam, A.J. Merer and D.M. Steunenberg, J. Chem. Phys. in press.

Address of Adam, Gerry and Merer. Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C V6T 1Y6, Canada.
Address of Ozier: Department of Physics, University of British Columbia, 6224 Agriculture Road, Vancouver, B.C. V6T 2A6, Canada.

MG12 (4:36)

LASER SPECTROSCOPY OF THE RYDBERG STATES OF H_3^*

C. M. BORDAS, L. J. LEMBO, H. HELM, AND D. L. HUESTIS

One-photon and two-photon excitation from the metastable $N = 0$ $\tilde{B}$ 2p A_2^* state of H_3 are used to investigate the np, nd, and nf Rydberg series converging to the $N^+ = 1$ and $N^+ = 3$ states of H_3^+. The excitation event is detected by monitoring H_3^+ ions formed by field-ionization, forced autoionization, and rotational autoionization.

The nd and nf Rydberg states are well described by Hund's case (d) since the quantum defects are quite small. On the other hand, the two $N = 2$ members of the np Rydberg series show strong mixing [or intermediate coupling between Hund's cases (b) and (d)] that is well described by MQDT using quantum defects $\mu_0 \approx 0.009$ and $\mu_1 \approx 0.4$.

The np and nd Rydberg series both show "giant" windows (or unexpectedly reduced intensity extending over several n values) near $n = 44$, and narrower windows at $n = 61$. The intensities of the lines in these windows are very sensitive to external electric fields (~ 0.1 V/cm) in the excitation region. Detailed studies now underway should allow the identification of the perturbing level and interaction mechanism responsible for these intensity variations.

Address of Bordas, Helm, and Huestis: Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

Current address of Lembo: TRW, 1 Space Park, Redondo Beach, CA 90278

MG13 (4:53)

Observation of Highly Vibrationally Excited $\widetilde{X}$ $^1\Sigma^+$ HCP by Stimulated Emission Pumping Spectroscopy

Yit-Tsong Chen, David M. Watt, Robert W. Field, and Kevin K. Lehmann

We have observed the stimulated emission pumping (SEP) spectra of highly vibrationally excited methinophosphide (HCP) at 16 000 cm^{-1} - 19 000 cm^{-1} above the zero-point energy of linear ground electronic $\widetilde{X}^1\Sigma^+$ state. At such high energy, HCP is predicted to undergo a large-amplitude-bending vibration, where the H atom is approximately half-way ($\angle$ HCP ~ 90°) from HCP to another chemical network, "HPC".[1] The observed SEP signals of large-amplitude-bending states (0, 26, 0), (0, 28, 0) and (0, 30, 0), and of a bending-C≡P stretching combination state (0, 24, 1), have enabled us to determine the rotational constants B ≈ 0.663 cm^{-1} for the highly vibrationally excited $\widetilde{X}^1\Sigma^+$ HCP. In comparison with the B ≈ 0.666 cm^{-1} values of those states with only a few vibrational quanta,[2] the rotational energy pattern of HCP remains almost unchanged even when large-amplitude-bending motions are excited. On the other hand, the energy separations between vibrational angular momenta ℓ=0 and ℓ=2 of the same vibrational level of $\widetilde{X}^1\Sigma^+$ HCP have increased from 17.5095 ± 0.0019 cm^{-1} for v_2=2 state, observed by infrared spectroscopy,[3] to 20.0 ± 0.5 cm^{-1} of the aforementioned v_2=24–30 states, determined by SEP.

1. K. K. Lehmann, S. C. Ross and L. L. Lohr, *J. Chem. Phys.*, 82, 4460 (1985).
2. J. W. C. Johns, H. F. Shurvell and J. K. Tyler, *Can. J. Phys.*, 47, 893 (1969).
3. J.-M. Garneau and A. Cabana, *J. Mol. Spectrosc.*, 87, 490 (1981).

Address of Y. T. Chen, D. M. Watt and R. W. Field : Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Address of K. K. Lehmann : Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

MG14 (5:10)

ANALYSIS OF THE 460nm BAND SYSTEM OF NiCl$_2$ PRODUCED IN A FREE JET EXPANSION.

S.H.Ashworth, F.J.Grieman and J.M.Brown.

Using a free jet expansion which incorporates a heated nozzle we have recorded the laser excitation spectrum of NiCl$_2$ at low rotational temperatures (< 40K). ^{35}Cl/^{37}Cl isotope shifts have been resolved which permit the assignment of the progressions involving the symmetric stretching vibrational mode ($\omega_1' = 357.69(5)^1$cm^{-1} $\omega_1'' \approx 360$cm^{-1}). Sequence bands involving the bending vibrational mode have been assigned. A triplet splitting attributable to fine structure effects has also been observed.

Work at higher resolution confirms the assignment of the ^{35}Cl/^{37}Cl isotope structure from the observed intensity alternation. Rotational analysis of the 1(1-0) bands (F$_1$ and F$_2$) allows the splitting due to the Ni isotopes (^{58}Ni/^{60}Ni/^{62}Ni) to be identified and a parity doubling parameter to be determined. (F$_2$ band $B'' = 0.056793(13)$cm^{-1} $B' = 0.054779(13)$cm^{-1} $q_{eff} = 0.1083(16)$cm^{-1})

---

^{1} 1σ in units of the last quoted decimal place.

Address of Ashworth and Brown: Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ. England.
Address of Grieman: Seaver Chemistry Laboratory, Pomona College, Claremont, California, 91711.

MH1 (1:30)

An Empirical Rule Relating Fundamental to Harmonic Frequencies

K. J. Miller and F. Ganda-Kesuma

An empirical approach to estimate the harmonic from the experimental fundamental vibrational frequencies is presented. It is based on a partitioning of the eigenvectors of each normal mode into internal motion components involving bond stretching, B_s, bond angle bending, A_s, torsional, T_s, and out-of-plane, O_s, motion. These normalized components, $B_s + A_s + T_s + O_s = 1$, are used in an empirical formula, $f_s = (1200B_s + 2000A_s + 1300T_s + 1600O_s)10^{-8}$ cm, which relates fundamental to harmonic frequencies with $v_s = \omega_s(1 - 2x_s) = \omega_s(1 - f_s\omega_s)$ when the anharmonic states follow a Morse expression, $v_{sn} = \omega_s(n+1/2) - \omega_s x_s(n+1/2)^2$, where $n=0, 1, 2,...$ denotes the vibrational states of mode s. This formula is tested with the available experimental data for v_s^{exp} and ω_s^{exp}. It allows one to estimate harmonic frequencies, ω_s, from experimental fundamental frequencies, v_s^{exp} in a self consistent procedure in cases where ω_s^{exp} are not known. Experimental data is available for approximately 20 molecules (and isotopes) including diatomics, CO_2, HCN, O_3, H_2O, H_2S, NH_3, CH_2O, C_2H_2, CH_4 and C_3H_8. The method, calibrated with these molecules, yields results which suggest that harmonic frequencies can be predicted accurately from experimental anharmonic frequencies. Therefore the empirical harmonic frequencies obtained from $v_s^{exp} = \omega_s^{emp} [1-f_s\omega_s^{emp}]$ can be used to adjust the force constants in Molecular Mechanics calculations until the theoretical eigenvalues, ω_s^{th}, agree with the empirical harmonic frequencies, ω_s^{emp}.

Address of Miller and Ganda-Kesuma: Rensselaer Polytechnic Institute, Troy, New York 12180

MH2 (1:47)

Potential Energy Functions for Stretching, Bending, and Torsional Energy and Fundamental Vibrational Levels

K. J. Miller and F. Ganda-Kesuma

A combined classical and quantum mechanical method is presented to calculate fundamental vibrational frequencies with anharmonic potential energy functions. The potentials are expanded in internal coordinate displacements, $g = r-r_{eq}$ and $\alpha-\alpha_{eq}$ for stretching and bending and a cosine function of ϕ for torsional interactions. For asymmetric motion in one internal coordinate about its equilibrium position a modified Morse potential, $kG^2/2$, is used where $G=[1 - e^{-\beta g}]/\beta_0$ and $\beta=\beta_0[1 + \beta_1u + \beta_2u^2]$. $\beta_0=[k/2D_e]^{1/2}$, with the force constant, k and dissociation energy, D_e. $u = g\gamma$, where $\gamma = exp[-\alpha g^2/(2l+1)]$, $\alpha = 2\pi[\mu k]^{1/2}/h$ and l is an integer, damps the potential to the Morse asymptotes. For symmetric motion in one internal coordinate about its equilibrium position, such as linear and out of plane motion, a modified harmonic potential, $kG^2/2$, where $G = g[1 + \beta_1g^2 + \beta_2g^4]^{1/2}$ is used. For torsional motion, functions of the form $[1 + \lambda/|\lambda|)\cos\lambda\phi]^n$, n> 1, are added for the anharmonic corrections. Standard correlation terms of second degree in the parameters G are introduced for stretch-stretch, bend-bend, stretch-bend, etc. At the minimum energy conformations, the second derivative energy matrix yields the normal coordinate directions, eigenvalues and force constants, k. A fit of an anharmonic potential with a fourth- and sixth-order polynomial along the normal modes permits adjustment of the parameters k, D_e, β_1 and β_2 to reproduce the experimental fundamental frequencies. Single term Hartree wavefunctions are obtained for the ground and excited states independently for each mode with all other modes in the ground state. The potential parameters are adjusted until the calculated and experimental fundamental frequencies are in good agreement. The product and sum rules are used to analyze and suggest corrections to the experimental harmonic frequencies.

Address of Miller and Ganda-Kesuma: Rensselaer Polytechnic Institute, Troy, New York 12180

MH3 (2:04)

Vibrational Overtone Spectrum of Pyrrolidine, 3-Pyrroline and Pyrrole

D.L. Snavely, F. Blackburn and Y. Ranasinghe

The vibrational overtone spectra of gaseous pyrrolidine and 3-pyrroline were obtained by laser photoacoustic spectroscopy for the region from 11,000 to 17,800 cm^{-1} at a resolution of 2 cm^{-1} Assignments of the vibrational absorption features were made by comparison of the spectra to those of pyrrole and its deuterated analogs. The absorption spectrum of pyrrolidine is similar to that of pyrrole, the main difference being a red shift in all the vibrational absorption bands of approximately 200 cm^{-1}.

The C-H oscillator absorptions fit a simple local mode model. However, multiple absorptions in the N-H stretching region of the spectra for all three compounds indicate the presence of strong vibrational coupling to other vibrational modes.

Address of Snavely and Blackburn. Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403

Address of Ranasinghe: Department of Chemistry, Purdue University,West Lafayette, Indiana 47907

MH4 (2:21)

OVERTONE AND COMBINATION SPECTRA OF TRIATOMIC MOLECULES
IN THE VIBRON MODEL

S. Oss

In this work we present some new calculations of vibrational energy spectra and infrared transition intensities within the framework of the vibron model[1]. This is an alternative approach to the usual techniques based on the solution of the Schrödinger equation or on the inclusion of higher order terms in a Dunham expansion. In the vibron model one replaces each interatomic bond with a Lie-algebraic structure. The Hamiltonian is then written in terms of generators of these algebras and, making use of group theory, one obtains energy levels and wave functions. We present here results for several triatomic molecules, both linear and bent, including CO_2, H_2S, OCS, N_2O, HCN and some isotopic species. Depending on the number of terms included in the algebraic expansion, r.m.s. errors in the vibrational energy levels fall in the $1-10$ cm^{-1} range.

The vibron model allows also one to compute the expectation values of any operator. We have computed intensities of IR transitions for some of the listed molecules, obtaining results in reasonable agreement with the most recent observations. Possible developments of this approach to the systematic study of tetra- and poly-atomic molecules will be also presented.

---

[1] F. Iachello, Chem. Phys. Lett. 78, 581-5 (1981); F. Iachello and R.D. Levine, J. Chem. Phys. 77, 3046-55 (1982).

Address: Department of Physics, University of Trento, 38050 Povo, (TN) ITALY

MH5 (2:33)

CHARGE FLOW CONTRIBUTIONS TO INFRARED ABSORPTION AND VIBRATIONAL CIRCULAR DICHROISM INTENSITIES OF 1-d-ETHANOL

F. MAURER, R.A. SHAW, R. DUTLER, A. RAUK, AND H. WIESER

Complete sets of charge flow parameters (CFPs) were determined for anti and gauche ethanol by an analytical derivation of *ab initio* Mulliken charges using several basis sets. These charges and CFPs, the latter consisting of bond charge derivatives with respect to local symmetry coordinates and describing charge redistributions along bonds accompanying molecular vibrations, were employed in the Charge Flow (CF) formalism to calculate infrared (IR) absorption and vibrational circular dichroism (VCD) intensities of anti and gauche 1-d-ethanol. The simulated spectra were compared with spectra calculated by Fixed Partial Charge (FPC), Atomic Polar Tensor (APT), and Vibronic Coupling methods, as well as with the experimental spectrum. These comparisons highlighted those normal and local symmetry modes which are most affected by CF contributions. A minimal CFP set, containing only main elements of the complete CFP matrix, reproduced the IR and VCD intensities with reasonable accuracy.

Address: Department of Chemistry, University of Calgary, Calgary, AB, Canada T2N 1N4.

Intermission

MH6 (3:05)

UNIQUE EVALUATION OF MOLECULAR CONSTANTS

P. THIRUGNANASAMBANDAM

Wilson's FG Matrix Method[1] appears to undergo a natural evolution into a comprehensive Integral Group Theoretical Method capable of providing unique force constants in molecules as a consequence of the recognition accorded to the fundamental role of Kinetic Constants[2] in molecular vibrations.

Besides the usual Raman-infrared spectral frequencies, the Integral Group Theoretical Method utilises two additional sets of equations herein called Static Symmetry Equations and Dynamical Symmetry Equations based on extensive studies relating to Kinetic constants in molecules. The Static Symmetry Equations enable us to eliminate the redundant force constants while the Dynamical Symmetry Equations are useful to reduce the number of independent force constants to just the number of spectral frequencies, paving the way for unique solution of the problem. The unique force constants lead, in turn, to unique values for other molecular constants, viz., Mean Amplitudes, Coriolis Coupling Constants and Centrifugal Distortion Constants with due regard to the experimental values concerned.

This method of arriving at unique molecular constants, beginning from our studies relating to XY_3 molecules, has been extended to a large number of molecules with interesting results thanks to the contributions of all our colleagues in this regard. Results relating to some molecules will be presented here. In addition, an interesting feature relating to the nature of molecular forces as revealed by the Static Symmetry Equations will also be discussed.

[1] E.B. Wilson, Jr., J.Chem.Phys., 7, 1047 (1939); 9, 76 (1941).

[2] P.Thirugnanasambandam, Proc. U.G.C. Seminar on Raman and Infrared Spectrosc., University of Kerala, India, 1964.

Address: Department of Nuclear Physics, University of Madras, Madras-600025. India.

MH7 (3:22)

REDUCED FORM OF THE ROTATION-INTERNAL ROTATION HAMILTONIAN

P. GRONER AND J. R. DURIG

The general Hamiltonian for a rotating asymmetric rotor molecule with internal rotation can be written as

$$\hat{H} = \tilde{P}\mu(\tau)P + (p_\tau - \tilde{P}\rho(\tau)) F(\tau)(p_\tau - \tilde{\rho}(\tau)P) + V(\tau) + \hat{H}_h,$$

where $\hat{H}_h$ contains the higher order terms of the components of the angular momentum. This Hamiltonian has been transformed according to

$$\tilde{H} = \exp(-i\hat{S}) \hat{H} \exp(i\hat{S})$$

with an appropriate operator $\hat{S}$ to bring the Hamiltonian into a reduced form. The qualitative features (order of terms, symmetry) of various reduction schemes are described and discussed (relation to PAM, IAM) and the numbers of determinable parameters are given. Detailed examples are presented for the reduction of pure internal rotor Hamiltonians.

Address: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

MH8 (3:39)

LOW FREQUENCY VIBRATIONAL SPECTRA, CONFORMATIONAL STABILITY, AND BARRIERS TO INTERNAL ROTATION FOR 3-BROMOPROPENE AND 1-BROMO-2-FLUOROETHANE

J. LIU, QUN TANG, T. S. LITTLE, AND J. R. DURIG

The far infrared spectra of gaseous 3-bromopropene (H_2CCHCH_2Br) and 1-bromo-2-fluoroethane ($BrCH_2CH_2F$) have been recorded at a resolution of 0.1 cm^{-1} in the region of 350 to 35 cm^{-1}. For 3-bromopropene, the fundamental asymmetric torsional frequencies of the more stable gauche (dih angle ∤CCCBr = 120.5°) and high energy cis (dih angle ∤CCCBr = 0°) conformers have been observed at 99 and 133.31 cm^{-1} in the Raman and infrared spectra of the gas, respectively, each with several excited states. For 1-bromo-2-fluoroethane, the fundamental asymmetric torsional frequencies of the more stable trans (two halogen atoms oriented trans to one another) and high energy gauche conformers have been observed at 125.3 and 111.3 cm^{-1}, respectively, each with excited states falling to lower frequency. From these respective data, the asymmetric torsional potential function governing internal rotation about the C-C bonds in both molecules have been determined. From studies of the Raman spectrum of 1-bromo-2-fluoroethane at variable temperature the conformational energy difference has been determined to be 383 ± 36 cm^{-1} (1.1 ± 0.1 kcal/mol) and 300 ± 46 cm^{-1} (0.9 ± 0.1 kcal/mol) for the gaseous and liquid phases, respectively. All of these data are compared to the corresponding quantities obtained from ab initio Hartree-Fock gradient calculations employing the STO-3G* basis set. Complete equilibrium geometries have also been determined for both conformers in both molecules.

Address: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

MH9 (3:56)

THE STRUCTURE OF METHYL CYANOFORMATE FROM MICROWAVE SPECTROSCOPY AND AB INITIO CALCULATIONS

JIE LIN, P. GRONER, J. R. DURIG AND B. VAN DER VEKEN

The microwave spectra of five isotopic species of methyl cyanoformate, $CD_3OC(O)CN$, $CD_2HOC(O)CN$, $CH_3OC(O)^{13}CN$, $CH_3OC(O)C^{15}N$ and $CH_3O^{13}C(O)CN$ have been measured and assigned. A barrier to internal rotation of 407 ± 1 cm^{-1} has been obtained for three species with symmetric internal rotors. The r_0 structural parameters for the s-trans conformer (CH_3 trans to CN) were determined from the rotational constants derived from the spectra. They are compared with the optimized structures calculated for both the s-trans and s-cis conformers by ab initio Hartree-Fock gradient calculations with the 3-21G and 6-31G* basis sets.

Address of Lin, Groner, Durig: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

Address of van der Veken: Laboratorium voor Anorganische Scheikunde, Rijksuniversitair Centrum Antwerpen, B-2020 Antwerpen, Belgium

MH10 (4:08)

VIBRATIONAL SPECTRA AND ASSIGNMENTS, CONFORMATIONAL STABILITY, STRUCTURE AND AB INITIO CALCULATIONS OF 2-METHYLPROPANAL AND 2-METHYLPROPANAL-d_7

W. E. BREWER, G. A. GUIRGIS, AND J. R. DURIG

The infrared spectra (3600 to 50 cm^{-1}) of the gaseous and solid states, and the Raman spectra (3600 to 10 cm^{-1}) of the gaseous, liquid and solid states of 2-methylpropanal (isobutyraldehyde), $(CH_3)_2CHCHO$, and the corresponding deuterium compound, $(CD_3)_2CDCHO$, have been recorded. Additionally, qualitative depolarization ratios have been obtained from the Raman spectra of the liquids. These data have been interpreted for the fluid phases on the basis that the gauche conformation (oxygen atom eclipsing a methyl group) is thermodynamically preferred over the high energy trans conformation (oxygen atom eclipsing the secondary hydrogen) and is the only rotamer present in the spectra of the annealed solids. From the relative intensities of the Raman lines of the liquid at 633 cm^{-1} (gauche) and 551 cm^{-1} (trans) as a function of temperature, the energy difference is found to be 440 ± 17 cm^{-1} (1.26 ± 0.05 kcal/mol). A complete vibrational assignment is proposed which is based on infrared band contours, depolarization values, isotopic shifts and group frequencies. The vibrational frequencies determined from experiment will be compared to the corresponding quantities obtained from ab initio Hartree-Fock gradient calculations employing the 3-21G and 6-31G* basis sets. Additionally, structural parameters previously provided will be compared to those determined from ab initio methods.

Address of Brewer and Durig: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

Address of Guirgis: Mobay Chemical Corporation, Analytical Research Laboratory, Charleston, South Carolina, 29411.

MH11 (4:25)

RAMAN TORSIONAL OVERTONE SPECTROSCOPY ON PROPANE AND DIMETHYLAMINE

R. ENGELN, D. CONSALVO, J. VAN BLADEL, A. VAN DER AVOIRD and J. REUSS

With an improved Ar^+-ion laser intracavity set-up many torsional transitions are observed, up to energies near to the torsional barrier. The analysis yields the interaction parameters between both internal rotors of these molecules. For dimethylamine - due to its pyramidal basic structure - new potential parameters occur, of significant influence on the (spontaneous) Raman spectrum for this molecule.

Address of Engeln and Reuss: Molecular and Laser Physics, Faculty of Sciences, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands
Address of Consalvo: Dipartimento di Chimica, Università la Sapienza, P.le A. Moro 5, I-00185 Roma, Italy
Address of v. Bladel and v.d. Avoird: Theoretical Chemistry, Faculty of Sciences, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

MH12 (4:42)

VIBRATIONAL CIRCULAR DICHROISM SPECTRA AND CONFORMATIONAL ANALYSIS OF DI-ISOCYANANO-CYCLOPROPANE

SRITANA C. YASUI, LIJIANG WANG AND T. A. KEIDERLING

We ha measured the vibrational circular dichroism (VCD) spectrum of trans-1,2-di-isocyanocyclopropane using a dispersive spectrometer in the C-H stretching and N=C=O asymmetric stretching regions. The C-H region resembles the spectra obtained for dicyano-cyclopropane, which until now was a unique VCD pattern for the series of trans disubstituted cyclopropanes. This is also one of the few CH stretching VCD spectra that, to date, are not ammenable to theoretical analyses even at the a priori level. The isocyanate stretch gives rise to a distorted couplet that can be interpreted with the coupled oscillator model. Our preliminary results indicate that the pattern observed is only compatible with a cis-trans conformation of the two isocyanates with respect to the ring. Due to sample stability problems, it was not possible to obtain mid-ir VCD.

Address of Wang and Keiderling: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, IL 60680 USA
Current Address of Yasui: U. S. Food and Drug Administration, 1141 Central Parkway, Cincinnati, OH 45202

MH13 (4:59)

MULTIPHOTON DISSOCIATION AND IONIZATION OF Ni(CO)$_4$ AND VARIOUS COBALT COMPLEXES IN A JET-COOLED MOLECULAR BEAM: COMPARISON WITH MPI OF WF$_6$

S.C. Lee and T.A. Keiderling

Mutiphoton ionization spectroscopy of Ni(CO)$_4$ and various cobalt complexes have been investigated. Their MPI spectra exhibited relatively sharp and narrow peaks, namely atomic lines, in the 410-510nm region. Two-photon resonance ionization spectra of metal atoms have been observed in Ni(CO)$_4$ and cobalt complexes. The multiphoton process for dissociation and ionization in these complexes will be discussed. However, MPI spectra of WF$_6$ have exhibited broad bands over the 450-500nm region. The MPI spectra of WF$_6$ are quite different than those of Ni(CO)$_4$ and cobalt complexes: no atomic bands have been observed. The spectra can be instead assigned to three-photon molecular resonance ionization of WF$_6$.

All the MPI spectra observed have been assigned and predicted pathways of the MPD/MPI mechanism have been postulated based on energetic thresholds and a power study. Comparison between molecular MPI and atomic MPI in the supersonic jet expansion will be discussed.

Address of Lee and Keiderling: Department of Chemistry, University of Illinois at Chicago, P.O.Box 4348 Chicago, Ill. 60680

TA1 (8:30)

FAR INFRARED VIBRATIONAL SPECTROSCOPY OF ArHBr USING A CO_2 LASER DIFFERENCE FREQUENCY SYSTEM

D.W. Firth, M.A. Dvorak, S.W. Reeve, R.S. Ford, and K.R. Leopold

We report the observation of the lowest Π bending vibration for both $ArH^{79}Br$ and $ArH^{81}Br$ in a continuously operated planar free jet expansion. The spectra were recorded with a high resolution tunable far infrared spectrometer which utilizes a metal-insulator-metal point contact diode to generate the difference frequency between two CO_2 laser frequencies[1]. The results are compared with recent calculations by Hutson[2] which employ a potential energy surface optimized to reproduce ground state microwave data for this species, and the agreement is found to be excellent. The data indicate strong coupling between the radial and angular degrees of freedom at angles sampled by the Π state. Comparison with related systems will be made.

(1) K.M. Evenson, D.A. Jennings, and F.R. Petersen, Appl. Phys. Lett., **44**, 576 (1984)
(2) J.M. Hutson, J. Chem. Phys., **91**, 4455 (1989)

Address of Firth, Dvorak, Reeve, Ford, and Leopold: Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

TA2 (8:47)

HIGH RESOLUTION INFRARED SPECTROSCOPY OF THE $Ar-H_2O$ VAN DER WAALS COMPLEX - VIBRATIONAL ENERGY TRANSFER IN WEAKLY BOUND COMPLEXES

Robert Lascola, Christopher M. Lovejoy, and David J. Nesbitt

We report the first near-infrared study of the $Ar-H_2O$ van der Waals complex. Three bands, all involving the asymmetric stretch of the H_2O subunit, are observed. In conjunction with far-infrared data of Cohen et al.[1], these allow determination of the intermolecular angular potential for the ground vibrational state of the complex. We find a smaller barrier for in-plane versus out-of-plane internal rotation of the water molecule within the complex. One of the bands exhibits perturbations of frequencies and line widths which reveal a resonance with a predissociative, H_2O symmetric stretch excited state. Analysis of the data provides evidence for both intra and intermolecular vibrational energy flow in the complex.

[1]R.C. Cohen, K.L. Busarow, K.B. Laughlin, G.A. Blake, M. Havenith, Y.T. Lee, and R.J. Saykally, J. Chem. Phys. **89**, 4494 (1988).

Address of Authors: Joint Institute for Laboratory Astrophysics, University of Colorado, and National Institute of Standards and Technology, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440

TA3 (9:04)

DETERMINATION OF THE INTERMOLECULAR POTENTIAL OF $AR-H_2O$ FROM TUNABLE FAR INFRARED LASER SPECTROSCOPY

R.C. COHEN AND R.J. SAYKALLY

The three-dimensional anisotropic intermolecular potential energy surface (PES) for argon interacting with a rigid H_2O in its ground vibrational state has been determined by least squares fitting an analytical form for the PES to data obtained using tunable far infrared laser spectroscopy.[1,2] We have extended a new numerical many-body method, the collocation method,[3] to three dimensions. This method provides a simple, efficient, and accurate route to calculation of the eigenvalues and eigenvectors of multidimensional systems. Comparison of the new AW1 potential determined in this work to previous approximate potentials will be presented.

[1] R.C. Cohen, K.L. Busarow, K.B. Laughlin, G.A. Blake, M. Havenith, Y.T. Lee, and R.J. Saykally, J. Chem. Phys. 89, 4494 (1988).

[2] R.C. Cohen, K.L. Busarow, Y.T. Lee, and R.J. Saykally, J. Chem. Phys. 92, 169 (1990).

[3] W. Yang and A.C. Peet, Chem. Phys. Letts. 153, 98 (1988); A.C. Peet and W. Yang, J. Chem. Phys. 90, 1746 (1989); A.C. Peet and W. Yang, J. Chem. Phys. submitted.

Address: Department of Chemistry, University of California and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

TA4 (9:21)

MICROWAVE AND TUNABLE FAR-INFRARED LASER SPECTROSCOPY OF WATER CONTAINING DIMERS.

R.E. Bumgarner and Geoffrey A. Blake

We have begun a systematic study of rotation-tunneling spectra of dimers containing water and small gas molecules using both microwave [1] and FIR laser sideband [2] techniques. Our ultimate goal for these studies is to produce accurate potential energy surfaces (PES's) which will be usefull for predicting properties of dissolved gases in water and water ices. Although we are currently a long way from having a complete and accurate PES for any of our dimers, water tunneling splittings have been measured for a number of different dimers. In this talk we will compare these water tunneling splittings and discuss the PES's for the tunneling coordinate. We will also discuss improvements made in the past year to both our microwave and laser sideband spectrometers.

[1] R.E. Bumgarner and G.A. Blake, Chem. Phys. Lett. 161,308(1989).

[2] G.A. Blake and R.E. Bumgarner, J. Chem. Phys. 91,7300(1989).

Division of Geological and Planetary Sciences 170-25, California Institute of Technology, Pasadena, Ca. 91125.

TA5 (9:38)

FAR-INFRARED LASER SIDEBAND SPECTRA OF $Ar-D_2O$ and Ar-HDO.

S. Suzuki, P.A. Stockman, Peter G. Green, R.E. Bumgarner and Geoffrey A. Blake.

Far-infrared spectra of weakly bound complexes formed in a planar supersonic nozzle expansion of an Ar /H2O/D2O mixture have been obtained using the CalTech far-infrared laser sideband spectrometer [1]. Weakly bound dimers of Ar-HDO, $Ar-D_2O$ and deuterated water dimers have been studied in the 500-700GHz range using the formic acid laser line at 584388MHz. Partial assignments of the spectra have been made. The spectroscopic parameters obtained from the data will be presented.

[1] G.A. Blake and R.E. Bumgarner, J. Chem. Phys., 91,7300(1989).

Address of the Authors: Division of Geological and Planetary Sciences 170-25, California Institue of Technology, Pasadena, Ca. 91125.

TA6 (9:50)

FAR INFRARED VIBRATION-ROTATION-TUNNELING SPECTROSCOPY AND THE INTERMOLECULAR POTENTIAL ENERGY SURFACE OF $Ar-NH_3$

CHARLES A. SCHMUTTENMAER, RONALD C. COHEN, R.J. SAYKALLY

Two new far infrared bands of $Ar-NH_3$ have been measured that share a common lower state with the band previously measured in our lab[1]. These three bands have all been assigned as transitions originating from the ground state[2]. One has been assigned as the first van der Waals stretching transition. The other two have been assigned as transitions to the levels resulting from the splitting of the j=1, k=0 rotational state of free NH_3 due to the anisotropic potential, as suggested by B.J. Howard[3].

An analysis using a least squares fit to an analytical form for the intermolecular potential has been carried out.

[1] D.H. Gwo, M.L. Hevenith, R.C. Cohen, K.L. Busarov, Y.T. Lee, R.J. Saykaly, Submitted for publication.

[2] D.D. Nelson, Jr., G.T. Fraser, K.I. Peterson, K. Zhao, W. Klemperer, F.J. Lovas, R.D. Suenram, J. Chem. Phys. 85, 5512 (1986).

[3] B.J. Howard, Private communication.

Address: Department of Chemistry, University of California, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

TA7 (10:07)

THE STRUCTURAL DEPENDANCE OF HF VIBRATIONAL RED SHIFTS IN Ar_nHF CLUSTERS VIA HIGH RESOLUTION INFRARED SPECTROSCOPY

Andrew McIlroy, Robert Lascola, Christopher M. Lovejoy, and David J. Nesbitt

The rotationally resolved HF stretching spectra of Ar_nHF, n=1-4, have been observed using a slit jet, difference frequency infrared laser spectrometer. The red shift of the HF vibrational frequency is shown to be sensitively dependent on the placement of the Ar with respect to the HF dipole moment; the largest incremental red shift is observed for the linear ArhF. The n=1-3 red shifts rapidly approach the values observed in an Ar matrix suggesting that only the nearest neighbors contribute significantly to the perturbation of the HF vibrational frequency. The observed Ar_4HF isomer places the fourth Ar in what would be the second layer from the HF and has little effect on the observed red shift. This supports the importance of the nearest neighbors in determining the HF vibrational frequency. In all spectra, no evidence for vibrational predissociation is observed, indicating an extremely long lived HF vibration within the cluster.

Address of Authors: Joint Institute for Laboratory Astrophysics, University of Colorado, and National Institute of Standards and Technology, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440

Intermission

TA8 (10:40)

JET COOLED EMISSION SPECTRA OF THE XYLENES AND XYLYL RADICALS

J. I. Selco and P. G. Carrick

Rotationally cooled gas-phase electronic emission spectra of the xylene and xylyl radicals were produced with a corona excited supersonic expansion. For each molecule, the emission is almost exclusively from the lowest vibrational level in the electronic excited state indicating efficient vibrational cooling Vibronic assignments were based on known infrared, Roman and torsional frequencies.

Address of Selco: Department of Chemistry, University of Redlands, P. O. Box 3080, Redlands, CA 92373-0999.

Address of Carrick: Air Force Astronautics Laboratory/LSX, Edwards Air Force Base, CA. 93523

TA9 (10:52)

SUBMILLIMETER SPECTROSCOPY OF $(H_2O)_2$ AND $(D_2O)_2$

E. ZWART, J.J. TER MEULEN and W. Leo MEERTS

Recently much work has been done on $(H_2O)_2$ and $(D_2O)_2$ in the microwave, FIR and infrared regions. We have extended this work by studying some new bands for these dimers in the submillimeter region. In $(H_2O)_2$ the bands $K=0 \rightarrow K=1$ (E_1 and A_1 symmetry) and $K=1 \rightarrow K=2$ (E_2 symmetry) have been measured, while in $(D_2O)_2$ the bands $K=1 \rightarrow K=2$ (E_1, A_1, B_1 and E_2 symmetry) were investigated. The dimers were formed in a continuous slit nozzle expansion. The submillimeter radiation was generated either by a tunable FIR laser sideband spectrometer or by direct multiplication of klystrons between 55 and 110 GHz.
The measured bands provide valuable information on the A rotational constant and the tunneling splittings for the dimers. In the search for $(D_2O)_2$, some bands of $Ar-D_2O$ were found as well, which have not been assigned yet.

Address of Zwart, ter Meulen and Meerts: Dept. Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

TA10 (11:09)

FAR INFRARED VIBRATION-ROTATION-TUNNELING SPECTROSCOPY AND TUNNELING DYNAMICS OF CH_4-H_2O

KERRY L. BUSAROW, RONALD C. COHEN, CHARLES A. SCHMUTTENMAER, Y.T. LEE, AND R.J. SAYKALLY

There has been a great deal of investigation into better understanding hydrophobic interactions in liquid phase systems. However, progress in understanding the most fundamental solute-solvent interactions has been impeded by the lack of accurate potential energy surfaces for these systems. In this talk, we present the far infrared spectrum of CH_4-H_2O, as well as a proposed energy level scheme for this dimer.
The experimental apparatus is a tunable far infrared laser spectrometer combined with a planar supersonic jet expansion. Over 200 lines have been observed, of which 110 lines have been assigned to nine different vibration-rotation bands at ~19 cm^{-1}, all of which, we propose are associated with the $\Sigma(1_{01}) \rightarrow \Pi(1_{10})$ transition in the water subunit [1]. Exact vibrational assignments have yet to be determined. In addition, preliminary results indicate that the CH_4-H_2O is considerably more strongly bound than $Ar-H_2O$ (D.E. $\Sigma(1_{01})$ ~137 cm^{-1} [2])

[1] R.C. Cohen, K.L. Busarow, Y.T. Lee, and R.J. Saykally, J. Chem. Phys.,92, 169 (1990).

[2] R.C. Cohen and R.J. Saykally, manuscript in preparation.

Address: Department of Chemistry, University of California and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

TA11 (11:26)

THE INFRARED SPECTRUM OF THE HCCH-N₂O VAN DER WAALS COMPLEX

Albert Hu, Ling Hong Sun, and J. S. Muenter

The infrared spectrum of the acetylene-nitrous oxide van der Waals complex has been observed in the three micron wavelength region, corresponding to excitation of the asymmetric hydrogen stretching vibration of the acetylene monomer. Preliminary analysis of this spectrum gives $A''=9385$, $B''=2834$, $C''=2170$, $A'=9390$, $B'=2830$, and $C'=2167$ MHz. The vibrational origin for the transition is 3281.544 cm^{-1}. The rotational constants are consistent with a geometry having the axes of the two monomers parallel to one another and the centers of mass of each monomer directly opposite each other. This geometry is almost indistinguishable from that of the acetylene-carbon dioxide complex.

Address of Hu, Sun, and Muenter: Dept. of Chemistry, University of Rochester, Rochester, N.Y. 14627.

TA12 (11:43)

FAR INFRARED SPECTRA OF HYDROGEN DIMERS

A.R.W. MCKELLAR

Studies of the infrared spectra of $(H_2)_2$ and its isotopes are continuing. These experiments are performed using a Bomem Fourier transform spectrometer and a special long path length (112 m), low temperature (20 K) absorption cell. The collected results for the vibrational fundamental (3000-5000 cm^{-1}) and first overtone (6000-8700 cm^{-1}) regions have now been published.[1]

New spectra have been obtained in the more difficult far-infrared region corresponding to the pure rotational transitions of the hydrogen monomers. As in the vibrational region, the most interesting spectrum is that of $(D_2)_2$, which is observed here accompanying the $S_0(0)$ rotational transition of D_2 in the 150-200 cm^{-1} region. With the help of ground state combination differences and of calculations by Danby,[2] it is possible to assign most of the $(D_2)_2$ spectrum and to derive an energy level diagram for the dimer in its $v_1,v_2=0,0$, $j_1,j_2=0,2$ / 2,0 state. Comparison of the observed and calculated levels provides a powerful means of refining the potential. The ultimate goal is to derive a (mostly) experimental six-dimensional potential energy surface for the hydrogen-hydrogen interaction.

---

[1] A.R.W. McKellar, J. Chem. Phys., to be published (March 15, 1990).
[2] G. Danby, J. Phys. B 22, 1785-1807 (1989).

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

TA13 (12:00)

THE ROVIBRATIONAL SPECTRUM, STRUCTURE AND INTERMOLECULAR DYNAMICS OF CO-Ar

Y.P. ZENG, S.W. SHARPE, C. WITTIG, AND R.A. BEAUDET

Spectroscopic studies have provided a large amount of data about the structures and nature of the intermolecular forces of weakly bonded complexes. Generally, for simple triatomic complexes, the rotational spectrum can be fit to rigid or semi-rigid rotor models, such as the Watson Hamiltonian.[1]

We have measured the ro-vibrational spectrum of CO-Ar by exciting the C-O stretching chromophore. The complex was formed in a pulsed free expansion nozzle, and the absorption spectrum was taken with a tunable diode laser in the 2145 cm^{-1} region. The absorption frequencies of ten perpendicular bands including P, Q and R branches with $K_a = 0,1$ and 2 have been obtained. However, the spectrum can not be explained by a simple rigid rotor Hamiltonian. A large and systematic shift in the band origin is required for each individual K_a value. At the present time, we ascribe this to a barrier in the potential curve for the van der Waals bending mode.

---

1. J. K. Watson, J. Chem. Phys. 46, 1935 (1967).

Address of the authors: Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482

TB1 (8:30)

FOURIER TRANSFORM EMISSION SPECTROSCOPY AT 13 μm : SiS
C. I. Frum, R. Engleman, and P. F. Bernath

The vibration-rotation spectrum of silicon monosulfide, an important astrophysical molecule, has been observed in emission between 640 and 800 cm^{-1} using the Fourier transform spectrometer associated with The McMath Solar Telescope at Kitt Peak.

Gas phase SiS was produced by the reaction of solid silicon with silicon disulfide, SiS_2, in an alumina heat pipe oven. The mixture was heated to 1000 °C and the emission was focused on the entrance aperture of the Fourier transform spectrometer. More than two thousand four hundred lines were assigned to four isotopomers ($^{28}Si^{32}S$, $^{28}Si^{34}S$, $^{29}Si^{32}S$ and $^{30}Si^{32}S$). The data for all the isotopomers series were fitted together using the mass-reduced Dunham expression including Watson's Born-Oppenheimer breakdown coefficients.

Address of Frum, Engleman and Bernath : Department of Chemistry, University of Arizona, Tucson, AZ 85721

TB2 (8:42)

FOURIER TRANSFORM SPECTROSCOPY OF THE VIBRATION-ROTATION BANDS OF THE IF MOLECULE.
C. I. Frum, R. Engleman, Jr. and P. F. Bernath

High resolution absorption spectra of the IF molecule in the $X^1\Sigma$ ground state have been observed with the Kitt Peak Fourier transform spectrometer in the transient products of a F_2/I_2 flame. Analyses of the (1,0) and (2,1) bands around 600 cm^{-1}. and the (2,0) band around 1200 cm^{-1} yielded accurate molecular constants Estimates of the IF concentration, temperature and linewidths were also made.

Address of Frum, Engleman and Bernath: Department of Chemistry, University of Arizona, Tucson, AZ 85721.

TB3 (8:54)

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE ν_3 MODE OF BeF_2
C. I. Frum, R Engleman, and P. F. Bernath

The infrared spectrum of the antisymmetric stretching mode, ν_3, of BeF_2 has been observed in emission near 1530 cm^{-1} using the Fourier transform spectrometer associated with The McMath Solar Telescope at Kitt Peak.

Gas phase BeF_2 was produced by heating solid beryllium difluoride to about 800 °C in a heat pipe oven. The spectrum was recorded at a resolution of 0.005 cm^{-1} using a KCl beam splitter and As:Si detectors. The rotational analysis is in progress.

Address of Frum, Engleman and Bernath : Department of Chemistry, University of Arizona, Tucson, AZ 85721

TB4 (9:06)

LASER SPECTROSCOPY OF GAS PHASE C_2D IN THE 2800 cm^{-1} REGION

W-B. YAN AND H. E. WARNER

The ethynyl radical, C_2H, is an important reaction intermediate in soot formation and is also widespread in interstellar space. Even though much work has been done on this molecule both in the solid matrix and in the gas phase, there is still controversy about the origin of the low-lying $^2\Pi - ^2\Sigma$ electronic transition, especially the frequency of the C$-$H stretch fundamental. We have recently studied the gas phase C_2D absorption spectrum in the C$-$D stretch region (~ 2800 cm^{-1}) using a high resolution difference-frequency laser spectrometer. The C_2D molecules were produced in a hollow cathode discharge in a mixture of C_2H_2 (~ 20 mTorr) and D_2 (~ 400 mTorr). Measurements were carried out using discharge modulation at 2 kHz with a current of about 500 mA. Total laser pathlength was 36 m in a White cell arrangement. Two bands were identified: one with a symmetry of $^2\Sigma - ^2\Sigma$ and the other $^2\Pi - ^2\Sigma$. The lower state of the $^2\Sigma - ^2\Sigma$ transition is the (0 0 1) level of the C_2D ground electronic state. The analysis of these bands will be presented.

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

TB5 (9:23)

OVERTONE SPECTRA OF HCCF VIA FTIR, OPTOACOUSTIC AND MODR SPECTROSCOPIES

S.L. Coy, J. Holland, K.K. Lehmann, I M. Mills and D. Newham

HCCF is being extensively studied in the fundamental and overtone regions primarily in Reading but with assistance of the laboratories in Princeton and MIT where double resonance experiments have been performed. The molecule is extremely interesting as a prototype system for intramolecular vibrational energy transfer due to the near 1:2:3 resonance of the C-H, C$\equiv$C and C-F modes which leads to a rich spectrum with many combination bands. The present state of the knowledge of the spectrum and its interpretation will be discussed.

Address of Holland, Newham, and Mills: Department of Chemistry, University of Reading, Reading RG6 2AD UK

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

Address of Lehmann: Department of Chemistry, Princeton University, Princeton NJ 08544

TB6 (9:40)

CHARACTERIZATION AND CALIBRATION OF THE BRUKER IFS 120 HR

M. Birk, D. B. Peterson, and H. M. Pickett

Absorption spectra of CO_2, N_2O and CS_2 have been recorded using the Bruker IFS 120 HR spectrometer. Absolute frequency calibration for the mid- infrared was completed using the CO_2 and N_2O absorption lines. The transitions were compared to previous data[1] and produced a RMS deviation of 0.00005 cm^{-1}. The CS_2 spectra at 2100 cm^{-1} was used to characterize the instrumental lineshape. After a correction for field of view effects an agreement of 0.03 % transmission was achieved between experimental and theoretical lineshapes. The results of the characterization and calibration will be discussed.

[1] C. R. Pollock et.al. J. Mol. Spec. 102, 112 (1983).

Address of the authors: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

TB7 (9:52)

WAVENUMBER STANDARDS IN THE 9-22 μm REGION.

J. W. C. Johns.

Bands of OCS, C_2H_2, CO_2 and N_2O have been recorded with a Fourier transform spectrophotometer at a resolution (FWHM of the instrument function) of 0.0014 cm^{-1}. The wavenumbers were calibrated using the 'laser bands' of CO_2 which were observed in absorption at a path length of 20 m at about 1 torr which was required to obtain adequate signal to noise ratio. All the fits showed measurement precision of better than 0.00003 cm^{-1} (1 MHz) and it is believed that the accuracy is of the same order.

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

Intermission

TB8 (10:20)

THE INFRARED ABSORPTION SPECTRUM OF C_2H_2 AROUND 1300 CM^{-1}

Y. KABBADJ, M. HERMAN, T.R. HUET and J. VANDER AUWERA

The absorption spectrum of C_2H_2 has been recorded with a resolution of $\sim$ 0.003 cm^{-1} using a Bruker IFS.120HR Fourier Transform Spectrometer, between 1200 and 1450 cm^{-1}. The spectrum, which was previously studied in the literature (1) at lower resolution, is reinvestigated. Several new bands will be reported. A full Hamiltonian dealing with vibrational and rotational ℓ-doubling interactions, inspired from (2,3), is used to improve the previous rovibrational constants concerning the ν_4 and ν_5 bending modes. The use of a unique model to deal simultaneously with all observed transitions will allow to consider relative intensities features between the various $\Delta\ell$ subbands.

It is hoped that this approach will help reconsidering the absolute intensities problem in an atmospheric context. This work is part of the belgian contribution to EUROTRAC, sponsored by the SPPS (Belgium).

(1) K.F. Palmer, M.E. Mickelson and K.N. Rao, J. Mol. Spectrosc. 44, 131-44 (1972).
(2) J. Pliva, J. Mol. Spectrosc. 44, 145-64 (1972), 44, 165-82 (1972).
(3) J.K.G. Watson, M. Herman, J.C. Van Craen and R. Colin, J. Mol. Spectrosc. 95, 101-132 (1982).

Address of authors : Laboratoire de Chimie Physique Moléculaire, C.P. 160, Université Libre de Bruxelles, 50 av. F.D. Roosevelt, 1050 Bruxelles, Belgium.

TB9 (10:32)

INTERPRETATION OF THE HIGH RESOLUTION FOURIER TRANSFORM SPECTRUM OF C$_2$H$_2$ IN THE 2.4 μm REGION.

Y. A. SARMA, R. D'CUNHA, G. GUELACHVILI, R. FARRENQ, K. QING LI, V. MALATHY DEVI, D. CHRIS BENNER AND K. NARAHARI RAO

The high resolution FTIR spectrum of acetylene in the 2.4 μm region has been obtained at a resolution of 0.005 cm^{-1}. The $(\nu_1+\nu_5{}^1)$ combination band of $^{12}C_2H_2$ as well as its associated hot bands $(\nu_1+\nu_4+\nu_5)^{2,0} \leftarrow \nu_4{}^1$ and $(\nu_1+2\nu_5)^{2,0} \leftarrow \nu_5{}^1$, have been analyzed. In the parametrization of the energy levels of the excited vibrational states, the various off-diagonal matrix elements due to vibrational and rotational ℓ-type resonances have been considered. Several Q branches overlapping in the 4070-4076 cm^{-1} region have been resolved and assigned to transitions of the different sublevels split by resonance effects. The $(\nu_1+\nu_5{}^1)$ band of $^{13}C^{12}CH_2$ present in the sample in its natural abundance has also been identified and assigned. The details of the analysis will be presented.

Address of Sarma and D'Cunha: Spectroscopy Division, Bhabha Atomic Research Center, Trombay, Bombay 400085, India.
Address of Guelachvili, Farrenq and Qing Li: Laboratoire d'Infrarouge, Université de Paris-sud, Associé au CNRS, 91405 Orsay Cedex, France.
Address of Malathy Devi and Benner: Department of Physics, The College of William and Mary, Williamsburg, VA 23185.
Address of Narahari Rao: Department of Physics, Ohio State University, 174 W 18th Avenue, Columbus, OH 43210.

82

TB10 (10:44)

DECOUPLING IN THE LINE MIXING OF ACETYLENE INFRARED Q BRANCHES

A.S. PINE AND J.P. LOONEY

The Q-branch profiles of the $\nu_1+\nu_5$, $\nu_3+\nu_4$ and $\nu_2+2\nu_4+\nu_5$ $\Pi_u-\Sigma_g$ combination bands in the 2.5 μm C-H stretch-bend region of acetylene have been recorded with a difference-frequency laser spectrometer at pressures from 1 to 500 Torr (0.13 to 66.7 kPa). The broadening coefficients, obtained from the $\nu_1+\nu_5$ band at pressures low enough to avoid significant spectral overlap, can be well fit with empirical rotationally-inelastic energy-gap scaling laws or satisfactorily modeled with semiclassical line broadening theory using known intermolecular potential parameters. At pressures when lines are overlapped, collisional interference or line mixing is manifest as a deviation of the Q-branch profiles from an additive superposition of individual transition components. However the line coupling given by the state-to-state collisional scaling laws used to fit the broadening coefficients predicts far more collisional narrowing or Q-branch collapse than is observed. We find that only about one third of the collisions that broaden the individual lines effectively couple the lines within the f-sublevel of the ℓ-doubled excited Π vibrational state observed in the Q branch. This decoupling indicates that there is little or no propensity for preserving the vibrational angular momentum sublevel upon collision, and that elastic reorientational collisions may also be significant. Additionally, we find that the collisional parameters and decoupling are independent of the vibrational state despite dramatically different spectral overlaps exhibited by the three bands studied and a close Fermi resonance between the lower two vibrations. This implies that vibrational relaxation and dephasing collision rates are negligible compared with rotationally-inelastic and reorientational rates and usually can be ignored for infrared spectral broadening.

Address of Pine* and Looney**: *Molecular Physics and **Temperature and Pressure Divisions, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

TB11 (11:01)

THE ν_3 / $\nu_2 + \nu_4 + \nu_5$ RESONANCE IN ACETYLENE

W.J. Lafferty and A.S. Pine

The energy levels of the ν_3 fundamental of $^{12}C_2H_2$ are accidentally perturbed by the levels of the close-lying combination band $\nu_2+\nu_4+\nu_5$. The interacting levels are so close that the resonance mixing causes the combination band to have very nearly the same intensity as the fundamental, and, in order to fit the observed line frequencies of either band to within the experimental uncertainties using conventional polynomial expansions in $J(J+1)$, it is necessary to use very high-order terms in the expansions. This resonance also affects the overtone and combination levels involving quanta of ν_3.

The interaction is not a just a simple 2x2 Fermi interaction, since the combination level has Σ^+, Σ^- ($\ell=0$), and Δ ($\ell=2$) components. The Σ levels of the combination state are linked via Coriolis-like ℓ-type resonance with the Δ levels, and this resonance, by virtue of the strong Fermi resonance, affects also the energy levels of the ν_3 fundamental. Although this system has been studied in a number of laboratories, as yet no successful analysis has been performed to account for the observed line frequencies to within experimental uncertainty.

During the course of a study of the $\Pi-\Sigma$ combination bands in the 2.5 μm region and the hot bands in the 3 μm region which have a common upper state with the 2.5 μm bands, we recorded as well the ν_3 and $\nu_2+\nu_4+\nu_5$ (Σ^+) bands with a BOMEM spectrometer at a resolution of 0.004 cm^{-1}. Although the Δ levels of the combination band have not been observed, we decided to attempt to fit the observed Σ^+ state line frequencies. In order to do this, an estimate of the unperturbed energies of the Σ states as well as the B rotational constant of ν_3 was made using the observed band centers and B values, and values of α_2, α_4 and α_5 which have been determined previously. The Σ^+ - Δ separation of the combination level was initially assumed to be that determined earlier in a study of the $\nu_4+\nu_5$ band system. A non-linear least-squares fitting program was used to determine the best estimate of the constants of the unperturbed bands. A 9 parameter fit yielded an experimentally limited standard deviation of 0.00036 cm^{-1}. The unperturbed frequency of ν_3 is 3288.7175(38) cm^{-1} and the Fermi interaction constant obtained is 6.46097(10) cm^{-1}.

The spectroscopic constants of the combination bands and hot bands studied will also be reported.

Address of Lafferty and Pine: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

TB12 (11:18)

THE ν_7 AND ν_6 BAND SYSTEMS OF CARBON SUBOXIDE

J. Vander Auwera and J.W.C. Johns

The analysis of the FIR spectrum of C_3O_2 (1) has been completed. Bands involving excitation of up to 8 quanta of the low frequency bending mode ν_7 have been analysed. The results will be presented.

The first contribution serves as a basis for further analysis of the IR spectrum of C_3O_2 in the region of the ν_6 fundamental, started four years ago (2). For this purpose, a new spectrum has been recorded from 520 to 580 cm^{-1} at -60°C with twice the resolution used previously, i.e. 0.002 cm^{-1}. The analysis has been extended and preliminary results will be presented.

(1) J.W.C. Johns and J. Vander Auwera, Proceedings of the 44th Symposium on Molecular Spectroscopy, p.143 (1989).
(2) P. Jensen and J.W.C. Johns, J. Mol. Spectrosc. 118, 248-266 (1986).

Address : Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles CP.160, 50 av. F.D. Roosevelt, 1050 Bruxelles, Belgium.

TB13 (11:30)

HIGH RESOLUTION FTS SPECTRUM OF SEVERAL BANDS OF ClO_2

J.B. Burkholder, C.J. Howard, J. Ortigoso, R. Escribano, and W.J. Lafferty

The spectra of all 3 fundamental bands and 2 overtone bands, $2\nu_1$ and $2\nu_3$, of OClO, have been obtained with a resolution of 0.004-0.006 cm^{-1}. The ClO_2 was prepared by flowing a mixture of 10% Cl_2 in He at a total flow rate of 1 cm^3/sec and 50 Torr total pressure through a glass tube filled with $\approx$ 50 g of $NaClO_2$. The ClO_2 flowed directly into a multiple pass absorption cell and was diluted with a He flow. The concentration of ClO_2 was measured using the UV absorption spectrum. The total path length was 97.3 m and the total pressure in the absorption cell was 1.5 Torr.

The unpaired electron of OClO in its ground electronic state (X^2B_1) gives rise to a weak coupling between the electronic spin and the overall rotation, and all the ro-vibronic transitions are doubled. An effective Hamiltonian which includes the corresponding interaction terms is necessary to account for the spectrum. A program has been written in which the Hamiltonian matrix is given using symmetric top basis functions times electronic spin functions which are appropriate for Hund's case (b). Quartic and sextic centrifugal distortion terms, as well as spin-rotation terms are explicitly treated in the model.

At this point, the ν_1 and ν_2 bands have been assigned. The data for the ν_1 band include transitions up to Ka=20 and N=45 for the ^{35}Cl species and up to K_a=18 and N=34 for the ^{37}Cl species. The data for the weaker and more blended ν_2 band are somewhat more limited. These data have been combined with extensive microwave data[1] to obtain an improved set of spectroscopic constants. The results are in good agreement with a laser Stark study[2] on the ν_1 band.

[1] T. Tanaka et al. J. Mol. Spectrosc. 116, 435 (1986) and earlier papers.
[2] K. Tanaka and T. Tanaka, J. Mol. Spectrosc. 98, 425 (1983).

Address of Burkholder and Howard: Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303.
Address of Ortigoso and Escribano: Instituto de Estructura de al Materia, Consejo Superior de Investigaciones Cientificas, Serrano 119, 28006 Madrid, Spain
Address of Lafferty: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

TB14 (11:47)

AN EXPERIMENTAL AND THEORETICAL REVIEW OF PRESSURE BROADENING AND SHIFT IN THE ROTOVIBRATIONAL SPECTRUM OF AMMONIA
G. BALDACCHINI, G. BUFFA AND O. TARRINI

Almost 500 transitions have been considered in this work, which is the first attempt to make a significant quantitative comparison between experiments and theory.

The self broadening, self shift and foreign gas (N_2, CO_2) broadening of transitions of the ν_2 and ν_4 ammonia vibrational bands are compared to theoretical calculations performed in the frame of ATC approximation.

The general agreement is satisfactory. In particular the relative r.m.s. discrepancy between theory and experiments for self broadening is about 0.10 for the majority of the transitions, while the absolute r.m.s. discrepancy for self shift is about 0.6 MHz/Torr.

Moreover we have determined some trends which show shortcomings in the experimental data and in the theoretical approach. Indications are given in order to improve further the description of collisional lineshape effects.

Address of G. Baldacchini: ENEA, TIB-FIS, P.O. Box 65, 00044 Frascati (Rome), Italy
Address of G. Buffa and O. Tarrini: Dipartimento di Fisica, Università di Pisa, 56100 Pisa, Italy.

TB15 (12:02)

FOURIER TRANSFORM SPECTROSCOPY OF CARBONYL SULFIDE FROM 1800 TO 3120 CM^{-1}.

A. BELAFHAL, V. MASSON, A. FAYT, AND G. GUELACHVILI

Four spectra of natural OCS have been recorded for the Handbook of Infrared Standards published by G. Guelachvili and K.N. Rao.

Spectrum 1	Pr = 0.0395 Torr	L = 20.17 m	7,426 lines
Spectrum 2	Pr = 0.275 Torr	L = 20.17 m	12,438 lines
Spectrum 3	Pr = 2.05 Torr	L = 20.17 m	16,509 lines
Spectrum 4	Pr = 24.68 Torr	L = 32.0 m	12,447 lines

The spectra have been calibrated within 2 10^{-5} cm^{-1} near 2000 cm^{-1} to 4 10^{-5} cm^{-1} near 3000 cm^{-1}. Practically all lines have been assigned. Thirteen isotopic species have been identified, some of them with an abundance of 0.002%.

As the $J(J+1)$ expansion of energies frequently diverges from anharmonic and l-type resonances, the analysis of each band has been applied on the deviations between the calculated frequencies from our global analysis[1] and the observed frequencies, according to a polynomial of order 1 or 2 (rarely 3) in $J(J+1)$. The new data have been introduced in the global analysis. Dealing with the intensities, we obtain smoothed values for the line strengths and finally the band strengths which appear to be in good agreement (± 20%) with the absolute measurements of R.H. Kagann[2].

[1] A. Fayt, R. Vandenhaute and J.G. Lahaye, J. Mol. Spectrosc., 119, 233-266 (1986).
[2] R.H. Kagann, J. Mol. Spectrosc., 94, 192-198 (1982).

Address of Belafhal, Masson and Fayt: Université Catholique de Louvain, Molecular Spectroscopy Laboratory — 2 chemin du cyclotron — B1348 Louvain-la-Neuve, Belgium
Address of G. Guelachvili, Laboratoire d'Infrarouge, Université de Paris-Sud, Bât. 350 — F91405 Orsay Cedex, France.

TC1 (8:30)

THE SUB-DOPPLER SPECTRUM OF TiO

J.E. SHIRLEY, L.M. RUSSON, K.Y. JUENG, AND T.C. STEIMLE

Numerous features in the $B^3\Pi(v=0)$-$X^3\Delta$ band system of titanium monoxide, TiO, have been recorded at a line width of <50 MHz(FWHM) using the technique of intermodulate fluorescence spectroscopy. Gas phase TiO was produced by in a flowing reaction chamber from the microwave discharge of a mixture of argon, a trace amount of O_2 and the vapor of a heated $Ti(C_5H_5)_2Cl_2$ sample. An attempt to identify magnetic hyperfine splitting of the features associated with the ^{47}TiO isotopic form. The identification of the spectral features were complicated by the low natural abundance of ^{47}Ti(-8%) and the presumable large magnetic hyperfine splitting. A series of predicted spectra were produced using realisitic estimates of the spectroscopic parameters for ^{47}TiO to aid in this identification.

Address of Shirley, Russon, Jueng and Steimle: Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604.

TC2 (8:42)

MOLECULAR BEAM OPTICAL STARK MEASUREMENTS OF ScF AND YF

J.E.SHIRLEY,C.T. SCURLOCK, AND T.C. STEIMLE

A molecular beam optical Stark spectrum of the $C^1\Sigma^+(v=0)$-$X^2\Sigma^+(v=0)(T_{00}=16092.0$ cm^{-1}) band system of scandium monofluoride, ScF, and the $B^1\Pi(v=0)$-$X^2\Sigma^+(v=0)(T_{00}=15885.8$ cm^{-1}) band system of yttrium monofluoride, YF, have been recorded and analyzed. An electron bombardment effusive oven was employed as the molecular beam source and collimation was sufficient to produce laser induced fluorescence line widths of <35 MHz (FWHM).

The low rotational levels of the $B^1\Pi$ state of YF exhibit a first order Stark shift from which an initial estimate of the permanent electric dipole moment is -1.0D. At higher field strengths (>800 V/cm), the optical spectra of both the ScF and YF also exhibit a second order Stark shift. The analysis of the second order shifts are in progress. Hyperfine splittings the $B^1\Pi(v=0)$-$X^2\Sigma^+(v=0)$ band system of YF have been observed and analyzed in terms of magnetic hyperfine interaction in the excited state.

The spectroscopic parameters are compared with sophisticated theoretical predictions[1], and those estimated from a simple molecular orbital model.

[1]S.R. Langhoff, C.W. Bauschlicher and H. Partridge, J. Chem. Phys. 89, 369(1988).

Address of Shirley, Scurlock and Steimle: Department of Chemistry, Arizona State University, Tempe. Arizona 85287-1604.

TC3 (8:59)

MOLECULAR BEAM-OPTICAL STARK SPECTROSCOPY OF THE $A^2\Pi$ $X^2\Sigma^+$ BAND SYSTEM OF ScO

J.E. SHIRLEY, C.T. SCURLOCK, AND T.C. STEIMLE

In a continuing study of first and second row transition metal monoxides, the molecular beam optical Stark spectrum of the $A^2\Pi$-$X^2\Sigma^+$ band system of scandium monooxide, ScO, has been recorded and analyzed. An electron bombardment effusive oven was employed as the molecular beam source. Collimation was sufficient to produce laser induced fluorescence line widths of <35 MHz (FWHM).

The $A^2\Pi_{3/2}$, $A^2\Pi_{1/2}$, and $X^2\Sigma^+$ states have first, pseudo-first, and second order Stark effects, the analysis of which produce permanent electric dipole moments of 4.06(3)D, 4.43(2)D, and 4.55(8)D, respectively. An analysis of the zero-field hyperfine splitting of the optical spectrum was also performed. The $X^2\Sigma^+$ parameters were held fixed to the previously determined values[1] and the $A^2\Pi$ state hyperfine parameters were optimized in a least-squares fashion to produce the values: a= 135(1) MHz, d= 177(2) MHz and eQq$_0$=-84 MHz.The experimental values are compared with theoretical predictions, simple one electron models and the previous results of Rice and Field[2].

[1]W.J. Childs and T.C. Steimle, J. Chem. Phys.88, 6168 (1988)
[2]S.F. Rice and R.W. Field, J. Mol. Spectrosc. 119, 331 (1986).

Address of Shirley, Scurlock and Steimle: Department of Chemistry, Arizona State University, Tempe. Arizona 85287-1604.

TC4 (9:16)

VISIBLE LASER SPECTROSCOPIC STUDIES OF FeH

D.A. FLETCHER, R.T. CARTER, J.M. BROWN AND T.C. STEIMLE

Laser induced fluorescence(LIF), resolved LIF, and resolved chemiluminescence studies of the blue/green bands of iron monohydride, FeH, have been performed. Approximately 50% of the lines observed in the King furnace emissions spectrum[1] were identified in the LIF spectra for the region covered (18600 cm^{-1}-19125 cm^{-1}). Preliminary dispersed fluorescence result on a number of the strong LIF features gives irregular PQR intensities and an initial estimate of B= 5.5 cm^{-1} and $\Delta G_{1/2}$= 1630 cm^{-1} for the lower state associated with these transitions. These values indicate that the lower state is not the $X^4\Delta$ state.

An attempt to record the intermodulated fluorescence spectrum of this band system is being made and the preliminary results will be given.

---

[1] P.McCormack and S. O'Connor. Ashton.[1] Astrophys. Suppl. 26,373 (1976).

Address of Fletcher, Carter and Brown: Physical Chemistry Laboratory, Oxford University, Oxford, England, OX1 3QZ.

Address of Steimle: Department of Chemistry, Arizona State University, Tempe, Arizona, 85287-1604.

TC5 (9:28)

THE EMISSION SPECTRUM OF InCl$^+$ REVISITED

W.J. BALFOUR, K.S. CHANDRASEKHAR, AND M.D. SAKSENA

Hollow cathode excitation spectra of InCl$_3$/In/He mixtures are rich in bands throughout the 320 - 335 and 360 - 420 nm regions. Some of these bands have hitherto been attributed to the InCl$^+$ ion[1], while others had been assigned to the neutral InCl species[2] or remained unassigned. These spectra have been critically re-examined, Franck-Condon factors have been computed, and virtually all of the observed bands can be satisfactorily accounted for. The so-called A' - X bands of InCl in the 360 - 420 nm region are shown to be due to InCl$^+$. Vibrational and rotational data in support of the assignments/reassignments will be presented.

---

[1] W.J. Balfour and K.S. Chandrasekhar, J. Mol. Spectrosc. 124, 443 (1987)
[2] K. Perumalsamy, S.B. Rai, K.N. Upadhya and D.K. Rai, Physica C 132, 122 (1985)

Department of Chemistry, University of Victoria, P.O. Box 1700, Victoria, B.C. Canada V8W 2Y2

TC6 (9:45)

U.V. SPECTRA OF InO AND InO$^+$

W.J. BALFOUR and M.D. SAKSENA

The emission spectrum of InO has been recorded using different excitation sources: a microwave discharge through a flowing mixture of InCl$_3$,O$_2$ and argon; a hollow cathode; and an indium metal d.c. arc in air. Twelve bands belonging to the Δv = +1 and 0 sequences of a $^2\Sigma$ - $^2\Sigma$ transition have been observed. The 0-0 and 1-0 bands lying respectively at 428.2 and 416.5 nm have been examined at high resolution and show marked effects of nuclear hyperfine coupling.

The InO$^+$ spectrum was also excited in the d.c. arc and microwave discharge experiments. Seven bands belonging to a $^1\Pi$ - $^1\Sigma$ transition in the 370 - 390 nm region have been assigned.

For both InO and InO$^+$, accurate vibrational and rotational constants have been determined for the first time.

Department of Chemistry, University of Victoria, Victoria, B.C., Canada V8W 2Y2

Intermission

TC7 (10:20)

Fluorescence-based laser intracavity spectroscopy and the electronic structure of NiH

E. J. Hill and R. W. Field

Two special problems confront the spectroscopist who studies transition-metal containing molecules: the dominance of nominally forbidden s-d and d-d metal-centered transitions, which make the application of nonlinear spectroscopies difficult; and the huge number of molecular states, which dilute the observable laser-induced fluorescence at a given detection wavelength. To combat both of these problems simultaneously, we have constructed a fluorescence-based, continuous wave, laser intracavity spectrometer which provides tunable laser light of high intensity (greater than 200 W/cm^2) over a large spatial region (greater than 0.1 cm^3), greatly increasing the amount of observable fluorescence and facilitating saturation of weak optical transitions as compared to extracavity spectroscopy. Using examples (saturation dip spectra of the hyperfine structure of the rare isotopomer ^{61}NiH and dispersed fluorescence spectra terminating in previously unobserved low-lying states of ^{58}NiH), we illustrate the capability of this spectrometer to rapidly and efficiently gather information crucial to the verification of electronic structure models.

Address of Hill and Field: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

TC8 (10:37)

Interpretation of the low-lying states of the NiH radical

M. Li, Th. Nelis and R. W. Field

The spectra of transition metal hydrides have become a challenging subject for both experimental and theoretical studies. Numerous electronic states, separated by only small energy differences, are coupled by often large spin-orbit and rotational interactions. We will show that the three lowest-lying electronic states of NiH, the $X^2\Delta$ ground state and $^2\Sigma$ and $^2\Pi$ first excited states, can be interpreted as arising from a single d^9 configuration, with a small admixture of d^{10} character in the $^2\Sigma$ wavefunction.

Address of Li, Nelis and Field: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

TC9 (10:54)

A NEW LOW-LYING STATE OF THE PtH MOLECULE.

R. Engleman, Jr., and P. F. Bernath

High resolution infrared emission spectra of the PtH molecule have been observed with the Kitt Peak Fourier transform spetrometer. The source was a platinum hollow cathode operating with argon containing a trace of hydrogen. It was possible to assign some weak lines around 8300 cm^{-1} to (0,0) and (1,1) bands of a 3/2-3/2 transition. The lower 3/2 state was previously known and is about 4000 cm^{-1} above the $X^2\Delta_{5/2}$ ground state Good molecular constants were derived for both states. Platinum isotope and hyperfine structure has been found for the higher J values of these bands.

Address of Engleman and Bernath: Department of Chemistry, University of Arizona, Tucson. AZ 85721.

TC10 (11:06)

THE GROUND STATE SPIN-ORBIT SPLITTING OF PtH

M.C. McCarthy and R.W. Field

We have observed several new bands in the electronic spectrum of PtH by laser excitation spectroscopy in the region 23,200-22,600 cm^{-1}. For one band at 4368 Å, a $\Omega'=3/2 \leftarrow$ X$^2\Delta_{5/2}$ (0,0) transition, it appears that the $\Omega'=3/2$ state we have observed is the same upper state seen by Kaving and co-workers[1]. The dispersed fluorescence spectrum of the 4368 Å band includes a strong transition to a state at ~3250 cm^{-1} above the X$^2\Delta_{5/2}$ ground state, probably the X"$^2\Delta_{3/2}$". Our spin-orbit splitting is approximately 2000 cm^{-1} larger than Kaving's prediction, but is consistent with recent theoretical calculations and the large atomic spin-orbit splitting of Pt. We will discuss this result as well as other progress made in the analysis of the electronic spectrum of PtH.

Address of McCarthy and Field: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

[1] B. Kaving and R. Scullman, Can. J. Phys. 49, 2264 (1971).

TC11 (11:23)

LASER SPECTROSCOPIC INVESTIGATION OF THE ORANGE BANDS OF SrO

R. F. W. HERRMANN, M. GRUNDLER, M. STEIN, AND W. E. ERNST

The flame reaction Sr + N$_2$O was investigated in a Broida-type oven by using laser excitation spectroscopy and dispersing the laser induced fluorescence with a 1/3m monochromator. The so far unclassified re- _nd orange bands in the region 14700 to 15700 cm^{-1} and 16600 to 16900 cm^{-1}[1] are undoubtedly attributed to SrO and partly share a common upper state.

Laser excitation in the particularly congested spectrum near 16800 cm^{-1} with a cw dye laser of about 1 cm^{-1} linewidth leads to emission into the X$^1\Sigma$ $^+$ ground state of SrO from two different states at 26360 and 26720 cm^{-1} above X$^1\Sigma^+$(v"=0).

The spectrum around a separate bandhead at 16852 cm^{-1} was recorded at rotational resolution with a single mode laser. Fluorescence from the excited upper state of this system into the ground state, the well resolved λ-doubling in the laser excitation spectra, and the determined rotational constants indicate that the lower state of this band is a$^3\Pi_1$[1] and that the upper state should be a Π state.

[1] K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. IV, "Constants of Diatomic Molecules," Van Nostrand-Reinhold, New York 1979.

Address of Herrmann and Ernst: Department of Physics, Penn State University, 104 Davey Lab, University Park, PA 16802.
Address of Grundler and Stein: Institut fur Molekulphysik, Freie Universitat Berlin, Arnimallee 14, D-1000 Berlin 33, West Germany

TC12 (11:35)

ROTATIONAL ANALYSIS OF THE $C^2\pi$ - $X^2\Sigma^+(0,0)$ SYSTEM OF CaF

W. E. ERNST, O. KNUPPEL, AND J. KANDLER

The $C^2\pi$ - $X^2\Sigma^+(0,0)$ system of CaF around 331 nm was investigated using Doppler-free laser spectroscopy. By applying UV light from a single mode ring dye laser with intracavity fequency doubling to a molecular beam of CaF, rotational spectra could be recorded between 30190 and 30232 cm^{-1} at 30 MHz linewidth. Two perturbations as well as the observation of additional unassigned lines indicate the presence of another electronic state close to the C state. About 200 lines of the C-X system were assigned and rotationally analyzed.

The main constants for the $C^2\pi$ state of CaF are I_0 = 30215.962(16) cm^{-1}, A_0 = 29.256(30) cm^{-1}, B_0 = 0.32341(7)cm^{-1}, p_0 = - 0.487(30)10^{-2} cm^{-1}, and q_0 = 0.105(2) 10^{-3} cm^{-1} (standard error in parentheses).

Address of Ernst: Department of Physics, Penn State University, 104 Davey Lab, University Park, PA 16802.
Address of Knuppel: Institut fur Molekulphysik, Freie Universitat Berlin, Arnimallee 14, D-1000 Berlin 33, West Germany.
Address of Kandler: VDI Technologiezentrum, Graf-Recke-Str., D-4000 Dusseldorf, West Germany.

TC13 (11:52)

The First Observation of a Gaseous Triatomic Containing a Transition Metal Atom: The Visible Spectrum of H-Y-N

B. Simard, W. J. Balfour, H. Niki and P. A. Hackett

Supersonic expansion of a NH_3/He gas mixture through a laser-produced plasma of yttrium atoms has yielded the formation of the HYN molecule which was studied by laser-induced-fluorescence. The carrier was confirmed by isotopic substitutions yielding $HY^{14}N$, $DY^{14}N$, $HY^{15}N$ and the magnetic hyperfine structure arising from the spinning Y nucleus. In the visible, fluorescence can be excited in only 3 regions centered around 700, 640 and 598 nm. For all the transitions analyzed so far the molecule appears to remain linear. The 700 nm region is characterized by two sub-bands assigned as the (0,0) band of a $^2\Pi$-$^2\Sigma$ transition in which the spin-orbit splitting is about 90 cm^{-1}. The 640 nm region is characterized by at least one strong band showing the features of a $^2\Pi$-$^2\Sigma$ transition. The 598 nm region is characterized by several bands among which the strongest is assigned as the (0,0) band of a $^2\Sigma$-$^2\Sigma$ transition. All the transitions examined so far appear to terminate on the same lower $^2\Sigma$ state that we assign as the ground state of HYN. The spectrum of the $^2\Sigma$-$^2\Sigma(0,0)$ band has been recorded at high resolution (120 MHz) and has yielded accurate spectroscopic constants which will be discussed. The spectrum is characterized by beautiful nuclear magnetic hyperfine structure which is due solely to the Y nucleus and which is attributable exclusively to the ground state. The coupling case follows a gradual transition from $b_{\beta s}$ to $b_{\beta J}$. High resolution studies on the other systems are currently underway and detailed analysis will be available at the time of the meeting.

Address of Simard and Hackett: Laser Chemistry Group, National Research Council of Canada, 100 Sussex Dr. Ottawa, Ontario, K1A OR6
Address of Balfour: Department of Chemistry, University of Victoria, Victoria, B.C., V8W 2Y2
Address of Niki: Institute of Laser Engineering, Osaka University, Osaka, Japan.

TD1 (8:30)

ROTATIONAL SPECTRA IN THE nv_8, n=1, 2, 3, v_7 AND v_4 VIBRATIONS OF THE $^{13}CH_3^{12}C^{15}N$ $^{13}CH_3^{13}C^{15}N$ MOLECULES FOR $1 \leq J \leq 5$ IN THE FREQUENCY RANGE 17-95 GHz*

M. Al-Share, G. K. Johri** and J. A. ROBERTS

The microwave spectrum of $^{13}CH_3^{12}C^{15}N$ and $^{13}CH_3^{13}C^{15}N$ for $1 \leq J \leq 5$ over the frequency range of 17-95 GHz was investigated for the vibrational states nv_8, n=1, 2 and 3, v_7 and v_4 to determine if systematic differences between theory and experiment as had been found for the $^{12}CH_3^{13}C^{15}N$ were also present in these two molecules for the A', $(K=\ell=+1)$, and A", $(K=\ell=-1)$, vibrational species.

Large departures observed in the rotational spectra of the molecular species of ^{13}C and ^{15}N substituted methyl cyanide seem to provide basis for a study of fundamental interactions in molecular systems with C_{3v} symmetry. The presence of each isotope alters the frequency position of each internal mode for the molecule and this substitution seems to bring some energy levels into closer resonance conditions with ensuing strong interaction between energy states.

Address of Al-Share and Roberts: Department of Physics, University of North Texas, Denton, Texas 76203.
Permananent address of Johri: D. A. -V. College (Kanpur University), Kanpur - 208 001, INDIA.

TD2 (8:47)

COLLISIONALLY COOLED SPECTROSCOPY: EXPERIMENTAL RESULTS AND APPROACHES TO A PARAMETERIZED THEORY

D. R. WILLEY AND F. C. DE LUCIA

By use of the collisional cooling technique, we have studied the helium pressure broadening of a number of species including CO, CH_3F, H_2S, NO, DCl, OCS, and HDO in the temperature region below 5 K. The size and variation with temperature of the cross sections can be qualitatively understood in terms of the rotational energy level density of the species and the depth of the shallow attractive well in the intermolecular potential. More quantitatively, Green[1] and Palma and Green[2] have shown for CO that 'exact' close coupled calculations based on numerical potentials obtained by *ab initio* techniques can provide a good description of the experimental results.

However, these numerical surfaces do not appear to be an appropriate starting point for a parameterized description of experimental results because the number of constants required to describe the surfaces is very large. Furthermore, most of these parameters are not closely related to basic molecular properties. Experimental results will be shown and compared with the calculations. The issue of appropriate parameterization of the intermolecular potential for the fitting and prediction of observables will also be considered.

[1] S. Green, *J. Chem. Phys.* 82, 4548 (1985).
[2] A. Palma and S. Green, *J. Chem. Phys.* 85, 1333 (1986).

Address of Willey: Department of Physics, Allegheny College, Meadville, PA 16335.
Address of De Lucia: Department of Physics, Duke University, Durham, NC 27706.

TD3 (9:04)

TEMPERATURE DEPENDENCE OF COLLISIONAL PROCESSES IN CH_3F

H. O. EVERITT, AND F. C. DE LUCIA

The temperature dependence of the cross sections for the vibrational swap process and the intrasymmetry rotational thermalization process has been studied in $^{12}CH_3F$ and $^{13}CH_3F$. This study, which utilized infrared / millimeter-wave double resonance techniques, was performed to discover more about the collision mechanisms responsible for these processes.

The cross section of the vibrational swap process fell smoothly as 1/T for the range of temperatures 120K to 400K. A variation of Anderson theory applied to resonant vibrational processes has been applied to account for this behavior. The theory, which used only well known, physically meaningful parameters, agreed extremely well with the experimental results.

The cross section of the intrasymmetry rotational thermalization process (*i.e.* the recently discovered thermalization process that follows the selection rules $\Delta K = 3n$ in CH_3F) is less well understood. At temperatures below 200K the cross section is very nearly the gas kinetic collision cross section. At temperatures above 200K the cross section rises dramatically to the point where this process appears to be the dominant collisional process at 400K. The implications of these results will be discussed in the context of collisional energy transfer in CH_3F and other methyl halides.

Address of Everitt and De Lucia: Department of Physics, Duke University, Durham, NC, 27706.

TD4 (9:21)

PRESSURE BROADENING bETWEEN 80 K AND 600 K

T. M. GOYETTE, J. J. HOLTON, W. GUO, W. L. EBENSTEIN, P. HELMINGER, and F. C. DE LUCIA

The results of recent pressure broadening experiments on NO_2, H_2O, and HNO_3 pressure broadened by O_2, N_2, and He will be presented. Nitrogen dioxide (NO_2) was studied over a wide range of quantum states at 300 K. The results are compared with previous Anderson theory calculations of Tejwani and Yeung.[1] Water (H_2O) was studied between 80 K and 600 K. Nitric acid (HNO_3) was studied between 80 K and 380 K. Results for the temperature dependence of the pressure broadening parameters are compared with predictions from Anderson theory. Low temperature measurements were made in a collisionally cooled cell[2] with a continuously variable temperature between 80 K and 300 K. Static measurements were made in a quartz cell enclosed in an oven with a continuously variable temperature between 80 K and 600 K.

[1] G .D. T. Tejwani, and E. S. Yeung, *J. Chem. Phys.* 63, 4562 (1975).
[2] Goyette, Ebenstein, and De Lucia ,*J. Mol. Spectrosc.* (in press).

Address of Goyette, Holton, Guo, Ebenstein, De Lucia: Department of Physics, Duke University, Durham, North Carolina 27706

Address of Helminger: Department of Physics, University of South Alabama, Mobile, Alabama 36688

TD5 (9:38)

THE PERTURBED MICROWAVE SPECTRUM OF CYCLOPROPYL BROMIDE

H. LI, M.C.L. GERRY and W. LEWIS-BEVAN

The microwave spectra of two isotopic species of cyclopropyl bromide, C_3H_5 ⁷⁹Br and $C_3H_5$⁸¹Br, have been measured in the frequency range 15-90 GHz. The molecule is a near-symmetric prolate rotor. The spectrum is dominated by strong a-type R branches; the anticipated c-type transitions are weak and difficult to identify.

Usually in this situation accurate values of only two rotational constants, B and C, are available. However, by taking advantage of perturbations in the Br quadrupole hyperfine structure, we have evaluated accurately all three rotational constants, using exclusively a-type transitions. This was done using a computer program for global least squares fitting to all spectroscopic constants.

As a result of these fits some c-type transitions could be identified, and accurate values for all rotational constants, quartic centrifugal distortion constants and Br quadrupole coupling constants have been obtained. The Br quadrupole coupling tensors have been diagonalized, and their structural implications, along with those of the rotational constants, have been deduced.

Address of Li and Gerry: Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B.C., CANADA V6T 1Y6.
Address of Lewis-Bevan: Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901-4409.

TD6 (9:55)

TWO-PHOTON MICROWAVE TRANSITIONS WITHIN A TWO-LEVEL SYSTEM
L. MARTINACHE, I. OZIER, and A. BAUDER

Two-photon pure rotational transitions in the symmetric top CF_3CCH have been observed with a pulsed beam Fourier transform crossed-cavity spectrometer modified to allow the application of a static Stark field. Transient one-photon emission signals at ν_0=17267 MHz for transitions between the levels (J=3,K,M) and (2,K,M) are generated for $KM \neq 0$ by the application of intense pulses at $\nu_0/2$. It has been demonstrated that the two-photon transitions occur within an effectively isolated two-level system as a result of the first order ac Stark effect. Quantitative studies of the intensities as a function of pulse length and power show that the two-photon transition probability in the microwave region is well represented by the theoretical model used earlier[1] to treat multiphoton transitions in a two-level system whose one-photon frequency is $\leq$ 1 MHz. A description is given of the spectrometer with emphasis on the modifications made for two-photon studies.

[1] W.L. Meerts, I. Ozier, and J.T. Hougen, J. Chem. Phys. 90, 4681 (1989).

Address of Martinache, Ozier, and Bauder:
Laboratorium für Physikalische Chemie, Eidgenössische Technische, Hochschule, CH-8092 Zürich, Switzerland.
Permanent Address of Ozier: Department of Physics, University of British Columbia, Vancouver, B.C. V6T 2A6, Canada.

TD7 (10:07)

GROUP-THEORETICAL FORMALISM FOR THE LARGE-AMPLITUDE VIBRATION-ROTATION PROBLEM IN METHYLAMINE-d_1
AND PRELIMINARY ANALYSIS OF THE GROUND-STATE MICROWAVE SPECTRUM

Motoki Oda, Nobukimi Ohashi, Kojiro Takagi and Jon T. Hougen

A group-theoretical formalism suitable for analyzing high resolution spectra of
monodeuterated methyl amine, CH_3NHD, has been derived. This formalism, which treats
simultaneously the methyl-group internal rotaion, the amino-group inversion, and the overall
rotation, is obtained using extended-group ideas, and represents a modification of the formalism
previously derived for treating normal methyl amine. The modification is necessary primarily
because the H and D atoms in the unsymmetrical amino group are expected to move different
distances during the inversion motion. The results of the treatment indicate that elements of
the Hamiltonian matrix can be expressed as three separate Fourier series in variables similar to
the usual Internal-Axis-Method variable $(2\pi/3)(\rho K-\sigma)$. One of the Fourier series can be
associated with splittings arising from the methyl-group internal rotation. tunneling. The other
two series can be associated with splittings arising from two symmetrically inequivalent amino-
group inversion tunneling paths. All matrix elements satisfying $\Delta K = 0$, ± 1 and ± 2 selection
rules have been derived in a form appropriate for carrying out a global fit of spectroscopic
data. Preliminary fits using a computer program based on this formalism lead to a standard
deviation of 0.8 MHz for a fit of 123 microwave transitions with $0 \leq K \leq 3$ and $0 \leq J \leq 15$ and 21
molecular parameters.

Address of Oda and Ohashi: Department of Physics, Faculty of Science, Kanazawa University,
Kanazawa, Ishikawa 920 Japan
Address of Takagi: Department of Physics, Faculty of Science, Toyama University, Toyama 930
Japan
Address of Hougen: Molecular Physics Division, National Institute of Standards and Technology,
Gaithersburg, Maryland 20899

Intermission

TD8 (10:40)

THE ROTATIONAL SPECTRUM AND STRUCTURE OF Cl_2O_3

M. BIRK, R. R. FRIEDL, AND E. A. COHEN

The products of the $Cl + OClO$ reaction have been studied using submillimeter wave spectroscopy. The
ClO initially formed reacts with the excess $OClO$ to give Cl_2O_3. The products of the ClO self reaction are
not apparent under the present experimental conditions. The spectra of the 35-35, 37-35, 35-37, and 37-37
species of Cl_2O_3 have been assigned and fitted. The rotational constants and chlorine substitution coordinates
are consistent with a classical chlorine chlorate structure. The experimental apparatus will be described. The
spectrum, molecular parameters and the role of Cl_2O_3 as a potential reservoir for active chlorine in the polar
stratosphere will be discussed.

Address of the authors: Jet Propulsion Laboratory, California Institute of Technology.
Pasadena, CA 91109

TD9 (10:57)

MICROWAVE SPECTRUM OF NS IN THE HIGHLY EXCITED VIBRATIONAL STATES.

TAKAYOSHI AMANO and TAKAKO AMANO

The NS free radical in the excited vibrational states up to $v = 20$ has been detected in a hollow cathode
discharge in a mixture of CS_2 (~1 mTorr) and N_2 (~40 mTorr) by microwave spectroscopy. This measurement
extends a previous microwave measurement of the vibrationally excited NS (up to $v = 5$) made by Anacona
et al[1]. The spectrum was recorded in the range of 75 to 385 GHz with a microwave system equipped with a
tripler-quadrupler. A least-squares analysis is being made to determine the spectroscopic constants in these
high-v states.

[1] J. R. Anacona, M. Bogey, P. B. Davies, C. Demuynck, and J. L. Destombes, Mol. Phys. 59, 81(1986).

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

TD10 (11:09)

MICROWAVE SPECTRUM OF NCS.

TAKAYOSHI AMANO and TAKAKO AMANO

A hollow cathode discharge in a mixture of CS_2($\sim$1 mTorr) and N_2($\sim$40 mTorr) is found to generate NS and CN radicals very well. In addition to these well-known species, the microwave spectrum of NCS free radical has been observed and the preliminary results were reported[1]. The ground electronic state of NCS is $^2\Pi$ and exhibits relatively large Renner effect upon excitation of the bending vibration. The spectrum was recorded in the range of 75 to 385 GHz with a microwave system equipped with a tripler-quadrupler. The lines in the excited bending vibrational states, $^2\Delta_{5/2}$ and $\mu^2\Sigma_{1/2}$, as well as those in the ground Π vibronic states have been observed. The molecular constants for the ground and the first excited bending vibrational excited states have been determined precisely from a least-squares fit.

[1] Takayoshi Amano and Takako Amano, The 44th Symposium on Molecular Spectroscopy, paper RF 1, 1989(Columbus, OH).

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

TD11 (11:26)

FIRST EXPERIENCES WITH AN AUTOMATIC PULSED MOLECULAR BEAM MICROWAVE FOURIER TRANSFORM SPECTROMETER

W. STAHL, U. ANDRESEN, H. DREIZLER, AND J. U. GRABOW

The pulsed molecular beam microwave Fourier transform (MB-MWFT) spectrometer turned out to be an extremely useful tool for the assignment of microwave spectra of stable as well as under normal conditions unstable molecules. This advantage arises mainly from the fact that in the molecular beam the rotational temperature is in the order of some Kelvin and therefore only a few low lying energy levels are populated which results in a rather clear rotational spectrum.

Due to the narrow bandwidth of the microwave cavity one usually observes only a small range of the spectrum in a single experiment. This disadvantage makes it rather tedious to scan wide frequency ranges if a completely unknown spectrum is to be measured, because the cavity has to be tuned manually after each single measurement. We now automated this process. The whole measuring sequence including the tuning of the cavity is computer controlled and after each measurement significant spectral lines are detected and recorded. This greatly increased the efficiency of the MB-MWFT spectrometer and gives more time to the spectroscopist to assign his spectra while the apparatus scans hundreds of MHz automatically.

Technical details of the MB-MWFT spectrometer of the University of Kiel and an application of the automatic scanning facility for the measurement and assignment of the rotorsional spectrum of tert-Butyl isocyanate will be presented in the talk.

Address of Stahl, Andresen, Dreizler and Grabow: Institut für Physikalische Chemie, Universität Kiel, Olshausenstr. 40, 2300 Kiel 1, Fed. Rep. of Germany.

TD12 (11:43)

MICROWAVE SPECTRA AND STRUCTURES OF THE NONLINEAR NNO-HCN, ^{15}NNO-HCN, AND NNO-DCN COMPLEXES

D. J. PAULEY, M. A. ROEHRIG, AND S. G. KUKOLICH

Microwave spectra were obtained for the bimolecular gas-phase complexes NNO-HCN, ^{15}NNO-HCN and NNO-DCN using pulse-beam Fourier transform microwave spectroscopy. These data were fit to determine values for $(A - D_K)$, B and C, and the quartic distortion parameters, D_J and D_{JK}. One quadrupole coupling parameter due to the HCN nitrogen in the complex was obtained by fitting low J transitions. Structural parameters were obtained using moments of inertia, quadrupole coupling, and single isotopic Kraitchman analysis. The first spectra for gas-phase N_2O-HCN complexes were measured with an infrared optothermal technique[1] by Dayton and Miller. In the present work two new sets of isotopic data for ^{15}NNO-HCN, and NNO-DCN combined with our previous microwave measurements on NNO-HCN have eliminated ambiguities in structure fits. The planar structure can be described with the distance $R_{cm} \approx 3.25 \pm 0.05$ Å, the angle $\theta \approx 90° \pm 6°$ between HCN and R_{cm}, and the angle $\phi \approx 77° \pm 6°$ between N_2O and R_{cm}. Analysis of the data indicate that the oxygen of N_2O is tilted slightly towards the hydrogen of HCN.
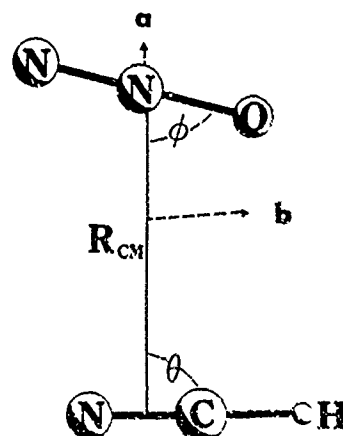
[1]   D.C. Dayton and R.E. Miller, 44th Symposium on Molecular Spectroscopy, Paper TF, The Ohio State University, Columbus, Ohio, June 1989.

Address of Pauley, Roehrig and Kukolich: Department of Chemistry, University of Arizona, Tucson, Arizona 85721

TD13 (11:55)

MICROWAVE SPECTRUM OF CHLOROMETHYLTHIIRANE

C. F. SU, M. T. HO, R. L. COOK, AND V. F. KALASINSKY

The microwave spectrum of chloromethylthiirane (3-chloropropylene sulfide) has been recorded in the R- and K-band regions. Only one conformer has been assigned in the microwave spectrum even though two conformers have been identified in an electron diffraction study [1] and in the vibrational spectra of the fluid phases. B-type transitions dominate the microwave spectrum, and the Stark effect and RFWM double resonance were used to confirm some assignments. Quadrupole hyperfine splittings were observed in some transitions as well. More than sixty Q- and R-branch transitions were used to determine the following rotational constants (MHz):

$$A = 7596.58 \quad \pm 0.01$$
$$B = 1708.568 \quad \pm 0.001$$
$$C = 1476.98 \quad \pm 0.001$$

These rotational constants are consistent with a gauche-1 structure in which the non-bonded chlorine-sulfur distance is very small. In the electron diffraction study, this conformer was determined to be approximately 18% abundant because it is less stable than the gauche-2 conformer (82%) in which the chlorine-sulfur distance is at a maximum. The reasons for the apparent discrepancy will be discussed along with other data which suggest the possible existence of three conformers of chloromethylthiirane.

1. Q. Shen and K. Hagen, J. Mol. Struct., 131, 309 (1985).

Address of Su, Ho, and Cook: Department of Physics and Astronomy, Mississippi State University, Mississippi State, Mississippi 39762

Address of Kalasinsky: Armed Forces Institute of Pathology, Walter Reed Army Medical Center, Washington, DC 20306

TE1 (1:30)

QUANTUM MECHANICAL TREATMENT OF TWO INTERACTING RIGID ROTORS: APPLICATION TO $(HCl)_2$

Michael D. Schuder and David J. Nesbitt

A simplified approach to the quantum mechanical description of two interacting rigid rotors is presented. The procedure is similar to that recently developed by Clary[1] with the intermolecular separation (R) being fixed at its equilibrium value. The potential energy surface is then described by the internal coordinates θ_1 and θ_2 between the HCl suounits and the intermolecular axis, and the torsional angle ϕ. The rotational tunneling spectrum is predicted using an electrostatic intermolecular potential and is compared to the experimentally determined $(HCl)_2$ spectrum. Of particular interest are the relative intensities of these tunneling transitions, which we have observed experimentally in combination with the HCl stretch. This technique can be applied to other rotor-rotor dimer systems such as $(HF)_2$ and $(HCCH)_2$.

[1] D.C. Clary, private communication

Address of Authors: Joint Institute for Laboratory Astrophysics, University of Colorado, and National Institute of Standards and Technology, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440

TE2 (1:47)

AN *AB INITIO* POTENTIAL ENERGY SURFACE AND RO-VIBRATIONAL CALCULATIONS FOR $(HCl)_2$

V. C. EPA, P. R. BUNKER, A. KARPFEN, H. LISCHKA, and M. KOFRANEK

An *ab initio* global potential energy surface has been computed for the dimer $(HCl)_2$ within the associated coupled pair functional (ACPF) framework using an extended polarized basis set. These 1058 points covering an energy range of up to 40000 cm^{-1} above the equilibrium have been fitted to a 6D analytical model containing 32 adjustable parameters with a weighted standard deviation of 23.5 cm^{-1}. The global minimum energy path, which is significantly different from that for $(HF)_2$, and the stationary point geometries and barrier heights have been determined. With this *ab initio* model, rotational-vibrational calculations, including those using an one-dimensional semi-rigid bender hamiltonian have been performed.

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

Address of Karpfen, Lischka, and Kofranek: Institut für Theoretische Chemie und Strahlenchemie, University of Vienna, Währingerstrasse 17, A-1090 Vienna, Austria.

TE3 (2:04)

INVESTIGATION OF H_2HCl AND H_2DCl COMPLEXES: H_2 ORIENTATION EFFECTS IN THE VAN DER WAALS COMPLEX

Michael D. Schuder and David J. Nesbitt

Recent high resolution infrared spectra recorded on a difference frequency and Pb-salt diode laser spectrometers have been obtained for H_2HCl and H_2DCl complexes, respectively. Analyses of these systems are used to characterize the internal rotor motion of the H_2 and the intermolecular potential which orients the subunits into a T-shaped asymmetric top complex. The spectra provide an opportunity to study any preferential orientation of DCl systems versus their HCl analogs. Such a differential intermolecular orientation has been demonstrated both theoretically[1] and experimentally[2] for rare gas - H(D)Cl complexes. The vibrationally averaged geometries of H_2HCl and H_2DCl are of interest since these systems provide a means of investigating photo initiated chemical insertion reactions of $D + H_2$ and $H + D_2$.

[1] J. Hutson, J. Chem. Phys. 89, 4550 (1988).
J. Hutson, J. Chem. Phys. 91, 4448 (1989).
[2] M.D.Schuder, D.D.Nelson, and D.J.Nesbitt (in preparation)

Address of Authors: Joint Institute for Laboratory Astrophysics, University of Colorado, and National Institute of Standards and Technology, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440

TE4 (2:21)

THEORETICAL CALCULATIONS OF THE TRANS-BEND, CIS-BEND AND TORSIONAL ENERGY LEVELS OF THE HF, HCL AND HBR DIMERS

S. C. ALTHORPE, D. C. CLARY AND P. R. BUNKER

For the HF, HCl AND HBr dimers, and their deuterated forms, we have calculated the positions and intensities of the trans-bend, cis-bend and torsional bands using purely electrostatic potential energy functions, and the monomer dipole moments. For the case of the HF dimer we have also done the calculation using the most recent ab initio potential of Bunker et al.[1]. The calculations have been performed with the intermolecular bond lengths and the HX bond lengths fixed. The results of the calculations will be compared with each other and with experiment.

[1]P. R. Bunker, P. Jensen, A. Karpfen, M. Kofranek, and H. Lischka *J. Chem. Phys.* in press.

Address of Althorpe and Clary: Department of Theoretical Chemistry, Cambridge University, Cambridge, England

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

TE5 (2:38)

THE STRETCHING VIBRATIONAL STATES OF THE HF DIMER

P. R. BUNKER, P. JENSEN, A. KARPFEN, H. LISCHKA, and M. KOFRANEK

For the HF dimer, and its deuterated forms, we have calculated the positions and intensities of the HF stretching fundamentals, overtones and combination bands for all states having $v_1 + v_2 < 4$, and we have also calculated the fundamental and overtone frequencies of the intermolecular (HF-HF) stretching vibration, using an ab initio surface and the previously developed Semirigid Bender Hamiltonian. The ab initio surface used involves the addition of 459 nuclear geometry points to the 1061 reported in our earlier work [1-3]. We determine that $\nu_1=3926$ cm^{-1}, $\nu_2=3875$ cm^{-1}, and $\nu_4=146$ cm^{-1}; the values obtained for ν_1 and ν_2 are in good agreement with experiment (3930.9 cm^{-1} and 3868.1 cm^{-1} respectively), and the value obtained for ν_4 could explain a perturbation observed in the ground state K=4 levels. We predict that the overtones $2\nu_2$ and $3\nu_2$ are very weak but that the combination tones $\nu_1 + \nu_2$, $\nu_1 + 2\nu_2$, and $2\nu_1 + \nu_2$ are relatively strong.

[1]M. Kofranek, H. Lischka and A. Karpfen, *Chem. Phys.* 121, 137 (1988).

[2]P. R. Bunker, M. Kofranek, H. Lischka and A. Karpfen, *J. Chem. Phys.* 89, 3002 (1988).

[3]P. R. Bunker, T. Carrington, P. C. Gomez, M. D. Marshall, M. Kofranek, H. Lischka and A. Karpfen, *J. Chem. Phys.* 91, 5154 (1989).

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

Address of Jensen: Institute of Physical Chemistry Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-6300 Giessen, Germany.

Address of Karpfen, Lischka and Kofranek: Institut für Theoretische Chemie und Strahlenchemie, Universität Wien, Währingerstrasse 17, A-1090 Vienna, Austria.

TE6 (3:00)

P-TYPE DOUBLING IN THE INFRARED SPECTRUM OF NO-HF

Wafaa M. Fawzy, Gerald T. Fraser, Jon T. Hougen and Alan S. Pine

The HF stretching band of the NO-HF open-shell complex has been recorded using a molecular-beam optothermal spectrometer. The spectrum exhibits P-type doubling indicative of an unpaired electron spin coupled to the rotational angular momentum of a bent complex with substantially quenched electron orbital angular momentum. From $\overline{B}'' = 0.111320(17)$ cm^{-1}, and an off-axis angle for the NO of 30°, the zero-point center-of-mass separation is estimated to be 3.4396(3) Å. The HF frequency shift of -84 cm^{-1} indicates that the complex is hydrogen bonded, and the spectral intensities imply that the HF axis is aligned closely to the center-of-mass axis and the NO is off axis by 30±15°. The Renner-Teller-like orbital quenching parameter is somewhat larger than the spin-orbit constant in the free NO molecule and increases substantially upon vibrational excitation. The transitions in this band exhibit vibrational predissociation broadening of 200±40 MHz (FWHM), similar to that observed for a number of closed-shell hydrogen-bonded HF complexes.

Address of Fawzy: Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, NY 11973
Address of Fraser, Hougen and Pine: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Intermission

TE7 (3:30)

SiS, C_2H_2, AND HCN IN IRC+10216; ASTRONOMY AT 12 - 14 MICRONS WITH A POSTDISPERSED FTS

D. E. JENNINGS, R. J. BOYLE, J. J. KEADY, AND G. R. WIEDEMANN

The circumstellar cloud of the late-type star IRC+10216 contains many molecules expected in a carbon-rich environment. In the infrared these are seen in absorption against the hot star and dense inner dust. During the past few years we have been studying the high resolution spectrum in this star at 12-14 microns. This region is dominated by C_2H_2 absorption lines, and also contains strong lines of HCN.[1] This effort has culminated recently in the identification of the v=0-1 band of SiS, the first infrared detection of this molecule. Intensities and lineshapes in these spectra probe the temperature, composition and chemistry in the circumstellar envelope.

Our high resolution observations in the thermal infrared are performed with a cryogenic postdisperser coupled to the FTS at the 4-meter telescope at Kitt Peak. The postdisperser[2] acts as a narrow bandwidth cold filter, thereby reducing the noise caused by radiation at the detector. The FTS produces resolutions as high as 0.01 cm^{-1}, the best presently achieved in this spectral region.

---

[1] G. R. Wiedemann, K. H. Hinkle, J. J. Keady, D. Deming, and D. E. Jennings 1990, Astrophys. J., submitted.

[2] G. R. Wiedemann, D. E. Jennings, R. A. Hanel, V. G. Kunde, S. H. Moseley, G. Lamb, M. D. Petroff, and M. G. Stapelbroek 1989, Applied Optics, 28, 139.

Address of Jennings and Wiedemann: Planetary Systems Branch, Code 693, Laboratory for Extraterrestrial Physics, NASA Goddard Space Flight Center, Greenbelt, MD, 20771
Address of Boyle: Department of Physics and Astronomy, Dickinson College, Carlisle, PA 17013
Address of Keady: T-4, MS-B212, Los Alamos National Laboratory, Los Alamos, NM 87545

TE8 (3:47)

Electronic Spectra and Relaxation Pathways of the Ne-CN and Ar-CN van der Waals Complexes.

Y. Lin, S. K. Kulkarni, and M. C. Heaven

Ne- or Ar-CN complexes were generated by photodissociation of ICN in expansions of pure Ne or Ar. The Ne - CN complex was observed by excitation of the B-X 0-0 transition, and detection of either resonance fluorescence, or emission from the CN $A^2\Pi$ photofragment (i.e. Ne-CN(B)$\rightarrow$ Ne + CN(A)). Detection of the complex via both A and B state emissions shows that electronic predissociation takes place at a rate which competes with radiative relaxation (τ = 62ns for CN(B)). Partial rotational resolution was achieved for two sub-bands of NeCN. A preliminary analysis of this data indicates a 'T' shaped geometry, with little change in the interaction potential on electronic excitation.

Ar-CN complexes were observed by excitation of the B-X system, and detection of the CN(A) photofragment. Emission from ArCN(B), or CN(B) from photodissociation was too weak to be detected. The excitation spectrum consisted of a broad gaussian-like continuum occuring on the high-frequency side of the CN B-X 0-0 transition. This continuum is thought to arise from direct excitation of the repulsive limb of the Ar-CN(B) potential surface.

Address of Lin, Kulkarni, and Heaven: Department of Chemistry, Emory University, Atlanta, GA 30322.

TE9 (4:04)

Electronic Spectra for the Ne OH and Ne OD van der Waals Complexes.

Y. Lin, S. K. Kulkarni, and M. C. Heaven.

Laser induced fluorescence spectra have been recorded for the $A^2\Sigma^+$- $X^2\Pi_{3/2}$ systems of Ne-OH and Ne-OD. Bands of the complexes were observed in conjunction with excitation of the OH/D 1-0 and 0-0 transitions. All of the bands originated from the ground state zero-point level. Ground state rotational constants of B_0 = 0.130 ± 0.003 and 0.127 ± 0.003 cm were found for the H and D isotopes, respectively. Bands corresponding to excitation of the van der Waals stretch and bend stretch combinations in the $A^2\Sigma^+$ state were seen. The energy ranges encompassed by these features provided lower limits for the van der Waals dissociation energies of D'_0 >61.8cm^{-1} (Ne-OH(A)) and 68.5 cm[1] (Ne-OD(A)). Analysis of the vibronic structure, based on ab - initio potential energy surfaces for the upper and lower electronic states, is in progress. Preliminary results indicate that NeOH(X) executes an almost free internal rotation. As a consequence, the LIF spectrum probes a large fraction of the excited state surface. Details of the experiment and analysis will be presented.

[1] L. Harding - private communication

Address of Lin, Kulkarni, and Heaven: Department of Chemistry, Emory University, Atlanta, GA 30322.

TE10 (4:21)

THE CHARACTERIZATION OF He_2Cl_2: SPECTROSCOPY AND DYNAMICS

W. D. SANDS, C. R. BIELER AND K. C. JANDA

The two color pump-probe technique has been used to obtain the X ← B excitation spectrum and the product state distribution of vibrational predissociation of the He_2Cl_2 van der Waals molecule. The excitation spectrum is well resolved, but does not give rise to simple rotational analysis as did He_2Cl_2[1] and Ar_2Cl_2.[2] We expect that the reason for this difference is due to the wide amplitude zero point motions of the He atoms. It is possible that it is not useful to picture the He_2Cl_2 complex as having a rigid structure. As is true with the previous rare gas - Cl_2 van der Waals species, parity selection during vibrational predissociation is observed. However, unlike the Ne_2Cl_2 dissociation, at least two quanta of Cl_2 stretch are consumed to dissociate the He atoms. This demonstrates that although one quantum of Cl_2 stretching vibration has sufficient energy to break all the van der Waals bonds, there is not sufficient intramode coupling to efficiently share the energy between both He - Cl_2 bonds.

[1] S. R. Hair, J. I. Cline, C. R. Bieler and K. C. Janda, J. Chem. Phys. 90, 2935 (1989).

[2] C. R. Bieler, D. D. Evard and K. C. Janda, manuscript in preparation.

Address of Sands, Bieler and Janda: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

TE11 (4:38)

$KrCl_2$ and $XeCl_2$: CHEMICAL COMPOUNDS OR VAN DER WALLS MOLECULES?

C. R. BIELER, K. E. SPENCE AND K. C. JANDA

The observation of van der Waals isomers of $KrCl_2$ and $XeCl_2$ by two-laser pump-probe spectroscopy is reported. Both clusters are found to be T-shaped in the ground electronic state and at least up to v=11 in the B excited electronic state. Analysis of the Cl_2 fragment rotational distribution yields a van der Waals dissociation energy of 235.6 ± 2.9 cm^{-1} for the ground state for $KrCl_2$ and 287.5 ± 1.1 cm^{-1} for the ground state for $XeCl_2$. All of these observations are consistent with previously studied rare gas-Cl_2 clusters; there is no evidence at this high excitation energy that there is any chemical rearrangement in the cluster. Work is currently in progress to observe the reaction $XeCl_2(B) \rightarrow XeCl(X) + Cl$.

Address of Bieler, Spence and Janda: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

TE12 (4:55)

Fluorescence Decay and Non-Radiative Relaxation Dynamics of the $A^2\Sigma^+$ States of OH-Ar and OD-Ar.

S. K. Kulkarni, Y. Lin, and M. C. Heaven

Fluorescence decay lifetimes of electronically excited OH-Ar and OD-Ar van der Waals complexes have been measured under collision-free conditions. The lifetimes for two vibronic levels of OD(A,v'=0)-Ar were identical to that of OD(A,v'=0), indicating that the A-X transition moment was unaffected by interactions between OD(A) and Ar. Lifetimes for two vibronic levels of OH(A,v'=0)-Ar were slightly shorter than that of OH(A,v'=0). This has been interpreted in terms of a weak predissociation (OH (A,v'=0)-Ar → OH(X,v" ~ 13)+ Ar).

Implications of these lifetime measurements with regard to the assignment of recently reported LIF and emission spectra for OH/D-Ar will be discussed.

Address of Kulkarni, Lin, and Heaven: Department of Chemistry, Emory University, Atlanta, Ga 30322.

TE13 (5:07)

VIBRATIONAL PREDISSOCIATION IN ACETYLENE AND HYDROGEN CYANIDE - HYDORGEN HALIDE COMPLEXES

P.A. Block, D.C. Dayton, and R.E. Miller

The opto-thermal detection technique has been used to obtain high resolution infrared spectra of a series of acetylene and hydrogen cyanide - hydrogen halide (HCl, DCl, HBr, and HI) binary complexes. Despite the fact that the acetylenic stretch in the acetylene - HX complexes is remote from the hydrogen bond, the homogeneous linewidths are observed to be large. Of particular interest are the results obtained for acetylene - HCl and DCl, which suggest that a near resonant V - V channel is present in the former, but not in the latter, and is responsible for the short lifetimes. In the hydrogen cyanide - HX complexes, the C-H stretch is again remote from the hydrogen bond; however, the transitions associated with the C-H stretch for the HCN complexes are narrow.

Address of Block, Dayton, and Miller: Department of Chemistry, University of North Carolina, CB 3290, Chapel Hill, North Carolina, 27599

TF1 (1:30)

MEASUREMENTS OF NITROGEN-SHIFTING COEFFICIENTS OF WATER VAPOR LINES BETWEEN 5000 AND 10700 CM^{-1}

J.-P. CHEVILLARD, J.-Y. MANDIN, J.-M. FLAUD, AND C. CAMY-PEYRET

About 150 values of nitrogen-shifting coefficients of the water molecule have been measured at 300 K, for vibro-rotational lines absorbing between 5000 and 10700 cm^{-1}. At the present time, the preliminary results show that, except for a few lines, the measured N$_2$- shifting coefficients are negative : they range between 0 and -0.022 cm^{-1}. atm^{-1}, with a mean value of -0.007 cm^{-1}. atm^{-1}. The estimated uncertainties are ranging from 0.0002 to 0.003 cm^{-1}. atm^{-1} according to the quality of the line.

Address of Chevillard, Mandin, Flaud and Camy-Peyret : Laboratoire de Physique Moléculaire et Atmosphérique, Tour 13, Université Pierre et Marie Curie et CNRS, 4, Place Jussieu 75252 Paris Cedex 05, France.

TF2 (1:36)

THE $\nu_2+3\nu_3$ BAND OF $^{16}O_3$ AT 2.7 μm: LINE POSITIONS AND INTENSITIES

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

The $\nu_2+3\nu_3$ band of $^{16}O_3$ has been analyzed based on room temperature absorption spectra of ozone recorded at a resolution of 0.01 cm^{-1} with the McMath Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. An extensive and accurate set of rotational energy levels of the (013) vibrational state has been determined. These experimental levels were very satisfactorily reproduced using a Hamiltonian which takes into account the Coriolis type resonance with the levels of the non-observed (112) vibrational state. Moreover, line intensities of the $\nu_2+3\nu_3$ band measured with a relative accuracy of about 8% were least squares fitted leading to the determination of the transition moment constants of this band. Finally, using these constants, a complete listing of line positions, intensities, and lower energy levels was generated.

Address of Malathy Devi: Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185.
Address of Perrin, Flaud and Camy-Peyret: Laboratoire de Physique Moléculaire et Atmosphérique, Tour 13, Université Pierre and Marie Curie et CNRS, 4 place Jussieu, 75252 Paris Cedex 05, France.
Address of Rinsland and Smith: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225.

TF3 (1:42)

PRESSURE BROADENING OF O$_3$ LINES IN THE 3 μm REGION

M. A. H. Smith, V. Malathy Devi, and C. P. Rinsland

We have recorded a series of high-resolution absorption spectra of ozone broadened by dry air, by N$_2$, and by O$_2$ 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 2600 cm^{-1} to 3500 cm^{-1} at a resolution of 0.01 cm^{-1}. Using recently-determined line positions, assignments, and intensities[1,2], we have analyzed these spectra to determine pressure broadening and line shift coefficients for a number of lines in the $\nu_1+\nu_2+\nu_3$ and 3ν_3 band systems.

[1] M. A. H. Smith, C. P. Rinsland, V. Malathy Devi, J.-M. Flaud, C. Camy-Peyret, and A. Barbe, J. Mol. Spectrosc., 139, 171-181 (1990).

[2] C. Camy-Peyret, J.-M. Flaud, M. A. H. Smith, C. P. Rinsland, V. Malathy Devi, J. J. Plateaux, and A. Barbe, J. Mol. Spectrosc., in press (1990).

Address of Smith and Rinsland: Atmospheric Sciences Division, Mail Stop 401A, NASA Langley Research Center, Hampton, VA 23665-5225.
Address of Malathy Devi: Physics Department, College of William and Mary, Williamsburg, VA 23185.

TF4 (1:54)

TEMPERATURE DEPENDENCE OF N_2 - BROADENING COEFFICIENTS IN THE ν_1 AND ν_3 BANDS OF OZONE

M. N. SPENCER AND C. CHACKERIAN, JR.

Pressure broadening coefficients of ozone are necessary for a number of applications dealing with understanding the health of the Earth's atmosphere. We report here measurements of the nitrogen broadening coefficients of selected rovibrational transitions of ozone in the ν_1 (1100 cm^{-1}) and ν_3 (1042 cm^{-1}) bands in the temperature range 296 K to 200 K. The temperature dependence is expressed as being proportional to the n'th power of T where n is the experimentally determined power dependence which for our experiments is in the vicinity of -0.75. Finally, we compare our values of n with theoretical calculations made by Gamache[1] which use quantum Fourier transform theory with improved dynamics (QFT-ID).

[1]R. Gamache, J. Mol. Spectrosc. 114, 31 (1985).

Address of Spencer and Chackerian: NASA AMES Research Center, MS 245/4, Moffett Field, CA 94035-1000.

TF5 (2:11)

MEASUREMENT OF COLLISION BROADENING BY HYDROGEN AND NITROGEN OF ACETYLENE LINES IN THE 14 μm REGION USING A TUNABLE DIODE LASER SPECTROMETER

J. F. BRANNON, JR., M. WEBER, AND W. E. BLASS

Using a tunable diode laser system at 0.0005cm^{-1} resolution, the line widths of acetylene, broadened by hydrogen and nitrogen, are currently being studied. Hydrogen and nitrogen have been previously used as perturbers in the ν_5 band of C_2H_2 by Blass and Chin,[1] while oxygen and nitrogen have been used as the perturbing gases by Lambot et al.[2] The collisional line widths are determined in a least mean squares sense from the aggregate set of observations using a stepwise multiple regression program with bi-weights.[3] The collision broadening coefficients will be determined for both hydrogen and nitrogen. Current work includes verification of previous results and the extension of line width measurements over a larger range of J values for ν_5 and several 14 μm hot bands.

[1]W. E. Blass and V. W. L. Chin, JQSRT 38, 185 (1987).
[2]D. Lambot, G. Blanquet and J.-P. Bouanich, J. Mol. Spec. 136, 86 (1989).
[3]K. F. Lin, W. E. Blass, and N. M. Gailar, J. Mol. Spec. 79, 151 (1980).

Address of Brannon, Weber, and Blass: Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200.

TF6 (2:23)

MOLECULAR PARAMETER RETRIEVAL FROM SPECTRA IN THE PRESENCE OF COMPLEX INTRAMOLECULAR ENERGY PIPELINES USING A SUPERCOMPUTER WITH A VECTOR PROCESSOR

W. E. BLASS

Retrieval of molecular parameters from the highest resolution molecular spectra is complicated by the existence of intramolecular energy conduits.[1-3] These energy pathways are referred to as accidental resonances and arise due to the model used in the characterization of rotation-vibration energies of gas phase molecules. Highly precise analyses are required to support the studies of planetary atmospheres including that of the earth. Without achieving the results that are the goal of this project, production of precise calculated spectral atlases for molecules such as acetylene and ethane in the 10 micrometer atmospheric window would not be possible.

A model including more than 20 interacting vibrational states for a symmetric deuterated halo-fluoride serves as the basis for a case study of the numerical retrieval of molecular parameters. This treatment of inverse eigenvalue problem uses the Hellman-Feynman Theorem[4-6] to calculate the changes in the molecular energies of the interacting states as a function of the molecular parameters in a necessarily iterative nonlinear least mean square analysis system.

Since hundreds of iterations are necessary to converge the system to physically meaningful results, the porting of the system to the vector 3090/200 makes explorations of the system possible. Typical iteration cycle times run to 15 minutes of cpu time at vectorization levels of from 50 to 70%. A complete analysis, presuming that no more than a few false paths are followed in the process, is estimated to consume 30 to 50 hours of 3090/200E cpu time at approximately 18 to 30 hours of vector facility time (60% vectorization). Performance enhancements of a factor of 40 over a 6 VUP system were achieved.

[1] H. H. Nielsen, Handbuch der Physik (S. Flugge, ed.)., Vol. XXXVI/1, p.173, Springer-Verlag, Berlin, 1959.
[2] G. Amat, H. H. Nielsen, and G. Tarrago, Rotation-Vibration of Polyatomic Molecules, Dekker, New York, 1971.
[3] W. E. Blass, Appl. Spectrosc. Revs. 23,1 (1987).
[4] H. Hellmann, Einfuhrung in die Quantumchemie, p.285, Deuticke, Vienna, 1937.
[5] R. P. Feynman, Phys. Rev. 56, 340 (1939).
[6] W. F. Rowe and E. B. Wilson, J. Mol. Spectrosc., 56, 163 (1975).

Address of Blass Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200

TF7 (2:40)

DETERMINATION OF ATOMIC AND MOLECULAR SPECIES IN SPECTRA USING ARTIFICIAL NEURAL NETWORKS

A. L. Sumner, S. K. Rogers, P. J. Grigsby, M. Kabrisky, and D. Norman

Spectral analysis involving the determination of atomic and molecular species present in a spectrum of multi-spectral data is a very time consuming task, especially considering the fact that there are typically thousands of spectra collected during each experiment. Due to the overwhelming amount of available spectral data and the time required to analyze this data, a robust automatic method for doing at least some preliminary spectral analysis is needed. This research focused on the development of a supervised artificial neural network with error correction learning, specifically a three-layer feed-forward, back-propagation perceptron. The objective was to develop a neural network which would do the preliminary spectral analysis and save the analysts from the task of reviewing thousands of spectral frames. The input to the network is raw spectral data with the output consisting of the classification of both atomic and molecular species in the source.

The idea that computers can do the spectral identification of molecular and atomic radiators goes back to the earliest days of computers. Most commercially available spectral identification programs use some type of statistical pattern recognition technique utilizing a database of known species. One of the greatest advantages of a neural network over traditional pattern recognition techniques is the ability of the neural network to learn. Once a neural network has been trained, it is able to make classifications with a general amount of robustness not normally found in statistical recognizers. One major advantage of neural networks over statistical methods is that new species can be recognized by just showing the neural network examples rather than the time consuming task of trying to statistically characterize the new species. Neural networks are not able to recognize everything and will never replace the analyst, but they can aid the analyst in picking out species where a statistical technique would have missed them.

Address of Sumner and Grigsby: Foreign Technology Division/SQDEO, Wright-Patterson Air Force Base, Ohio, 45433-6508
Address of Rogers, Kabrisky, and Norman: Air Force Institute of Technology/ENG, Wright-Patterson Air Force Base, Ohio, 45433-6583

Intermission

TF8 (3:10)

BAND AND LINE STRENGTHS OF FIFTEEN MICRON CARBON DIOXIDE BANDS FROM GAS SAMPLES AT HIGH TEMPERATURES

MICHAEL HOKE AND MARK ESPLIN

Spectral data of samples of carbon dioxide, of natural isotopic abundance, heated to 800 K are being analyzed to yield estimates of band and line strengths. The sample cell windows are necessarily at room temperature[1]; consequently the gas sample temperature is not homogenous. Analysis techniques are being developed to cope with this problem. The interferometric measurements were made using the GL (Geophysics Laboratory/ AFSC) high resolution Fourier transform spectrometer[2] employing a maximum resolution of 0.004 cm^{-1}.

This work was supported by the Air Force Office of Scientific Research (AFOSR) as part of GL task 2310G1.

[1]William S. Dalton and Hajime Sakai, Applied Optics 19, 2413 (1980).
[2]Mark P. Esplin and Laurence S. Rothman, J. Mol. Spec. 116, 351 (1986).

Address of Hoke: OPI/GL(AFSC), Hanscom AFB, Bedford, Ma. 01731.

Address of Esplin: Stewart Radiance Laboratory, Utah State University, 139 The Great Road, Bedford, Ma. 01730.

TF9 (3:22)

LINE POSITIONS OF CO_2 IN THE 580 TO 940 CM^{-1} REGION AT ELEVATED TEMPERATURES

MARK P. ESPLIN AND MICHAEL HOKE

A CO_2 sample of natural isotopic abundance has been heated to 800 K in a high temperature absorption cell of pathlength 1 3/4 meters. Sample pressures ranged from 5 to 40 torr. The spectral measurements were made using the AFGL (Air Force Geophysics Laboratory) high resolution Fourier transform spectrometer with resolutions of up to 0.004 cm^{-1}. Many "hot bands" were clearly seen in the experimental spectra. Line positions determined from the measurements made at different pressures were merged into a single data set, and then a weighted least-squares fit was used to obtain improved vibration-rotation constants. Effective vibration-rotation constants for these bands will be presented at the symposium.

This work was supported by the Air Force Office of Scientific Research (AFOSR) as part of AFGL Task 2310G1.

Address of Esplin: Stewart Radiance Laboratory, Utah State University, 139 The Great Road, Bedford, Ma 01730.

Address of Hoke: OPI/Air Force Geophysics Laboratory, Hanscom AFB, Bedford, Ma 01730.

TF10 (3:34)

CENTRIFUGAL CORRECTIONS TO ROTATIONAL INTENSITIES

H. M. PICKETT

Centrifugal corrections to rotational intensities for asymmetric rotors involve intensity borrowing from infrared transitions, as well as corrections to the rigid rotor wave functions. The latter type of correction is easily accomplished by using rotational programs that diagonalize the full rotational Hamiltonian instead of just the rigid rotor part. Intensity borrowing calculations require knowledge of the sign and magnitude of the infrared transition dipoles. Traditionally intensity corrections have been made using perturbation theory. The approach taken here is to directly diagonalize the Hamiltonian for the ground state and fundamentals using theoretical off-diagonal elements. When this calculation is used to refit the ground state energies, the resulting second order centrifucal constants should approach zero. In addition, the first order perturbations of the infrared intensities should be reproduced. It will be shown   effects of Watson indeterminancies and planarity conditions are accounted for in this type of calculation.

Results of calculations for ozone and water will be shown. The calculations for water reproduce previously calculated corrections on the AFGL tapes, but corrections for ozone have not been done previously. Corrections for water range from 0.95 to 1.55, while corrections for ozone range from 0.78 to 1.25. However, the biggest corrections tend to be for the weaker lines.

Address of the author: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

TF11 (3:51)

HERMAN-WALLIS FACTORS FOR CARBON DIOXIDE CALCULATED BY DIRECT NUMERICAL DIAGONALIZATION (DND)

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

Calculations of Herman-Wallis factors for observed isotopic variants of carbon dioxide have been made by including the mixing of the perpendicular and parallel components of the dipole moment function which results from the Coriolis diagonalization. Comparisons with experiment and recent calculations using perturbation theory will be presented.

Comparison of the observed and calculated Herman-Wallis parameters for the P- and R-branches will be shown for several bands in the 5- and 3-μm regions. Good agreement has been obtained for most of the perpendicular bands in these regions. One particular band at 1881 cm^{-1} (20003 - 01101) has an experimental band intensity about one half that of the DND prediction. This prediction is effected strongly by the correlation with the ground state transition at 1932 cm^{-1} (11102 - 00001). When the effective transition intensities are plotted as functions of m for the P- and R-branches of the 1881 cm^{-1} band, one realizes much better agreement with the actual observed line intensities.

The Q-branch Herman-Wallis parameters for the 15-μm region also show excellent agreement with recent observations.[1] A phenomenon which has not been fully appreciated before is the presence of a separate term linear in J, derived from the Coriolis interaction of Q-branch lines. The effect in this region is that the J(J+1) dependence of the Q-branch Herman-Wallis factors, as derived for example by Watson,[2] is not strictly correct. This effect is even more striking in the 5- and 3-μm regions.

1. J.W.C. Johns and J. Vander Auwera, J.Mol.Spectrosc. (in press).
2. J.K.G. Watson, J.Mol.Spectrosc. 125, 428-441 (1987).

Address of Wattson and Newburgh: Visidyne, Inc., 10 Corporate Place, S. Bedford St., Burlington, MA 01830

Address of Rothman: Optical Physics Division, Air Force Geophysics Laboratory, Hanscom AFB, MA 01731-5000

TF12 (4:08)

DIODE LASER SPECTRA OF SiS IN THE REGION FROM 700 TO 800 CM^{-1}. ROTATIONAL CONSTANTS AND FOREIGN-GAS BROADENING PARAMETERS.

D. C. REUTER, AND J. KURTZ

Infrared spectra of the SiS molecule have been obtained using the GSFC tunable lead-salt diode laser spectrometer[1]. The spectrometer was used in the single beam mode and spectra were acquired by multi-sweep averaging. Frequency calibration was performed using precisely known C_2H_2 transition frequencies and a high-finesse etalon.

Molecular SiS was made by heating a quartz cell containing a mixture of SiS_2 and Si to temperatures in the range of 770 to 1100 C. At these temperatures spectra may be obtained for J-values ranging up to ~ 100. Several hot-band transitions were also evident. Foreign-gas broadening parameters were measured for N_2 and He. The usual rotational constants were derived.

[1] D. E. Jennings, Appl. Opt 19, 2695 (1980).

Address of Reuter and Kurtz: Planetary Systems Branch, Code 693, Laboratory for Extraterrestrial Physics, NASA Goddard Space Flight Center, Greenbelt, MD, 20771

TF13 (4:25)

HALFWIDTH AND PRESSURE-INDUCED LINESHIFT COEFFICIENTS IN THE ν_3, $\nu_2+\nu_4$, $\nu_3+\nu_4$ AND $\nu_1+\nu_4$ BANDS OF $^{12}CH_4$

D. Chris Benner, V. Malathy Devi, Curtis P. Rinsland and Mary Ann H. Smith

Air-broadened halfwidth and pressure-induced lineshift coefficients were determined for transitions in the ν_3 fundamental and the $\nu_2+\nu_4$, $\nu_3+\nu_4$ and $\nu_1+\nu_4$ combination bands of $^{12}CH_4$ by analyzing room temperature absorption spectra in the 2800 to 3000 and 4136 to 4400 cm^{-1} spectral regions recorded at 0.01-cm^{-1} resolution. In addition, N_2-broadened halfwidth and pressure-induced lineshifts were determined for the ν_3 and $\nu_2+\nu_4$ bands. The data were obtained with the McMath Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. A high purity natural sample of methane diluted by dry air or N_2 to a mixing ratio of ~0.01 in a 5 cm to 1.5 m absorption cell was used to obtain the data. The total gas sample pressures ranged from 60 to 550 Torr. The halfwidth and pressure-shift coefficients were retrieved using a non-linear least-squares curve fitting technique. Determination of the unshifted line positions was improved by fits to spectra of pure methane at low pressures. The vibrational dependence of the retrieved parameters will be discussed by comparing the values with those obtained for similar transitions in other methane bands.

Address of Benner and Malathy Devi: Department of Physics, College of William and Mary, Williamsburg, VA 23185.
Address of Rinsland and Smith: Mail Stop 401A, Atmospheric Sciences Division, NASA Langley Research Center, Hampton, VA 23665-5225.

TF14 (4:42)

PRELIMINARY RESULTS ON THE ANALYSIS OF THE PENTAD OF $^{13}CH_4$

J.M.JOUVARD, B.LAVOREL, J.P.CHAMPION and L.R.BROWN

Preliminary results on the simultaneous analysis of infrared and Raman data of $^{13}CH_4$ in the 3-μm region $(\nu_1,\nu_3,2\nu_2,\nu_2+\nu_4,2\nu_4)$ will be presented.

The infrared spectrum of $^{13}CH_4$ (90% enriched) has been recorded with the Fourier Transform Spectrometer at Kitt Peak National Observatory. Line positions have been mesured with a relative accuracy of 0.0001 cm^{-1} (for well isolated lines) using 0.0118 cm^{-1} resolution spectra.

In order to compensate for the lack of infrared information about low J transitions of vibrational bands forbidden in infrared, two spectra of the $\nu_1(A_1)$ and $2\nu_2(A_1)$ Q-branches have been recorded in Dijon by Inverse Raman Spectroscopy with an instrumental resolution of 0.0022 cm^{-1}. They were recorded at room temperature and at pressures of 3 torr for ν_1 and 36 torr for $2\nu_2$. Line positions have been measured with a precision of 0.001 cm^{-1} using a profile fitting procedure.

Raman and infrared data were combined in a weighted least-squares fit to determine vibration-rotation constants. We used an effective tensorial Hamiltonian taking into account all interactions within the pentad up to the fourth-order of approximation (206 parameters).

The preliminary analysis has been carried out throughout J=13 involving 1200 data reproduced with a standard deviation of 0.0007 cm^{-1}, approximately 30 times better than the most recent results published on the $^{12}CH_4$ pentad.

Address of J.P.Champion, J.M.Jouvard and B.Lavorel:
    Laboratoire de Spectronomie Moléculaire et Instrumentation Laser,
  Université de Bourgogne, U.A. CNRS N°777, 6 Bd Gabriel 21100 Dijon, France.

Address of L.R.Brown:
    Jet Propulsion Laboratory, California Institute of Technology,
        4800 Oak Grove Drive, Pasadena, California 91109.

TF15 (4:54)

BROADENING AND SHIFTS OF CH₄ LINES IN THE ν₄ BAND AT LOW TEMPERATURES

M. A. H. Smith, V. Malathy Devi, C. P. Rinsland, and D. C. Benner

We have recorded a series of high-resolution absorption spectra of methane broadened by dry air and by N_2 at low temperatures using the McMath Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. The spectra cover a wavenumber range from approximately 500 cm^{-1} to 1500 cm^{-1} at a resolution of 0.01 cm^{-1}. A 50 cm double-walled Pyrex absorption cell cooled by circulating chilled ethanol enabled us to obtain spectra over a temperature range from 2°C to -63°C. These spectra have been analyzed to determine pressure broadening and line shift coefficients at low temperatures for a number of lines in the ν₄ fundamental band of $^{12}CH_4$. These values, along with previously-determined room-temperature coefficients[1], have been used to examine the temperature-dependence of the air- and N_2-broadening and shift coefficients for these CH₄ lines.

[1] C. P. Rinsland, V. Malathy Devi, M. A. H. Smith, and D. C. Benner, Appl. Opt. 27, 631-651 (1988).

Address of Smith and Rinsland: Atmospheric Sciences Division, Mail Stop 401A, NASA Langley Research Center, Hampton, VA 23665-5225.
Address of Malathy Devi and Benner: Physics Department, College of William and Mary, Williamsburg, VA 23185.

TF16 (5:11)

COLLISIONAL LINE BROADENING CALCULATIONS FOR HF-He

Mark Thachuk and Frederick R. W. McCourt

A study of collisional line broadening calculations using a variety of theoretical methods on an atom-diatom system has been performed. The full close coupled quantal calculation is compared with the centrifugal sudden approximation (CSA), the "corrected" centrifugal sudden approximation (CCSA), the infinite order sudden approximation (IOSA) and a semiclassical trajectory method for the HF-He interaction. The accuracy and relative cost of each method will be discussed.

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

TG1 (1:30)

QUADRUPOLE N₂ LINES AT 4.1 μm STUDIED WITH A DIODE LASER AND AN ABSORPTION PATH OF 5.016 km-UPDATE

PAUL P. BALOG, MICHAEL E. MICKELSON, AND K. NARAHARI RAO
Ohio State and Denison Universities

Three quadrupole vibration-rotation absorption lines of molecular nitrogen were detected using second derivative spectroscopy in the 4.1 micron region, using a high resolution diode laser spectrometer and a White-type multiple reflection absorption cell, adjusted to a path length of 5.016 km. Accurate line positions, pressure broadening parameters, integrated absorption coefficients, and quadrupole moment derivatives were determined for two of these transitions. The S(10) quadrupole line was scanned at three pressures in the range 730 to 837 Torr, while the S(12) line was studied at five pressures, ranging from 729 to 950 Torr, to determine pressure-broadened line widths. All the measurements were carried out at a temperature of 297°K.

The line shapes and the full-width-at-half-maximum values provided some evidence of collisional narrowing.

Address of Balog and Rao: Department of Physics, The Ohio State University, Columbus, Ohio 43201.
Address of Mickelson: Department of Physics and Astronomy, Denison University, Granville, Ohio 43023.

TG2 (1:47)

INTEGRATED ABSORPTION COEFFICIENT OF GENERAL ZERO-PHONON DOUBLE TRANSITION OF THE TYPE $(\Delta J=\ell)_{v_1 \leftarrow 0} + S_{v_2 \leftarrow 0}(0)$ IN SOLID PARA HYDROGEN

T.K. BALASUBRAMANIAN, R.D'SOUZA, ROMOLA D'CUNHA, AND K. NARAHARI RAO

In continuation of our theoretical efforts[1,2] relating to the (induced) infrared spectrum of solid H_2, we have treated zero-phonon double transitions in which the multipolar induction proceeds via the anisotropic part of the polarizability of H_2. This has led us to develop a general formula for the integrated absorption coefficient of a double transition in which one para molecule undergoes the rovibrational transition $(v'=v_1, J'=\ell) \leftarrow (v''=0, J''=0)$ and another para molecule the $S(\Delta J=2)$ transition $S_{v_2 \leftarrow 0}(0)$, following the absorption of a photon. Using this we could estimate the absorption intensities of some W+S type double transitions in solid para H_2. Details of the theory will be discussed.

[1] T.K. Balasubramanian, R. D'Souza and K. Narahari Rao, 43rd Symposium on Spectroscopy, Columbus, Ohio, (1988) Paper RF2.

[2] T.K. Balasubramanian, R. D'Souza, Romola D'Cunha and K. Narahari Rao, Can.J.Phys. 67, 79 (1989).

Address of Balasubramanian, D'Souza and D'Cunha: Spectroscopy Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay- 400 085, India.

Address of Narahari Rao : Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210.

TG3 (1:59)

PREDICTED INTENSITY OF THE $S_0(0) + S_0(0) + S_0(0)$ TRIPLE
TRANSITION IN THE INFRARED SPECTRUM OF SOLID ORTHODEUTERIUM

R. H. Tipping, Q. Ma, and J. D. Poll

The predicted intensity of a new absorption feature in the spectrum of solid o-D_2 corresponding to three molecules making simultaneous rotational transitions from $J = 0$ to $J = 2$ is calculated. This transition should occur near 555 cm^{-1}, and arises primarily through the mixing of rotational levels by the quadrupole-quadrupole interaction. Although the calculated intensity is small (less than 1% of that of the weak $W_0(0)$ transition), it nevertheless may be observable. Such an observation would be of interest, because by comparing the experimental intensity with that predicted on the basis of mixing of levels, one can set an upper limit to the contribution to such a feature from non-additive (three-body) dipoles.

Address of Tipping and Ma: Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL 35487-0324.

Address of Poll: Department of Physics, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

TG4 (2:11)

HIGH RESOLUTION INFRARED SPECTROSCOPY OF SOLID HYDROGEN: ANALYSIS OF THE FINE STRUCTURE OF THE $Q_{1\leftarrow0}(1)$ TRANSITION OF ORTHOHYDROGEN IMPURITY IN SOLID PARAHYDROGEN

MAN-CHOR CHAN AND TAKESHI OKA

Complicated structure consisting hundreds of transitions with typical linewidth of ~20 MHz was observed in the Q branch of the fundamental band of solid p-H_2 (containing ~0.2% o-H_2) using high resolution difference frequency infrared laser spectroscopy.[1] Similar to the microwave spectrum due to orientational splittings of the nearest neighbor and the next nearest neighbor of o-H_2 pairs in the ground vibrational state,[2] our spectrum may also be ascribed to the orientational splittings of the vibrational transition of a pair of interacting o-H_2 molecules. However, infrared spectroscopy allows us to observe splittings of interacting pairs which are further apart. These splittings appear as features close to the $Q_{1\leftarrow0}(1)$ transition (at 4146.5673 cm^{-1}) of isolated o-H_2. Our spectrum also shows an additional complexity arising from the hopping of the vibrational excitation energy between the interacting pair. The analysis of this effect and the preliminary assignment will be discussed.

[1] M.-C. Chan, M. Okumura, B. D. Rehfuss, and T. Oka, TG1, Forty-fourth Symposium on Molecular Spectroscopy, The Ohio State University, 1989.

[2] W. N. Hardy and A. J. Berlinsky, *Phys. Rev. Lett.* **34**, 1520 (1975).

Address of Chan and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, the University of Chicago, Chicago, IL 60637.

TG5 (2:28)

HEXADECAPOLE-INDUCED $\Delta J = 4$ INFRARED TRANSITIONS OF SOLID DEUTERIUM

MAN-CHOR CHAN AND TAKESHI OKA

Rovibrational transitions of solid deuterium in the 3 μm region were studied using Fourier transform infrared spectroscopy. Spectra of solid ortho enriched and normal deuterium have illustrated a variety of interesting phenomena of collision induced absorption in solid state.[1] Observed transitions were assigned to be the U bran~' 1) of the fundamental band of deuterium. In addition to the previously observed $U_{1\leftarrow0}(0)$ transition,[2] we o. ·' $_{1\leftarrow0}(1)$ transition. From the experimental integrated absorption intensity, the transition hexadecapole moment was uc.~mined using the analytic expression of Poll and Tipping.[3] The effect of $J = 1$ paradeuterium on the intensities and linewidths of the transitions will be discussed.

[1] J. Van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).

[2] S. B. Baliga, R. Sooryakumar, K. N. Rao, R. H. Tipping, and J. D. Poll, *Phys. Rev. B* 6, 2496 (1987).

[3] J. D. Poll and R. H. Tipping, *Can. J. Phys.* 56, 1165 (1978).

Address of Chan and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, the University of Chicago, Chicago, IL 60637

TG6 (2:45)

2-D IMAGES OF DENSITY DISTRIBUTIONS OF O_2 IN SPECIFIC v,J QUANTUM STATES OBTAINED VIA PREDISSOCIATIVE LASER INDUCED FLUORESCENCE

GYUNG-SOO KIM, LYNNE M. HITCHCOCK, AND ERHARD W. ROTHE, GENE P. RECK

We report data from a new method, originally described by P. Andresen[1] et al., that produces instantaneous 2-D images of state-specific molecular concentrations, and is ideal for observation of gaseous, turbulent reacting systems. This excimer-laser based approach yields state-specific 2-D distribution for each of a number of constituents and it should also yield temperature fields. The method applies within a wide temperature and pressure range because it is based upon a novel variant of laser induced fluorescence (LIF) which eliminates the collisional quenching that limits the quantitative use of normal LIF to pressures <≈10 torr. This limitation is overcome by exciting molecules that are in a selected ground quantum state to predissociating states which are so short-lived (1-10ps) that there is no time for quenching collisions. The imaging technique uses a ribbon of narrow-band laser-light that passes through a medium. The laser's wavelength is tuned, in the range 193-193.8nm, to a desired transition. Fluorescence light is recorded by an intensified CCD camera that is pointed at 90° to the path of the light-ribbon. Our narrow-band laser is bright enough that a single pulse yields a 2-D image. The laser is also a "flashbulb" that determines the time scale. Our laser pulse lasts ≈15ns which is essentially "stop action" for turbulent phenomena. If we assume a molecular velocity of one km/s, a molecule would move only ≈15μm during the pulse. As an example, we show 2-D images of vibrationally excited O_2 in several types of open flames.

[1] P. Andresen, A. Bath, W. Gröger, H. W. Lülf, G. Meijer, and J. J. ter Meulen, Appl. Opt. 27, 365 (1988).

Address of Kim, Hitchcock and Rothe: Department of Chemical Engineering, Wayne State University, Detroit, MI 48202
Address of Reck: Department of Chemistry, Wayne State University, Detroit, MI 48202

Intermission

TG′1 (3:00)

VIBRATIONAL CIRCULAR DICHROISM STUDIES OF AZIDOMETHEMOGLOBIN AND AZIDOMETMYOGLOBIN

T. B. FREEDMAN, N. RAGUNATHAN, L. A. NAFIE, P. J. LARKIN, S. A. ASHER, B. SPRINGER, S. SLIGAR AND R. W. NOBLE

We have investigated the vibrational circular dichroism associated with the antisymmetric stretch of azide ion bound to several methemoglobins (human, carp) and metmyoglobins (horse, sperm whale, reconstituted with modified heme, and mutant). There is no VCD intensity corresponding to the absorption feature arising from azide bound to high-spin iron. A negative VCD feature ($g = -1.3 \times 10^{-3}$) is observed for azide ion bound to low-spin iron; this feature is absent in a mutant myoglobin in which the distal histidine is replaced with glycine. For the normal proteins, the VCD anisotropy ratio is slightly larger in myoglobin compared to hemoglobin, but is not affected by using D_2O rather than H_2O solvent. Our results differ in magnitude from those originally reported by Marcott et al.[1] The relationship between the structure of the ligand binding site in the heme proteins and the VCD intensity will be discussed.

[1]Marcott, C.; Havel, H.A.; Hedland, F.; Overend, J.; Moscowitz, A. In *Optical Activity and Chiral Discrimination*, Mason, S. F., Ed., Reidel, Dordrecht, 1979, pp 289-292.

Address of Freedman, Ragunathan, and Nafie: Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100.
Address of Larkin and Asher: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.
Address of Springer and Sligar: Department of Biochemistry, University of Illinois, Urbana, IL 61801.
Address of Noble: Department of Medicine and Biochemistry, State University of New York, Buffalo, NY 14215.

TG′2 (3:12)

VIBRATIONAL CIRCULAR DICHROISM STUDIES OF DEHYDROPHENYL ALANINE PEPTIDES

M. G. PATERLINI, T. B. FREEDMAN, C. PRATESI, O. PIERONI

The solution conformations of three peptides containing dehydrophenyl alanine (Δ^Z - Phe) have been determined from their NH-, CH- and C = O- stretching vibrational circular dichroism spectra. We have found that the peptides Ac-Δ^Z-Phe-L-Ala-OMe (1), Ac-Δ^Z-Phe-Δ^Z-Phe-L-Ala-OMe (2), and Boc-L-Ala-Δ^Z-Phe-Gly-Δ^Z-Phe-L-Ala-OMe (3) are all stabilized in chloroform solution by intramolecular hydrogen bonds. The conformation of the C_7-ring in peptide 1 and C_{10}-ring (type I β-turn) in peptide 2 involving the Δ^Z-Phe residues is determined by the formation of a C_5-ring in the terminal L-Ala residue. Peptide 3 assumes several intramolecularly hydrogen-bonded conformations including a type III β-turn.

Address of Paterlini and Freedman: Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100.
Address of Pratesi and Pieroni: Instituto di Biofisica, 56100 Pisa, Italy.

TG′3 (3:29)

THEORETICAL AND EXPERIMENTAL COMPARISON OF INCIDENT CIRCULAR POLARIZATION (ICP) AND SCATTERED CIRCULAR POLARIZATION (SCP) RAMAN OPTICAL ACTIVITY

L. HECHT, D. CHE AND L.A. NAFIE

A complete theory of natural Raman optical activity (ROA) covering all forms of ROA, ICP, SCP and DCP (dual circular polarization), as a function of scattering angle and incident or scattering polarizer angle, has been recently developed in our laboratory.[1] We use the results of this theory to predict differences in ICP and SCP ROA experiments. In the cases of (+)-trans-pinane and (-)-α-pinene, we have measured depolarized ICP and SCP and ROA for 90° scattering angle and find no difference in ROA intensity to within experimental error. Theoretical justification of this result and predictions of where differences between ICP and SCP ROA are expected to occur will be discussed.

[1]L. Hecht and L.A. Nafie (unpublished results).

Address: Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100

TG´4 (3:46)

INVESTIGATIONS OF THE THERMOLYSIS KINETICS OF DIDEUTERIOCYCLOPROPANE BY VIBRATIONAL CIRCULAR DICHROISM AND FTIR SPECTROSCOPIES

L. A. NAFIE, T. B. FREEDMAN, K. M. SPENCER, S. J. CIANCIOSI AND J. E. BALDWIN

The gas-phase thermolysis kinetics of R,R-cyclopropane-1,2-d_2 have been monitored by using vibrational circular dichroism to follow the loss of optical activity due to the production of the *trans* S,S-enantiomer and the achiral *cis* isomer, and by using partial least squares fitting of the FTIR bands in the 1000 cm^{-1} region to measure the production of the *cis* isomer. The results of these measurements and their implications for the mechanism of ring opening deduced from both of the kinetic measurements will be discussed.

Address: Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100

TG´5 (3:58)

ROTATIONALLY RESOLVED MAGNETIC VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF NO

R. K. YOO, B. WANG, P. V. CROATTO, AND T. A. KEIDERLING

We have measured the magnetic vibrational circular dichroism (MVCD) spectrum of NO at 0.5 cm^{-1} resolution using an FTIR spectrometer with a superconducting magnet operated at 8T. These spectra were so intense that saturation effects were evident. The MVCD of individual rotational bands could be interpreted in large part as psuedo-A terms arising from coupling of the spin-orbit split components of the $^2\Pi$ ground term. In the P branch these components can be resolved, and the B term associated with the stronger absorbing $^2\Pi_{3/2}$ lines were positive and those with the weaker $^2\Pi_{1/2}$ lines were about the same intensity but negative. The unresolved Q branch has a negative B term. The ease of observation of the NO MVCD is consistent with earlier observations of Zeeman modulated absorption spectra of radicals including NO. Actual signal size increases by an order of magnitude in going from 2 cm^{-1} to 0.5 cm^{-1} resolution. Attainment of the higher resolution required a modification of our FTIR system to create an artificial center burst on the polarization modulated signal.

Address: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, IL 60680 USA

TG´6 (4:15)

MOLECULAR ZEEMAN SPECTROSCOPY IN THE EXCITED STATE. ROTATIONALLY RESOLVED MAGNETIC VCD SPECTRA OF CH_4

B. WANG, R. K. YOO, P. V. CROATTO, AND T. A. KEIDERLING

We have measured the magnetic vibrational circular dichroism (MVCD) spectrum of CH_4 in the t_2 symmetry deformation mode at ~1300 cm^{-1} using 0.5 cm^{-1} resolution on an FTIR spectrometer with the sample contained in the bore of a superconducting magnet operated at 8T. The MVCD spectra were partially rotationally resolved, evidencing identifiable single bands in the R branch. The MVCD of these individual bands consisted of negative A terms having a relatively constant A_1/D_0 value. This is consistent with an interpretation that the magnetic moment measured depends only on the change in rotational angular momentum. These spectra mark the first observation of molecular Zeeman spectra in a molecule with no permanent dipole moment.

Address: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, IL 60680 USA

TG′7 (4:32)

VIBRATIONAL CIRCULAR DICHROISM SPECTRA AND NORMAL MODE ANALYSES OF THF

A. A. EL-AZHARY, J. S. CHICKOS AND T. A. KEIDERLING

We have measured the vibrational circular dichroism (VCD) spectrum of $3,4$-d_2·tetrahydrofuran (d_2-THF) using an FTIR spectrometer. These spectra were broad and weak compared to previously studied isotopically chiral molecules but reliable features could be identified for several mid-ir bands. To interpret these spectra, a new force field for THF was developed based on an *ab initio* calculated force field with C_2 symmetry. For comparison, force fields with C_s and C_{2v} symmetries were also calculated. The C_2 geometry is calculated to be lowest in energy, and that force field gives the best fit after scaling to the ir and Raman data we have re-obtained from five isotopomers. Calculated VCD spectra obtained using Stephen's *a priori* model agree with experiment for many but not all modes. Fixed partial charge results are worse.

Address: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, IL 60680 USA

TG′8 (4:49)

THE VIBRATIONAL CIRCULAR DICHROISM SPECTRUM OF 2-METHYLTHIETANE

R.A. SHAW, N. IBRAHIM, AND H. WIESER

The vibrational circular dichroism (VCD) spectrum is reported for 2-methylthietane in the region of 800-1500 cm^{-1}. Based on optimized geometries and force fields at the 3-21G and 6-31G* levels of *ab initio* theory for the equatorial and axial conformers,[1] the infrared absorption and VCD intensities are calculated with the Fixed Partial Charge (FPC), Charge Flow (CF), and Atomic Polar Tensor (APT) models.

Empirically a distinction can be made for selected modes that can be used as reliable configuration markers being insensitive to conformation change, and conformation indicators reversing the VCD sign upon ring inversion while being insensitive to the absolute configuration.

Generally none of the three VCD models agree with all the observed VCD features. From the inability to predict the VCD intensities of specific modes and by comparison with analogous situations for 2-methyloxetane,[2] inferences are drawn about the adequacy of the models in certain circumstances.

[1] R.A. Shaw, N. Ibrahim, and H. Wieser, Can. J. Chem., in press.
[2] R.A. Shaw, N. Ibrahim, and H. Wieser 94, 125-133 (1990).

Address: Department of Chemistry, University of Calgary, Calgary, AB, Canada T2N 1N4.

TG '9 (5:06)

THE VIBRATIONAL CIRCULAR DICHROISM SPECTRA OF SELECTED METHYL SUBSTITUTED 6,8-DIOXABICYCLO[3.2.1]OCTANES

T. EGGIMANN, N. IBRAHIM, AND H. WIESER

The experimental infrared absorption and vibrational circular dichroism (VCD) spectra of a series of methyl substituted 6,8-dioxabicyclo[3.2.1]octanes are reported in the region 800 - 1500 cm^{-1}. Vibrational intensities were calculated with the models of atomic polar tensor (APT), fixed partial charge (FPC), and charge flow (CF), based on the scaled and refined SCF *ab initio* 3-21G force fields.

In general, APT and FPC reproduce the intensities satisfactorily and poorly, respectively, in accord with the results for the parent compound 6,8-dioxabicyclo[3.2.1]octan. In order to correct for the major shortcoming of the FPC model, different sets of charge flow parameters were employed, derived originally for propane, dimethyl ether and ethanol. It is demonstrated that only few parameters are necessary for reasonably accurate predictions of the absorption and VCD intensities. It appears that the charge flow parameters may be transferable between structurally related molecules.

---

[1] T. Eggimann, R.A. Shaw, and H. Wieser, J. Phys. Chem., submitted.

Address: Department of Chemistry, University of Calgary, Calgary, AB, Canada T2N 1N4.

TH1 (1:30)

A LIF STUDY OF RENNER-TELLER, SPIN ORBIT AND FERMI RESONANCE INTERACTIONS IN $X^2\Pi$ NCS

F. J. NORTHRUP AND <u>T. J. SEARS</u>

We report detailed measurements of a large number of bending and bend-stretch combination levels in the NCS radical in its ground $X^2\Pi$ state. The experimental data comes from a variety of laser induced fluorescence techniques, including stimulated emission pumping (SEP), conducted in a free jet cooled sample of the radical. The data include information on all the bending vibronic states up to and including three quanta of bend and the associated bend-stretch combinations of similar energy. These data have been fit to a quantum mechanical model that includes the Renner-Teller, spin orbit and Fermi resonance interactions. We found it necessary to include a new term in the effective Hamiltonian that derives from second order perturbation theory involving $H_{SO} \times H_{RT}$. This interaction, when combined with a simple single state perturber model, enables the separation of the dipolar and quadrupolar contributions to the familiar Renner-Teller interaction parameter, ε.

<u>Address of Northrup and Sears</u>: Department of Chemistry, Brookhaven National Laboratory, Upton, N.Y. 11973.

TH2 (1:47)

STIMULATED EMISSION PUMPING SPECTROSCOPY OF JET COOLED C_3

F. J. NORTHRUP, <u>T. J. SEARS</u> AND E. A. ROHLFING

We have measured the energies of many vibration-rotation states of $X^1\Sigma_g^+$ C_3 in pure bending and bend-stretch combination levels up to nearly 10000 cm^{-1} above the zero point level. The levels accessed have up to 34 bending quanta of excitation and up to 10 units of vibrational angular momentum. Combination states with up to 3 quanta of symmetric stretch have been measured at Brookhaven while those with up to 4 quanta of antisymmetric stretch have been measured at Sandia. All the bending and symmetric stretch levels can be well described as having a linear average structure albeit with very large amplitude bending motion. In contrast, excitation of the antisymmetric stretch causes the molecule to become bent. We are attempting to use our data together with the semi-rigid bender model[1] to extract effective bending potentials as a function of stretching state and progress will be reported at the meeting.

[1]P. R. Bunker and B. M. Landsberg, J. Mol. Spectro <u>67</u>, 374 (1977).

<u>Address of Northrup and Sears</u>: Department of Chemistry, Brookhaven National Laboratory, Upton, N.Y. 11973.
<u>Address of Rohlfing</u>: Combustion Research Facility, Sandia National Laboratories, Livermore, CA. 94551.

TH3 (2:04)

LASER INDUCED FLUORESCENCE OF RADICAL SPECIES PRODUCED IN A PULSED DISCHARGE AND COOLED BY SUPERSONIC EXPANSION
<u>S.-J. TSAY</u>, T. A. MILLER, AND V. E. BONDYBEY

The temperature of radicals produced in a discharge can be greater than 1000 C. In the present study, a supersonic expansion technique is used to lower the temperature of the radical species--CN, C_2 and OH produced in a pulsed D.C. discharge. From the laser induced fluorescence spectra, the rotational temperature for OH is found to be about 11 K, for CN, about 65 K.

<u>Address of Authors</u>: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

TH4 (2:16)

THE SIMPLEST HETERONUCLEAR METAL CLUSTER: LiBe-DIMER

K. PAK, R. SCHLACHTA, I. FISCHER, P. ROSMUS, AND V. E. BONDYBEY

An electronic transition with an origin near 19203 cm^{-1} is observed in vapour produced by YAG laser vaporization of a pressed pellet of Li and Be powders and assigned to LiBe diatomic. Vibrational analysis yields a $\Delta G_{\chi}'' = 295$ cm^{-1} and $\Delta G_{\chi}' = 188$ cm^{-1}. A preliminary rotational analysis gives $r_0'' \approx 2.59$ Å and $r'_0 \approx$ 3.04 Å. The spectroscopy and the electronic structure are discussed and the experimental molecular constants show a very good agreement with our recent state-of-the-art *ab initio* calculated values.

Address of Pak: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

Address of Fischer and Schlachta: Institut für Physikalische und Theoretische Chemie der Technischen Universität München, D-8046 Garching, Federal Republic of Germany.

Address of Rosmus: Fachbereich Chemie der Universität Frankfurt, D-6000 Frankfurt, Federal Republic of Germany.

Addresses of Bondybey: Institut für Physikalische und Theoretische Chemie der Technischen Universität München, D-8046 Garching, Federal Republic of Germany and Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

TH5 (2:28)

HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF ArOH AND ArOD VAN DER WAALS COMPLEXES
BOR-CHEN CHANG, DAVID W. CULLIN, JAMES M. WILLIAMSON, BRENT D. REHFUSS, LIAN YU and TERRY A. MILLER

ArOH and ArOD van der Waals complexes are of interest because they are prototypical molecules for studying the interactions between an open-shell radical and an inert gas atom. Recently, several groups have reported spectroscopic investigations of these complexes.[1,2] In particular, Fawzy and Heaven found that there are two distinct band types in ArOH. Much work has been done on the spectra, but questions remain. In collaboration with Fawzy and Heaven, we have observed LIF spectra of ArOH with higher resolution with the aim of getting more detailed information about the complex. The experiments on ArOD are also in progress. Implications of the high resolution spectra of these open-shell van der Waals complexes will be discussed.

[1]K. M. Beck, M. T. Berry, M. R. Brustein and M. I. Lester, Chem. Phys. Lett. 162, 203 (1989) and references therein.

[2]W. M. Fawzy and M. C. Heaven, J. Chem. Phys. 92, 909 (1990) and references therein.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210.

TH6 (2:45)

HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF AN INERT GAS-RADICAL VAN DER WAALS COMPLEX, NeOH
BRENT D. REHFUSS, BOR-CHEN CHANG, DAVID W. CULLIN, JAMES M. WILLIAMSON, LIAN YU AND TERRY A. MILLER

Rotationally resolved electronic spectra of NeOH have been recorded in a free jet expansion from a slit nozzle. The cluster is formed in a He/Ne expansion after photolysis of the precursor, HNO_3, with an ArF excimer laser and then probed downstream. The probe laser system is an Ar^+ pumped ring dye laser, which is fed into an excimer pumped pulsed amplifier. The pulse amplified output is then frequency doubled in a KDP crystal that is angle tuned for maximum conversion efficiency. The total fluorescence is collected and imaged through optical slits onto a photomultiplier. Analysis of the spectra is in progress and will also be discussed.

Address: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210.

TH7 (2:57)

ANTICROSSING RESONANCES IN THE FIR LMR SPECTRUM OF FO₂: A CLASSIC EXAMPLE

P. B. DAVIES, T. J. SEARS AND F. TEMPS

We have detected strong laser magnetic resonance (LMR) spectra of the FO_2 radical on two closely spaced laser lines around 919 μm. The spectra show two distinct types of pattern, one has an extended progression of narrow resonances while the other exhibits an extremely strong, broad, doublet with an unsymmetrical lineshape. We have assigned these spectra following predictions of nearby zero field transitions using our earlier mm-wave results[1]. The patterns arise from a very complicated set of anticrossings involving seven different rotational levels and give information on the off diagonal elements of the spin-rotation and spin g-factor tensors. Although the observed spectra are complicated, it is likely that similar mechanisms will dominate the FIR LMR spectra of all heavier asymmetric top radicals.

[1] M. Bogey, P. B. Davies, C. Demuynck, J. L. Destombes and T. J. Sears, Molec. Phys. 67 1033 (1989).

Address of Davies: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, U. K.
Address of Sears: Department of Chemistry, Brookhaven National Laboratory, Upton, N.Y. 11973, U.S.A.
Address of Temps: MPI für Stroemungsforschung, Bunsenstr. 10, 3400 Göttingen, W. Germany.

Intermission (3:04-3:20)

TH8 (3:25)   THIS PAPER WILL BE PRESENTED AS RD 7

A THEORETICAL STUDY OF C_2S AND C_3S.

D.J. PEESO, D.W. EWING, AND T.T. CURTIS

Two molecules recently observed in interstellar space, C_2S and C_3S, were studied via ab initio calculations. Bond lengths, rotational constants, stabilities, dipole moments, and vibrational frequencies were obtained from Hartree-Fock and second and third order many-body perturbation theory calculations. Double zeta, and double zeta plus polarization basis sets were used.
Both molecules were found to be linear with cumulated double bonds. Ground electronic configurations were found to be analogous to those of C_2O and C_3O. Calculated rotational constants are in good agreement with experiment.

Address of Peeso, Ewing, and Curtis: Department of Chemistry, John Carroll University, Cleveland, OH 44118.

TH9 (3:37)   THIS PAPER WILL BE PRESENTED AS RD 9

ACCURATE PREDICTIONS OF ROTATIONAL CONSTANTS
FOR LINEAR CARBON CHAIN MOLECULES

D.W. EWING AND D.J. PEESO

Rotational constants via ab initio theory have typically been calculated in the recent literature by using double-zeta plus polarization (DZP) basis sets, and including electron correlation to third order in the many-body perturbation scheme (MP3). An empirical correction factor, usually obtained from studies on species isoelectronic to the one of interest, is then applied to bring the predicted rotational constant closer to the experimental value.
It is shown here that using triple-zeta basis sets which include two sets of polarization functions (TZ2P), but including electron correlation to only second order (MP2) gives rotational constants which are in closer agreement to experiment without resort to empirical scaling. Furthermore, since algorithms for analytically computing energy gradients at MP2 are routinely available, much less effort is required. MP2/TZ2P rotational constants are compared to MP3/DZP and MP2/DZP rotational constants for C_3O, C_2S, and C_3S. MP2/TZ2P rotational constants for other linear carbon chain molecules are presented.

Address of Ewing and Peeso: Department of Chemistry, John Carroll University, Cleveland, OH 44118.

TH10 (3:49)

New Pattern Recognition Methods Applied to Spectra
in Transition from Regularity to Chaos:
C_2H_2 Stimulated Emission Pumping, and NO_2 MODR

S.L. Coy, K.K. Lehmann, R.J. Silbey, and R.W. Field

New pattern recognition methods have been developed, based on an multi-dimensional extended autocorrelation method. The new methods are capable of discriminating between rotational and vibrational order in unassigned spectra, can be tailored to expected spacing and intensity patterns and to expected errors in intensity measurements and line positions, and are rather insensitive to spectral noise, especially for multi-line patterns. This method also suggests a quality factor which may be applied to evaluate combination-difference combinations in assigning complex spectra.

These methods are applied to the stimulated emission pumping spectrum of C_2H_2 at energies between the regular and ergodic regions, and to NO_2 microwave optical double resonance spectra at different energies and J values. These results are related to other measures,

including the Fourier transform, Δ_3 and Σ^2 .

Lehmann: Dept. of Chemistry, Princeton U., Princeton, N.J.
Others: Dept. of Chemistry, MIT, Cambridge, Mass. 02139

TH11 (4:01)

Relaxation in $\tilde{A}\ ^1A_2\ \nu_4=1\ D_2CO$: Evidence for Coupling to a
Lumpy Continuum from Single State Depopulation Rates, and a
Reversible Intersystem Crossing Interpretation of Fluorescence Decay

S. Halle, S.L. Coy, J.L. Kinsey, and R.W. Field

We have performed two types of experiments in $\tilde{A}\ ^1A_2\ \nu_4=1\ D_2CO$: He- and self-broadened population decay measurements by transient gain spectroscopy (TGS) on several single rotational levels (SRL's), self-broadened undispersed fluorescence decay measurements on the $^rR_0$ head.

The SRL depopulation measurements allow a comparison between collisional inelastic rotational or vibrational relaxation, enhanced in self-broadening, and collisional electronic quenching, which is a larger fraction of the He-broadened rate. The large irregular variation in He-broadened SRL depopulation rates indicates that collisional electronic quenching rates vary strongly in a way consistent with the large range of S_1-S_0 matrix elements found by Polik et. al.[1].

The fluorescence decay curves at low pressures between 0.9 mTorr and 13.0 mTorr are accurately modeled by single exponential curves with a decay rate linear in pressure, in disagreement with Ref. [2]. At high pressures, the decays become strongly non-exponential. In light of recent measurements on V-V transfer in $\nu_2=1\ NH_3$ (a comparable non-planar system) [3], and of other V-V measurements, we interpret this data with a reversible intersystem crossing model, rather than the V-V model of Ref [4].

1. W.F. Polik, C.B. Moore, W.H. Miller, J.Chem.Phys. 89,3584 (1988).

2. J.Weisshaar, A.Baronavski, A.Cabello, C.B.Moore, J.Chem.Phys. 69, 4720 (1978).

3. M. Shultz, J. Wei, to be published in J. Chem. Phys.

4. J.Weisshaar, D.Bamford, E.Specht, C.B.Moore, J.Chem.Phys. 74, 226
(1981).

Kinsey: Rice U., P.O. Box 1892, Houston, Texas 77251
Others: Dept. of Chemistry, MIT, Cambridge, Mass. 02139

118

TH12 (4:18)

MONOTONIC BEHAVIOUR OF DATA FOR MAIN-GROUP TRIATOMIC MOLECULES

R. HEFFERLIN, B. D. HARTMAN, and A. M. HARPER

We are investigating the data for a variety of properties for main-group, neutral, ground-state triatomic molecules. We are seeking a simple combination of the row numbers with respect to which the data will be on smooth, monotonic (in the same direction, increasing or decreasing, for a given property) curves for all group-number combinations and for the all properties. We have been guided by (1) a conviction that the function will reduce to R_1*R_2, with which data for diatomic molecules correlate impressively well,[1] or R_1+R_2, with which they correlate somewhat less well,[1] when one atomic row number is removed; by (2) studies on the asymptotic behaviours of various properties in the heavy-molecule limit[2]; and by (3) the hypothesis that the function should not treat differently the central of the three atoms. We have investigated the functions $R_1+R_2+R_3$, $R_1*R_2*R_3$, and $R_1*R_2+R_1*R_3+R_2*R_3$, to which criterea (1) and (3) pertain; we will try others. We are doing this for dissociation energy, partition function, and equilibrium constant data,[3] and for ionization potential[4] and entropy data,[5] for growing number of column-number combinations (such as 7,2,7 -- alkaline-earth dihalides including such molecules as ClFMg). We are aware that an empirical search such as this can never be totally convincing, but some of our plotted curves appear to be predictively useful.

[1] R. Hefferlin, "Periodic Systems and their Relation to the Systematic Analysis of Molecular Data," Edwin Mellen Press, Lewiston, NY, 1989.
[2] J. F. Mucci and N. H. March, J. Chem. Phys. 22, 5099 (1985).
[3] A. J. Sauval, unpublished communication.
[4] L. V. Gurvich et al, "Energii Razryva Khimicheskikh Svyazei," Nauka, 1974.
[5] K. S. Krasnov et al, "Molekulyarnye Postoyannye Neorganicheskikh Soedineni," Khimiya, 1979.

Address of all authors: Physics Department,
Southern College, Collegedale, TN 37315-0370

TH13 (4:30)

PERIODIC BEHAVIOUR OF DATA FOR MAIN-GROUP TRIATOMIC MOLECULES

R. HEFFERLIN, R. L. MARSA, R. J. CAVANAUGH, AND K. A. LINDERMAN

We suggest that all neutral ground-state triatomic molecules (including permutation isomers) be arranged in a cubic lattice on Z_1, Z_2, and Z_3. We then create a new lattice by (1) pulling out, perpendicular to each axis, molecules with H and He, with transition-metal atoms, and with rare-earth atoms, and then (2) shoving the outer portions inward so that the lattice is again uninterrupted from its least massive member (Li_3) outward along each axis. On the basis of the behaviours of atomic and diatomic molecular[1-3] data, of the group-dynamic analyses of periodic systems,[3,4] and of previous studies of triatomic molecules,[3] we propose that data for various properties of these main-group triatomics are periodic, with a "wavelength" of 8 and with "phase" zero at rare-gas molecules, moving parallel to each axis of this new lattice. We detail this behaviour -- especially the group-number regions where the most stable molecules are found -- by (1) preparing a data base containing quality tabulated data for molecules with known structure, and (2) plotting data as color-coded balls in (cubical blocks of) the lattice (defined by fixed row numbers R_1, R_2, and R_3) and then (3) pointing out similarities in the color patterns from block to block. We supplement the demonstration by (1) preparing another data base which includes more molecules (those whose ABC order is unknown), and (2) plotting the data using Kong's method.[2]

[1] R. Hefferlin, R. Campbell, D. Gimbel, H. Kuhlman, and T. Cayton, J. Quant. Spect. Rad. Transfer 21, 315 (1979).
[2] F. A. Kong, J. Mol. Struct. 90, 17 (1982).
[3] R. Hefferlin, "Periodic Systems and their Relation to the Systematic Analysis of Molecular Data," Edwin Mellen Press, Lewiston, NY, 1989.
[4] R. Hefferlin, G. V. Zhuvikin, K. E. Caviness, and P. J. Duerksen, J. Quant. Spect. Rad. Transfer 32, 257 (1984).

Address of all authors: Physics Department,
Southern College, Collegedale, TN 37315-0370

TH14 (4:42)

SiH₃ ELECTRONIC STATES OBSERVED BY 2+1 AND 3+1 RESONANCE ENHANCED MULTIPHOTON
IONIZATION SPECTROSCOPY.

R. D. Johnson III, J. W. Hudgens

Electronic spectra of SiH₃ (silyl radical) have been observed previously[1] by
2+1 Resonance Enhanced Multiphoton Ionization (REMPI) Spectroscopy.
Predominantly transitions from the silicon $3p_z$ orbital (the HOMO) to np Rydberg
states were observed. These two-photon transitions seem to obey the atomic-like
selection rule of $\Delta l = 0, \pm 2$, which allows transitions to np and nf Rydberg
states. New spectra covering the same energy region but using three-photon
absorptions have been observed. In these three-photon spectra the transitions
to np Rydberg states are practically absent and transiti~ s to ns Rydberg
states are strong.

---

[1] J. Chem. Phys. **91**, 3340 (1989)

Address: Chemical Kinetics Division, National Institute of Standards and
Technology, Gaithersburg, Maryland 20899

TH15 (4:59)

THE SUB-DOPPLER OPTICAL STARK SPECTRUM OF $A^2\Pi$-$X^2\Sigma^+$ BAND OF CaOH.

D.A. NACHMAN, J.E.SHIRLEY, T.C. STEIMLE, S.R. LANGHOFF AND C.W.
BAUSCHLICHER

The intermodulated fluorescence spectrum of the 000-000 $A^2\Pi$-$X^2\Sigma^+$ band system of
CaOH has been recorded in the presence of a dc electric field. The low rotational levels of
the $A^2\Pi_{3/2}$ state are expected to have a first order Stark shift, yet no significant splitting of
the $P_2(2.5) + Q^2(1.5)$ line was observed at the maximum obtainable dc field strength of -200
V/cm. This observation establishes an upper limit of the permanent electric dipole moment of
<1D for the $A^2\Pi$ state, which is substantially less than the equivalent states of the alkaline
earth monohalides. At the maximum obtainable resolution of the IMF spectrum (-70 MHz
FWHM) no evidence of proton magnetic hyperfine splitting was observed.
These observations are consistent with a recent ab initio results which predict
$\mu(A^2\Pi)=.5D$, $\mu(X^2\Sigma^+)=.9D$ and are also consistent with our failure to detect the
microwave optical double resonance signal. Simple models that have been successfully used
to predict the dipole moments of the alkaline earth monohalides appear not to work for the
monohydroxides.

Address of Nachman, Shirley and Steimle: Department of Chemistry, Arizona State
University, Tempe, Arizona 85287-1604.

Address of Langhoff and Bauschlicher: NASA Ames Research Center, Moffett Field,
California, 94035.

TH16 (5:11)

PREDISSOCIATION LINE WIDTHS OF THE SCHUMANN-RUNGE BANDS OF $^{18}O_2$ and $^{16}O^{18}O$

S.S.-I. CHIU, A.S.-C. CHEUNG, K. YOSHINO, J.R. ESMOND, D.E. FREEMAN and W.H. PARKINSON

Predissociation line widths of the (3,0)–(11,0) Schumann-Runge bands of $^{18}O_2$ and $^{16}O^{18}O$ in the wavelength
region 180-196 nm have been obtained from the published measurements of the absolute absorption cross sections
of Yoshino et al.[1,2] and spectroscopic constants of these molecules of Cheung[3,4]. The line widths are determined
as parameters in the non-linear least squares fitting of calculated to measured cross sections. Predissociation
maxima are found at upper vibrational levels with v'= 4, 7 and 10 for $^{18}O_2$ and $^{16}O^{18}O$. Our predissociation line
widths are mostly greater than previous experimental values for both isotopic molecules.

---

[1] K. Yoshino, D.E. Freeman, J.R. Esmond, R.S. Friedman and W.H. Parkinson, Planet. Space Sci. **36**,
1201-1210 (1988).

[2] K. Yoshino, D.E. Freeman, J.R. Esmond, R.S. Friedman and W.H. Parkinson, Planet. Space Sci. **37**, 419-426
(1989).

[3] A.S.-C. Cheung, K. Yoshino, D.E. Freeman and W.H. Parkinson, J. Mol. Spectrosc. **131**, 96-112 (1988).

[4] A.S.-C. Cheung, K. Yoshino, D.E. Freeman, R.S. Friedman, A. Dalgarno and W.H. Parkinson, J. Mol.
Spectrosc. **134**, 362-389 (1989).

Address of Cheung and Chiu: Chemistry Department, University of Hong Kong, Hong Kong.
Address of Yoshino, Esmond, Freeman and Parkinson: Harvard-Smithsonian Center for Astrophysics, 60 Garden
St., Cambridge, MA 02138

TH14 (4:42)

SiH₃ ELECTRONIC STATES OBSERVED BY 2+1 AND 3+1 RESONANCE ENHANCED MULTIPHOTON
IONIZATION SPECTROSCOPY.

R. D. Johnson III, J. W. Hudgens

Electronic spectra of SiH_3 (silyl radical) have been observed previously[1] by
2+1 Resonance Enhanced Multiphoton Ionization (REMPI) Spectroscopy.
Predominantly transitions from the silicon $3p_z$ orbital (the HOMO) to np Rydberg
states were observed. These two-photon transitions seem to obey the atomic-like
selection rule of $\Delta l = 0, \pm2$, which allows transitions to np and nf Rydberg
states. New spectra covering the same energy region but using three-photon
absorptions have been observed. In these three-photon spectra the transitions
to np Rydberg states are practically absent and transitions to ns Rydberg
states are strong.

[1] J. Chem. Phys. 91, 3340 (1989)

Address: Chemical Kinetics Division, National Institute of Standards and
Technology, Gaithersburg, Maryland 20899

TH15 (4:59)

THE SUB-DOPPLER OPTICAL STARK SPECTRUM OF $A^2\Pi$-$X^2\Sigma^+$ BAND OF CaOH.

D.A. NACHMAN, J.E.SHIRLEY, T.C. STEIMLE, S.R. LANGHOFF AND C.W.
BAUSCHLICHER

The intermodulated fluorescence spectrum of the 000-000 $A^2\Pi$-$X^2\Sigma^+$ band system of
CaOH has been recorded in the presence of a dc electric field. The low rotational levels of
the $A^2\Pi_{3/2}$ state are expected to have a first order Stark shift, yet no significant splitting of
the $P_{21}(2.5)$ + $Q^2(1.5)$ line was observed at the maximum obtainable dc field-strength of ~200
V/cm. This observation establishes an upper limit of the permanent electric dipole moment of
< 1D for the $A^2\Pi$ state, which is substantially less than the equivalent states of the alkaline
earth monohalides. At the maximum obtainable resolution of the IMF spectrum (~70 MHz
FWHM) no evidence of proton magnetic hyperfine splitting was observed.

These observations are consistent with a recent ab initio results which predict
$\mu(A^2\Pi)$=.5D, $\mu(X^2\Sigma^+)$=.9D and are also consistent with our failure to detect the
microwave optical double resonance signal. Simple models that have been successfully used
to predict the dipole moments of the alkaline earth monohalides appear not to work for the
monohydroxides.

Address of Nachman, Shirley and Steimle: Department of Chemistry, Arizona State
University, Tempe, Arizona 85287-1604.

Address of Langhoff and Bauschlicher: NASA Ames Research Center, Moffett Field,
California, 94035.

TH16 (5:11)

PREDISSOCIATION LINE WIDTHS OF THE SCHUMANN-RUNGE BANDS OF $^{18}O_2$ and $^{16}O^{18}O$

S.S.-I. CHIU, A.S.-C. CHEUNG, K. YOSHINO, J.R. ESMOND, D.E. FREEMAN and W.H. PARKINSON

Predissociation line widths of the (3,0)-(11,0) Schumann-Runge bands of $^{18}O_2$ and $^{16}O^{18}O$ in the wavelength
region 180-196 nm have been obtained from the published measurements of the absolute absorption cross sections
of Yoshino et al.[1,2] and spectroscopic constants of these molecules of Cheung[3,4]. The line widths are determined
as parameters in the non-linear least squares fitting of calculated to measured cross sections. Predissociation
maxima are found at upper vibrational levels with v'= 4, 7 and 10 for $^{18}O_2$ and $^{16}O^{18}O$. Our predissociation line
widths are mostly greater than previous experimental values for both isotopic molecules.

This work is supported by NASA grant NAG 5-484 to Smithsonian Astrophysical Observatory.

[1] K. Yoshino, D.E. Freeman, J.R. Esmond, R.S. Friedman and W.H. Parkinson, Planet. Space Sci. 36, 1201-1210 (1988).
[2] K. Yoshino, D.E. Freeman, J.R. Esmond, R.S. Friedman and W.H. Parkinson, Planet. Space Sci. 37, 419-426 (1989).
[3] A.S.-C. Cheung, K. Yoshino, D.E. Freeman and W.H. Parkinson, J. Mol. Spectrosc. 131, 96-112 (1988).
[4] A.S.-C. Cheung, K. Yoshino, D.E. Freeman, R.S. Friedman, A. Dalgarno and W.H. Parkinson, J. Mol. Spectrosc. 134, 362-389 (1989).

Address of Cheung and Chiu: Chemistry Department, University of Hong Kong, Hong Kong.
Address of Yoshino, Esmond, Freeman and Parkinson: Harvard-Smithsonian Center for Astrophysics, 60 Garden
St., Cambridge, MA 02138

WA4

IMPROVED OZONE LINE PARAMETERS FROM MICROWAVE TO MID-INFRARED

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

The ever increasing need for improvements in the accuracy of remote sensing measurements of ozone in the Earth's atmosphere has motivated the effort we began several years ago to undertake a comprehensive program to improve the microwave and infrared spectroscopy of this molecule. High resolution (0.005 to 0.01 cm^{-1}) laboratory spectra of natural, pure $^{16}O_3$, and ^{18}O-enriched samples recorded with the Fourier transform spectrometer at Kitt Peak have been analyzed to derive assignments, accurate positions, and accurate line intensities for all of the $^{16}O_3$ band systems between 3.3 and 14.3 μm and the three fundamental bands of $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$. Combining these results with the best experimental measurements in the microwave as well as powerful theoretical methods, it has been possible to generate a comprehensive compilation of improved line positions, intensities, and lower state energies for ozone bands occurring between 0 and 3400 cm^{-1}. More than 160,000 vibration-rotation lines belonging to about 75 cold and hot bands have been calculated including the hot and cold pure rotation bands and the three fundamentals of $^{16}O^{18}O^{16}O$ and $^{16}O^{16}O^{18}O$. Different examples showing comparisons of high resolution laboratory and atmospheric spectra with corresponding simulated spectra generated with the new line parameters will be presented. These comparisons illustrate the extensive improvements obtained with the new line parameters as well as the importance of the absorption by hot and the ^{18}O-monosubstituted isotopic bands.

Address of Rinsland and Smith: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225.
Address of Flaud and Camy-Peyret: Laboratoire de Physique Moléculaire et Atmosphérique, Tour 13, Université Pierre and Marie Curie et CNRS, 4 place Jussieu, 75252 Paris Cedex 05, France.
Address of Malathy Devi: Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185.

WA5

Ab Initio Prediction of Vibration-Rotation Spectra: HCCF, HFCO, SiH₃⁺, and CH₂

William H. Green, Andrew Willetts, Dylan Jayatilaka, Roger D. Amos, Stuart Carter, Peter J. Knowles and Nicholas C. Handy
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

ABSTRACT

Knowledge of a force field expanded through quartic displacements, together with a dipole field expanded through cubic displacements, yields all the harmonic and anharmonic molecular properties of interest to infrared spectroscopists. Such force fields may also explain much of the mechanism behind IVR.

The ab initio quantum chemist can now calculate these fields, either at the SCF level or with the inclusion of electron correlation effects. For accurate predictions, it is important to include electron correlation effects for at least the quadratic part of the force fields. Here we report three studies using the MP2 method with large basis sets for the full quartic fields: HCCF, for which a large quantity of experimental data has been recently analysed by Holland, Newnham and Mills. The MP2 calculations are so accurate that errors in the experimental assignments became apparent. HFCO, where the theoretical anharmonic constants are helpful in interpreting the highly excited vibrational states probed by Moore and coworkers. SiH₃⁺, whose high resolution absorption spectra has recently been detected in the Davies group. This straightforward way of calculating spectroscopic properties is an extremely valuable tool for the understanding of spectroscopy.

More exact calculations have been performed on singlet methylene, in an attempt to understand the very complex visible spectra. The potential energy surfaces of the two electronic states, which interact by the Renner-Teller effect, are calculated using the internally-contracted multi-reference configuration interaction technique. The full rotation-vibration Hamiltonian is solved variationally, including Renner-Teller coupling elements calculated ab initio. This calculation demonstrates the state of the art in the ab initio prediction of rovibronic spectra of triatomic molecules, and improves our understanding of the experimental data.

Seminar: George Pimental Remembered,

WE1 (1:30)   K.S. Pitzer

WE2 (2:00)   M. Jacox

WE3 (2:10)   M. Tsumi

WE4 (2:27)

NEW HORIZONS IN MATRIX ISOLATION SPECTROSCOPY. INFRARED SPECTRA OF SOME NITROGEN OXIDE IONS AND DIMER IONS

MARILYN E. JACOX AND WARREN E. THOMPSON

When NO, NO_2, or N_2O, mixed with a large excess of neon, is codeposited at a temperature approaching 4 K with a beam of neon atoms which has been excited in a microwave discharge, a number of monomer and dimer ions are isolated in the solid. Isotopic substitution experiments support the identification of infrared absorptions of such species as NO^+, N_2O^+, NO_3^-, and at least two isomeric forms of $N_2O_2^-$. A survey of these results will be presented, and the magnitude of the matrix shift for such species trapped in solid neon will be considered.

Address of Jacox: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.
Address of Thompson: National Science Foundation, Washington, DC 20550.

WE5 (2:44)

TRANSITION-METAL DIATOMICS: GROUND STATE PROPERTIES OF MnNi, MnPd, and MnPt

R. J. VAN ZEE, Y. M. HAMRICK, AND W. WELTNER, JR.

These isovalent, 17 valence-electron, molecules were found to have ground states $X^6\Sigma$ (MnNi), $X^4\Sigma$, (MnPd and MnPt). This was established via electron-spin-resonance spectroscopy in neon and argon matrices at 4 K. Hyperfine interaction with ^{55}Mn was observed for all molecules and also ^{105}Pd in the case of MnPd.

The electronic and magnetic properties of these molecules will be discussed and comparison made with the 13 valence-electron ($X^2\Sigma$, ScNi,...[1]) and 15 valence-electron ($X^4\Sigma$, VNi,...[2]) series.

[1] R. J. Van Zee and W. Weltner, Jr., Chem. Phys. Lett. 150, 329 (1988).
[2] M. Cheeseman, R. J. Van Zee, and W. Weltner, Jr., High Temp. Sci. 25, 143 (1988).

Address of authors: Department of Chemistry, University of Florida, Gainesville, FL 32611-2046.

Intermission

WE6 (3:15)

MATRIX ISOLATION STUDIES OF WEAK HYDROGEN BONDING: ALKYNE AND ALKENE COMPLEXES
Mei-Lee H. Jeng and Bruce S. Ault

The matrix isolation technique has been combined with infrared spectroscopy for the isolation and characterization of weakly hydrogen bonded molecular complexes. The systems studied all employed the C-H group as the proton donor in the complex. A series of alkynes were codeposited with lone electron pair donors containing N, O, S, P, Se and As donor atoms into argon matrices. Distinct evidence of hydrogen bond formation was observed, primarly through a red shift of the C-H stretching mode and a blue shift of the CCH bending mode. Perturbation to the triple bond stretch of the alkyne was also noted, leading to a small red shift. The C-H stretching mode shifted between 50 and 300 cm^{-1}, depending on the base and on the substituents on the alkyne. The observed shifts correlated well with the proton affinities of the base and the Hammett substituent constants for the alkyne substituents. Recent studies have extended these complexes to alkenes, where hydrogen bond formation was again observed, but with significantly smaller shifts. Most recently, the interaction of anions, particularly F^-, with alkynes has been examined. Here much larger shifts were observed, in keeping with the very strongly basic nature of the fluoride anion.

Address of Jeng and Ault: Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221

WE7 (3:32)

ULTRAVIOLET SPECTRA OF MATRIX-ISOLATED CYTOSINE AND SOME OF ITS DERIVATIVES, AND THE EFFECT OF FURTHER ULTRAVIOLET IRRADIATION

M. SZCZESNIAK AND W. B. PERSON

We report here the UV spectra measured for cytosine isolated in an Argon matrix, together with similar studies for 1-methylcytosine and several cytosines halogenated at the 5- position. It is shown that the UV spectrum of this isolated cytosine can be interpreted as the sum of the spectra of 1-methylcytosine and of 5-fluorocytosine. Since the latter is a model for the hydroxy tautomer of cytosine, and the former is a model for the oxo tautomer of cytosine, this observation provides further confirmation of the conclusion[1] that both tautomeric forms exist in equilibrium in this hydrophobic environment.

Previous studies of the infrared spectra of cytosine isolated in an argon matrix[1] have shown that UV photolysis of the isolated cytosine results in the selective photodecomposition of the oxo form of the molecule, leaving higher concentrations of the hydroxy tautomer in the matrix after the irradiation. We believe that the key to understanding this selective photodecomposition is provided by the comparison of the transmittance of the CsI filter through which the matrix was irradiated with the absorption from each of the two model compounds 1-methylcytosine (as a model for the oxo tautomer), and 5-fluorocytosine (as a model for the hydroxy tautomer).

---

[1] M. Szczesniak, K. Szczepaniak, J. S. Kwiatkowski, K. KuBulat, and W. B. Person, J. Am. Chem. Soc., 110, 8319, (1988); see also M. J. Nowak, L. Lapinski, J. Fulara, Spectrochim. Acta, to be published.

Address of both authors: Department of Chemistry, University of Florida, Gainesville, FL 32611-2046.

WE8 (3:49)

FT SPECTROSCOPY OF THE ν_3 VIBRATION OF SiC_2 IN THE FAR IR[*]

J.D. PRESILLA AND W.R.M. GRAHAM

FTIR studies, in the 40-2500 cm^{-1} range, of SiC_2 produced by vaporizing mixtures of silicon and carbon-12 or carbon-13 at 2900K and quenching the products in argon at 10K, have enabled the identification for the first time of the $\nu_3(b_2)$ vibrational mode. The observed frequency at 160.4 cm^{-1} is in agreement with the predictions of *ab initio* calculations.[1] Optimized force constants have been derived using the frequencies of the newly assigned mode and the previously reported, $\nu_1(a_1) = 1741.3$ and $\nu_2(a_1) = 824.3$ cm^{-1} vibrations, together with their values on single and double carbon-13 substitution. Two alternative structures of the molecule, both of C_{2v} symmetry, cyclic and T-shaped, will be discussed.

---

[1]G. Fitzgerald, S.J. Cole, and R.J. Bartlett, J. Chem. Phys. 85, 1701 (1986).

Address of Presilla and Graham: Department of Physics, Box 32915, Texas Christian University, Fort Worth, TX 76129.

WE9 (4:01)

FTIR STUDY OF TRICARBON HYDRIDE RADICALS (C_3H_n, $n \leq 5$) TRAPPED IN AN ARGON
MATRIX AT 10 K[*]

JIUNWOEI HUANG AND W.R.M. GRAHAM

An FTIR study of the products of the vacuum uv photolysis of CH_3CCH,
methylacetylene and its partially and fully deuterated istopomers has revealed
new information on the vibrational spectra of a variety of tricarbon hydride
radicals, C_3H_n $(n \leq 5)$. New vibrations for C_3H, propynylidyne; C_3H_2, cis- and
trans-propenediylidene, and C_3H_3, cyclopropenyl are proposed. Also observed
are the cyclopropenylidene, vinylidenecarbene, and propargylene isomers of
C_3H_2, and the C_3H_5, allyl radical. On the basis of isotopic data previous
vibrational assignments are confirmed, and in some cases, revisions are
suggested.

Address of Huang and Graham: Department of Physics. Box 32915, Texas
Christian University, Fort Worth, Texas 76129.

WE10 (4:18)

OBSERVATION OF C-H and C$\equiv$C STRETCHING VIBRATIONS OF THE C_4H BUTADIYNYL RADICAL
TRAPPED IN AN ARGON MATRIX[*]

L.N. SHEN AND W.R.M. GRAHAM

An FTIR isotopic study of vacuum UV photolyzed diacetylene (C_4H_2),
1,3-butadiene (C_4H_6), and their various deuterated and carbon-13 substituted
isotopomers has enabled the assignment of the ν_1, C-H stretching, and the ν_2,
C$\equiv$C stretching vibrations, as well as confirmed the previous assignment of a
band at 2060.5 cm^{-1} to ν_3, the second C$\equiv$C vibration.[1] Based on the isotopic
data, a study of concentration effects, and the results of the calculations
by the Wilson GF matrix technique, absorptions at 3307.4 cm^{-1} and 2083.9 cm^{-1}
are identified as the ν_1 and ν_2 stretching vibrations of C_4H, respectively.

[1]K.I. Dismuke, W.R.M. Graham, and W. Weltner, Jr., J. Mol. Spectrosc.
57, 127, (1975).

Address of Shen and Graham: Department of Physics, Box 32915, Texas
Christian University, Fort Worth, Texas 76129.

WE11 (4:35)

INFRARED SPECTRUM OF SULFINIC ACID HSO_2H

Matthew A. Fender, Yasmin M. Sayed, and Frank T. Prochaska

Sulfinic acid is a reactive molecule that has been postulated as an
intermediate in a number of chemical reactions. Its infrared spectrum has not been
reported.

Visible-ultraviolet photolysis of mixtures of sulfur dioxide and hydrogen
sulfide in solid argon produced eight new infrared absorptions that we have
assigned to the HSO_2H molecule. These same absorptions are produced upon
photolysis of mixtures of hydrogen iodide and sulfur dioxide in an argon matrix.
Oxygen-18 and deuterium isotopic substitution studies, as well as normal coordinate
calculations, support the assignment of these eight absorptions to vibrational
frequencies of the sulfinic acid molecule. The structure and bonding of sulfinic
acid will be discussed.

Address of Fender and Prochaska: Department of Chemistry and Physics, Western
Carolina University, Cullowhee, NC, 28723

Address of Sayed: Department of Chemistry, University of Wyoming, Laramie, WY,
82070

124

WE12 (4:52)

USING MONTE-CARLO SIMULATIONS OF MATRIX SHIFTS TO CHARACTERIZE TRAPPING SITES IN RARE GAS MATRICES

Mark R. Davies and *Robert J. Le Roy*

When a chromophore is trapped inside a rare gas matrix, its characteristic vibrational frequencies shift from those of the free molecule. The magnitude of these shifts are dependent on the nature of the vacancy site occupied by the chromophore. Application of Monte-Carlo averaging techniques to a realistic model for the chromophore-rare gas interaction and a means of estimating its perturbation by the atoms of the matrix, allows one to probe the effect of the shape of the trapping site on the vibrational spectra. This paper describes the use of this approach for the case of SF_6 and SiF_4 in Ar and Kr matrices.

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario
N2L 3G1, Canada.

WE13 (5:09)

SPECTROSCOPIC SEARCH FOR MATRIX-ISOLATED ACETYLNITRENE

Robert F. Ferrante

Early mechanistic proposals regarding the well-known Curtius rearrangement of carbonyl azides (R-CON₃) into alkyl isocyanates (R-NCO), with loss of nitrogen, focused much interest on the carbonylnitrenes (R-CON). However, there is little chemical evidence, and virtually no spectroscopic proof of the existence of these species. The facility of the thermal rearrangement (now known to be concerted) of the parent azide, as well as the high reactivity of the singlet nitrene, have precluded their observation. Even less is known about the triplet ground states of the simple carbonylnitrenes, which are not readily produced by standard methods, since intersystem crossing rates from the singlet are quite slow.

In this study, preliminary evidence for the trapping of triplet acetylnitrene in nitrogen matrices has been obtained. These features were produced when the parent acetyl azide was subjected to metastable energy transfer (MET) fragmentation by interaction with excited N₂ produced in a microwave discharge. This MET method has been shown to favor production of triplet state nitrenes in related azide systems. New signals attributable to CH₃CON include a weak ESR line near 8200 G, characteristic of a triplet molecule with D = 1.6 cm⁻¹, and IR bands near 1770, 1380, and 1350 cm⁻¹ associated with C-O, CH₃ and C-N vibrations. None of these signals can be produced by direct photolysis of the parent, which causes quantitative conversion to methyl isocyanate, CH₃NCO. A structured UV absorption system may also be associated with the new molecule. These observations and additional experiments will be discussed.

Address: Department of Chemistry, U.S. Naval Academy, Annapolis, MD 21402

WF1 (2:15) L. Nemes

WF2 (2:48)

OBSERVATION OF TRANSFERRED SPIKES IN INFRARED-INFRARED FOUR-LEVEL DOUBLE RESONANCE IN $^{12}CH_3F$[1]

UHYON SHIN, QUAN SONG, AND R. H. SCHWENDEMAN

The resonance frequency of the $^QR(11,9)$ transition in the ν_3 fundamental band of $^{12}CH_3F$ is approximately 26 MHz below the frequency of the 9P(22) laser transition in $^{12}C^{18}O_2$. We have used this laser coincidence to pump molecules into the $\nu_3 = 1$ vibrational state of $^{12}CH_3F$ while observing double resonance effects in transitions in the ν_3 fundamental band and in the $2\nu_3 \leftarrow \nu_3$ hot band by means of an infrared microwave sideband laser spectrometer. Both three-level and four-level double resonance effects were observed and were separated from single resonance absorption by means of a double-modulation scheme. The experiments were performed at room temperature with sample pressures of 10-40 mTorr in a cell with one-meter path.

The double resonance effects observed in the hot-band transitions strongly parallel the effects recently reported for $^{13}CH_3F$.[2] Sharp transferred spikes are seen in transitions originating in states with K = 9 and with 9 < J < 20. Evidence for broader spikes are seen for transitions with K = 3 and K = 6, confirming the $\Delta k = \pm 3r$ selection rules for collisionally-induced rotational transitions. The lineshapes of the transferred spikes have been analyzed by means of a theoretical equation derived by assuming a Keilson-Storer[3] collision kernel. The width of a spike, which is related to the r.m.s. change in velocity upon collision, is greater for larger values of the absolute value of difference between the J value of the lower level of the probe transition and the J value (12) of the level pumped. This result can be explained by assuming that the number of collisions required to transfer molecules from the pumped to the probed level increases with this difference. The widths of the transferred spikes observed for several fundamental transitions are not so easily explained because both levels involved in the transition are pumped. Nevertheless, a rationalization will be described.

---

[1]Supported in part by the National Science Foundation.
[2]Y. Matsuo and R. H. Schwendeman, J. Chem. Phys. 91, 3966-3975 (1989).
[3]J. Keilson and J. E. Storer, Q. Appl. Math. 10, 243-253 (1952).

Address of Shin, Song, and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322.

WF3 (3:05)

VELOCITY DEPENDENCE OF COLLISIONALLY TRANSFERRED SPIKES OBSERVED BY INFRARED-INFRARED FOUR-LEVEL DOUBLE RESONANCE[1]

QUAN SONG AND R. H. SCHWENDEMAN

The center frequency of a collisionally-induced transferred spike observed by infrared-infrared four-level double resonance depends on the difference between the frequency of the pump laser and the center frequency of the pumped transition. This difference determines the component of the velocity of the pumped molecules in the direction of propagation of the pump laser. The r.m.s. speed of the pumped molecules increases with this difference. In order to change the r.m.s. speed of the pumped molecules, we have locked the frequency of the pump laser to the frequency of the saturation dip in a laser-Stark absorption in a separate sample cell outside the laser cavity. By varying the Stark field it has been possible to stabilize the laser at any frequency within ±15 MHz from the usual saturation dip in the CO_2 fluorescence. This technique has been used to stabilize the frequency of the 9P(32) transition of a $^{12}C^{16}O_2$ laser by means of the J,k,m = 5,1,5 ← 4,1,4 transition in $^{13}CH_3F$.

The laser stabilization scheme just described has been used in double resonance experiments to pump the $^QR(4,3)$ transition in $^{13}CH_3F$ with offset frequencies between 8 and 38 MHz. The variation in the collisionally-transferred spikes in several transitions in the $2\nu_3 \leftarrow \nu_3$ band of the same species were probed by means of an infrared microwave sideband laser spectrometer. The lineshapes of the transferred spikes have been analyzed by means of an equation derived from the Keilson-Storer[2] collision kernel. The r.m.s. change in velocity for the overall collisionally-induced transition from the upper level of the pump transition to the lower level of the probe transition has been deduced for each lineshape by this analysis. The change in velocity has been found to be ~ 15% larger for 38-MHz offsets than for 8-MHz offsets. Some differences in the lineshapes with increasing offsets have also been noted. Possible interpretations of these results will be discussed.

---

[1]Supported in part by the National Science Foundation
[2]J. Keilson and J. E. Storer, Q. Appl. Math. 10, 243-253 (1952).

Address of Song and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322.

WF4 (3:22)

TIME-RESOLVED MEASUREMENTS OF TRANSFERRED SPIKES IN INFRARED-INFRARED DOUBLE RESONANCE IN $^{13}CH_3F^1$

UHYON SHIN AND R. H. SCHWENDEMAN

A recent report from this laboratory describes the observation of collisionally-induced transferred spikes in the lineshapes of transitions in the $2\nu_3 \leftarrow \nu_3$ hot band of $^{13}CH_3F$.[2] The spikes, which were produced by pumping the $^Q R(4,3)$ transition in the ν_3 fundamental band by means of a 9P(32) CO_2 laser, were recorded by means of an infrared microwave sideband laser spectrometer. Sample pressures were 10-50 mTorr. The transferred spikes were observed in many transitions originating in K = 3 levels of the v_3 = 1 state. We have now succeeded in time-resolving the probe signals both upon switching on and upon switching off the pump laser. The pump laser output is turned on or off by the combination of an electro-optic crystal and a Fresnel rhomb. By switching an electric field across the crystal between appropriate positive and negative values, the plane of polarization of the radiation can be changed by 90° in ~0.5 μs. A polarizer blocks the beam during one-half the cycle. Although the electronics allow switching at a rate up to 10 kHz under TTL control, most of the experiments to date have been performed at 100 Hz to allow establishment of near steady-state conditions before each change in the pump power applied to the sample.

The steady-state lineshape of the four-level double-resonance transition in the hot band is a superimposition of a narrow transferred spike and a Gaussian component that has the expected Doppler width. We have interpreted the spike to be the result of collisionally-induced rotational transitions bringing a pumped molecule to the lower level of the probe transition, whereas the Gaussian part is the result of a swapping of vibrational energy between a pumped molecule and a molecule in the ground vibrational state. The time-resolved spectra show that the effect of double-resonance pumping of the transferred spike is a much faster process than pumping the Gaussian part. The rate of appearance or disappearance of the transferred spike also decreases as J(probe) - J(pump) increases. Other characteristics of the time-resolved spectra will be described.

[2]Y. Matsuo and R. H. Schwendeman, J. Chem. Phys. 91, 3966-3975 (1989).

Address of Shin and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322.

WF5 (3:39)

INFRARED-INFRARED DOUBLE RESONANCE AND POLARIZATION LABELING SPECTROSCOPY OF METHYL FLUORIDE

CYNTHIA M. FAUST, L. PETER GOLD, AND ROBERT A. BERNHEIM

We have observed for the first time infrared-infrared double resonance and polarization-labeling spectra. A CO_2 laser operating at 10 μm was used to pump rotation-vibration transitions in the v_3 bands of $^{12}CH_3F$ and $^{13}CH_3F$ and a Bomem DA3 Fourier-transform spectrometer was used to observe at high resolution (0.004 cm^{-1}) pumped molecules in the region of the $2v_3 \leftarrow v_3$ transitions. The experiments employed a multi-pass cell to give a path length of about 20 m. The observed spectra display the great simplification which is a principal advantage of the double resonance technique.

Address of Faust, Gold, and Bernheim: Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802.

WF6 (3:56)

ROTATIONAL PARTITION FUNCTIONS FOR SYMMETRIC TOPS

ROBIN S. McDOWELL

A simple, accurate closed-form expression for the rotational partition functions of symmetric-top molecules is derived, which includes the effects of nuclear-spin statistics (significant at very low temperatures), quartic and sextic centrifugal distortion terms (moderate and high temperatures), and inversion (all temperatures):

$$Q_r \sim \sigma*(\pi m)^{1/2}e^{\beta(4-m)/12}\beta^{-3/2}\{1 + \beta^2(1-m)^2/90\}(1 + \delta)(1 + \rho_1\beta^{-1} + \rho_2\beta^{-2} + \rho_3\beta^{-3})(1 - \beta\Delta G/2B),$$

where $\beta = hcB/kT$, $m = B/A$ for prolate tops or B/C for oblate tops, and $\sigma* = \Pi_i(2I_i+1)/\sigma$ where I_i is the spin of nucleus i and σ is the classical symmetry number. The low-temperature nuclear-spin correction is

$$\delta \approx 2(2I_Y+1)^{-2}\exp\{\pi^2 m(\beta m-6)/54\beta\}$$

for C_{3v} XY_3 and WXY_3 molecules; similar expressions hold for other molecular models. The ρ's are functions of the centrifugal distortion constants D_J, D_{JK}, D_K, H_J, etc., and ΔG is the inversion splitting in the ground vibrational state. Applications to the partition and thermodynamic functions of NH_3, CH_3D, CHD_3, allene (C_3H_4), and ethane, including isotopic variants, will be discussed.

Address: University of California, Los Alamos National Laboratory, Los Alamos, N.M. 87545

WF7 (4:13)

LOCAL MODE ROTATIONAL STRUCTURE IN THE (3000), (4000) AND (5000)
STRETCHING OVERTONE BANDS OF SILANE: (1) EXPERIMENTS AND RESULTS

QING-SHI ZHU, BAO-SHU ZHANG, HAI-BO QIAN, YUE-REN MA AND HUI MA

The (3000), (4000) and (5000) stretching overtone bands of silane have been recorded on a BOMEM Fourier transfer spectrometer equipped by a multipass absorption cell, which had an effective length of up to 100 meters and was capable of holding the sample pressure almost constant over two days continuous scan. A symmetric top rotational structure, similar to that observed in the (3000) band of germane[1], was clearly demonstrated, indicating that the upper states were very near the local mode limit. The band origins agree well with the model vibrational calculation[2]. In addition, some interesting intensity anomalies and perturbations were found in these spectra and will be reported here.

[1] Q.Zhu, B.A.Thrush and A.G.Robiette; Chem. Phys. Lett., 150 (1988) p181
[2] M.S.Child and L.Halonen; Adv. Chem. Phys., 57 (1984) p1

Address: Dalian Institute of Chemical Physics, P.O.Box 110, Dalian 116023, China.

WF8 (4:25)

LOCAL MODE ROTATIONAL STRUCTURE IN THE (3000), (4000) AND (5000)
STRETCHING OVERTONE BANDS OF SILANE: (2) ROTATIONAL ANALYSIS

QING-SHI ZHU, BAO-SHU ZHANG, HAI-BO QIAN, YUE-REN MA AND HUI MA

The observed rotational lines are fit well to the transition frequency expression of symmetric top parallel band. It is found that when stretching quantum number n increases from 3 to 5, the rotational constant B decreases one order of magnitude faster than A, which suggests that molecules in these states should be thought of as vibrating with all Si-H stretching quanta localized in one bond, so that the molecular symmetry reduces from T_d to C_{3v}.

The symmetric top rotational structure can also be explained by a close coupling of the $n\nu_i$ and $(n-1)\nu_i + \nu_j(F_2)$ vibrational states. The Hamitonian matrix was set up and then diagonalized to give the eigenvalues and eigenfunctions. The molecular constants were derived by least-squares fitting, and the A_i-F_2 vibrational separation was estimated to be less than 0.01 cm^{-1}, which indicated that the inter-bond energy transfer period (neglecting the stretch-bend coupling) was $t \gg 3ns$, which was much greater than the vibrational and rotational period.

Address: Dalian Institute of Chemical Physics, P.O.Box 110, Dalian 116023, China.

WF9 (4:42)

INFRARED DIODE LASER AND FOURIER TRANSFORM SPECTROSCOPY OF THE NO_3 RADICAL

Eizi Hirota, Kentraou Kawaguchi, Takashi Ishiwata, and Ikuzo Tanaka.

The band of NO_3 at 1492 cm^{-1} reported previously [J. Chem. Phys. 82, 2196 (1985)] has been reinvestigated by extending the observations so as to take ground-state combination differences. A slight revision of the assignment now removes all anomalies from the ground state. On the other hand, a small, but finite spin-orbit interaction term exists in the upper state. The first-order Coriolis coupling constant which was observed differs much from the calculated value. This and other anomalous features in the upper state are discussed in light of a few models including a dynamical C_{2v} structure.

WF10 (4:54)

HIGH RESOLUTION OVERTONE SPECTROSCOPY OF BENZENE USING IR-UV DOUBLE RESONANCE TECHNIQUE

D-J. Liu, A. Stolow, M. J. Vrakking, E. F. Cromwell, A. H. Kung and Y. T. Lee

Two transform-limited laser systems were used to study the overtone spectroscopy of benzene at v = 2 and v = 3 levels in a supersonic molecular beam via infrared-ultraviolet double resonance detection technique.

A frequency-doubled, Raman-shifted UV radiation(probe laser) was tuned to $S_1 \leftarrow S_0$ transition of benzene with a single (J, K) state selection and benzene ion was generated by REMPI. A narrow band infrared radiation with bandwidth of 120 MHz (pump laser) was spatially overlapped with UV. The resonance of the overtone transitions was detected by the ion depletion.

A fully rotationally resolved spectrum was obtained for v = 2 level. The vibration state density of 20 to 50 /cm^{-1} was observed in the most congested spectrum region. A careful power dependance study showed that the linewidth is only dominated by the laser bandwidth. For v = 3 level, we observed a broad feature with FWHM = 7 cm^{-1}. No narrow linewidth transition was resolved even with the transformed-limited laser resolution.

Address of Liu: Chemistry Division, Argonne National Laboratory, Argonne, Ill 60439.
Address of Stolow, Vrakking, Cromwell, Kung and Lee: Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry , University of California at Berkeley, Berkeley, CA 94720.

WG1 (2:15)

INFRARED SPECTROSCOPY AND STRUCTURE OF CH_4 ON NaCl(100)

Laura Quattrocci and George E. Ewing

Physisorption of methane on a single crystal of NaCl(100) was investigated in a cyrogenic UHV chamber using Fourier Transform Infrared Spectroscopy. Spectra were recorded under equilibrium conditions for the saturated monolayer. Both the ν_3 stretching and ν_4 bending modes are triply degenerate in the gas phase. This degeneracy is partially lifted when methane is adsorbed, giving rise to doublets. Polarized infrared spectra give the direction of the transition dipoles. Measurements of degeneracy splitting and polarization are consistent with a monolayer structure with one molecule per unit cell and two hydrogens pointing toward the surface.

Address of Quattrocci and Ewing: Department of Chemistry, Indiana University, Bloomington, IN 47405

WG2 (2:32)

STRUCTURAL DETERMINATION FOR ACETYLENE PHYSISORBED ONTO NaCl(100)

S. Keith Dunn and George Ewing

The IR absorption spectrum of monolayer acetylene on a single crystal of NaCl was obtained in 3200 cm^{-1} region. From results using E_s and E_p polarized light, the molecular axis of acetylene was determined to lie parallel to the substrate surface. Results were found to be consistent with a monolayer made up of a series of hydrogen-bonded chains in which half of the acetylene molecules act as proton acceptors and half act as proton donors. This monolayer structure is directly analogous to the T-shaped gas phase dimer.

Address of Dunn and Ewing: Department of Chemistry, Indiana University, Bloomington, IN 47405

WG3 (2:49)

INFRARED SPECTRA OF H_2O, D_2O, and HDO ON ALKALI HALIDE FILMS*

L. GIANCARLO, B. STONE, AND C.A. BAUMANN

The infrared spectrum of water adsorbed onto sublimated alkali halide films has been observed and characterized from submonolayer to multilayer coverage. Potential surfaces for a variety of modes of adsorption have been calculated. Vibrational frequency shifts induced by the adsorption potential are consistent with a mode of adsorption in which the oxygen is above a surface cation and the molecular dipole is normal to the surface.

Address of Giancarlo and Baumann: Department of Chemistry, University of Scranton, Scranton, PA 18510.

Address of Stone: Department of Chemistry, San Jose State University, San Jose, CA 95192.

WG4 (3:06)

SPECTRA OF GAS-PHASE CRYSTALLINE MICROPARTICLES

J.P. DEVLIN AND F. FLEYFEL

A simple cold cell for the FT-IR study of large gas-phase clusters has been used to obtain spectra for several molecular systems in various phases. Results for ice, ethers and CO_2 will be noted while particular attention will be directed to the case of HCl(s) clusters for which longitudinal optic modes dominate the spectra. Such results are indicative of the information on morphology of microcrystals contained in the spectra.

Address of Devlin and Fleyfel: Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

WG5 (3:23)

INFRARED SPECTROSCOPY OF LARGE WATER CLUSTERS

Robert Disselkamp and George E. Ewing

Water clusters were formed by passing an argon gas stream through a mixture of 97% H_2O/ 3% D_2O which was admitted to a large cryogenic cell cooled to 77K. The resulting suspension of clusters, which contain on the order of 10^3 molecules/cluster, were spectroscopically studied as a function of time using FTIR techniques. The clusters have been observed to disappear over a period of hours which we attribute to diffusion to the cell walls. Successfully computer modeling of the diffusion process will be discussed which has allowed us to estimate an average cluster size. An explaination for the infrared structure in the O-H and O-D stretching regions of the clusters will also be presented.

Address of Ewing and Disselkamp: Department of Chemistry, Indiana University, Bloomington, IN 47405.

WG6 (3:40)

PHOTOCHEMISTRY OF PHYSISORBED KETENE

Otto Berg, R.W. Anthony Huff and George Ewing

Sodium chloride is an excellent substrate for the spectroscopic study of adsorbed molecules. It is transparent to infrared, visible, and ultraviolet light. It is also chemically passive; adsorbates are bound through van der Waals forces. We have used infrared spectroscopy to probe molecules adsorbed to highly divided sodium chloride films[1]. We are extending this technique to the study of surface photochemistry. Gas-phase ketene, (CH_2CO), has become a model system for exploring photochemical mechanisms[2]. Infrared spectra of the adsorbed molecule and its trapped photolysis products indicate that a surface can alter photochemical behavior.

[1] H.H. Richardson, C. Baumann, and G.E. Ewing, Surf. Sci. 185 (1987) 15.

[2] H. Bitto, D.R. Guyer, W.F. Polik, and C.B. Moore, Faraday Discuss. Chem. Soc. 82 (1986) 149.

Address of Berg and Ewing: Department of Chemistry, Indiana University, Bloomington, IN 47405

Address of Huff: Department of Chemistry, University of California, Berkeley, CA 94720

WG7 (3:57)

FT-IR SPECTRA OF EPITAXIALLY GROWN CLATHRATE HYDRATES

F. FLEY EL AND J. P. DEVLIN

The spectroscopic study of clathrate hydrates of small polar molecules have been greatly simplified since the development of methods for their preparation based on the vacuum codeposition of water with guest molecules at cryogenic temperatures. However, these methods have not proved directly adaptable to nonpolar guest molecules, presumably because of much longer structural-relaxation times of such hydrates. The continued development of the cryogenic methods has revealed that nonpolar-guest hydrates will grow quite readily epitaxially to the clathrate hydrates of certain polar molecules. Spectra for epitaxially grown structure I and structure II clathrate hydrates of CO_2 will be discussed and the dependence of the growth on the nature of the clathrate substrate will be examined in terms of the role that point-defect activities play in the formation of icy solids.

Address of Fleyfel and Devlin: Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078.

WG8 (4:14)

SPECTROSCOPIC OBSERVATIONS ON DEFECT ACTIVITIES IN AMORPHOUS ICE

M. FISHER AND J. P. DEVLIN

Defect activities (ionic and orientational) have previously been characterized for cubic ice through FT-IR monitoring of isotopic exchange reactions that produce HOD from D_2O isolated in protiated ice. This technique has been extended to amorphous ice in an effort to identify the temperature of onset of orientational defect motion. The orientational defects are best monitored by following the decoupling of vibrationally-coupled neighbor HOD pairs. Techniques for preparing amorphous ice rich in neighbor HOD pairs will be described and decoupling results compared with observations for crystalline ice.

Address for Fisher and Devlin: Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

WG9 (4:31)

OPTIMIZATION OF THE FOURIER DECONVO-
LUTION TECHNIQUE TO ENHANCE INFRARED
SPECTRA. J. Miletic, M. Trudel, and C. CHAPADOS

The Fourier self-deconvolution technique was developed by Kauppinen
et al. using a Lorentz band shape to enhance intrinsically overlapped
bands in ir spectra by narrowing the bandwidth of bands so that the compo-
nents in a massive absorption become separated.[1] In this presentation,
the theory of Fourier deconvolution using Cauchy-Gauss product functions
is developed that permits to enhance an experimental infrared spectra more
adequately than using pure Cauchy (or Lorentz) functions. Two methods
can be used to obtain the inverse Fourier transform of the lineshape func-
tion: an analytical and a numerical method. The numerical method gives
some errors which limit the degree of enhancement. The analytical method
overcomes these difficulties but necessitates a mathematical development.
The numerical method is the only way to obtain an inverse Fourier transform
of an experimental spectrum, and some aliasing is introduced by the algorithm
used. The infrared spectra of the carbonyl containing compounds are used
to illustrate the effectiveness of the procedure described.

[1] J.K. Kauppinen et al. App. Spectros. 35 (1981) 271-276.

Address of Trudel and Chapados:

Département de chimie-biologie
Université du Québec à Trois-Rivières
C.P. 500, Trois-Rivières
Québec, Canada   G9A 5H7

Address of Miletic:

Département de physique
Université du Québec à Trois-Rivières
C.P. 500, Trois-Rivières
Québec, Canada   G9A 5H7

Send correspondence to:

Camille Chapados, Professeur
Département de chimie-biologie
Université du Québec à Trois-Rivières
Trois-Rivières, Qué.
Canada \ G9A 5H7

WG10 (4:43)

BAND SHAPE OF KETONE CARBONYLS IN SOLU-
TION. G. PETIT and C. CHAPADOS

In solid solutions of large molecules of biological interest such as chlo-
rophylls and proteins, the infrared spectra show large structureless bands.
These characteristics are due to overlapping bands.[1] To separate the com-
ponents in the massive absorptions it is necessary to know the band shapes
and bandwidths of the functional groups involved in the absorption.

We have used acetone in CS_2 solutions as a model system for the ketone
carbonyl bands of solid solutions of chlorophyll. The spectra at several
concentrations were obtained and concatenated to obtain a spectrum free
of noise. Three bands were readily observed: one band was a combination
band which was in Fermi resonance with the second band assigned to the
ketone carbonyl, the third band was an isotope satellite. Two more broader
and weaker bands were situated on each side of the carbonyl band. These
bands were assigned to the combination of the carbonyl band with the
rotational-translational band situated in the far ir.

After Fourier deconvolution of the bands situated in the carbonyl region,
several satellite bands were observed. These were assigned to different
conformers of the molecule. Using the simulation technique of Pitha and
Jones we have fitted the bands to determine the relative concentration,
the bandwidth and band shape of each conformers. Complications arising
from the Fermi resonance will be discussed.

[1] C. Chapados, Photochem. Photobiol. 47, 115-132 (1988)

Address of Petit and Chapados:

Département de chimie-biologie
Université du Québec à Trois-Rivières
C.P. 500, Trois-Rivières
Québec, Canada
G9A 5H7

Send correspondence to:

Camille Chapados, Professeur
Département de chimie-biologie
Université du Québec à Trois-Rivières
Trois-Rivières, Qué.
Canada \ G9A 5H7

WH1 (2:15)

HIGH RESOLUTION $S_1 \leftarrow S_0$ FLUORESCENCE EXCITATION SPECTROSCOPY OF THE TAUTOMERS OF
2-HYDROXYPYRIDINE.[1]

A. HELD, D. F. PLUSQUELLIC, AND D. W. PRATT

Three separate $S_1 \leftarrow S_0$ electronic origins are known to exist for 2-hydroxypyridine (2HP).[2]
The highest energy origin is thought to belong to the lactim (2-pyridinol) tautomeric form
while the two lower energy origins are thought to belong to two different conformers of the
lactam (2-pyridone) form. We have examined these two origins at high resolution using the
molecular beam laser spectrometer and determined the inertial parameters of both the S_0 and S_1
zero-point vibrational levels (ZPL's) in both 2HP and hydroxy-deuterated 2HP (2DP). We also
have performed geometry optimizations of both tautomers at the Hartree-Fock level using a
3-21G basis set. The rotational constants of the S_0 ZPL's participating in the two lower
energy origins in 2HP are the same within experimental error ($\pm$ 0.1 MHz), showing that both
transitions originate in the same tautomeric (and conformeric) form. This form is shown to be
the lactam form of 2HP by comparing the theoretical geometries and the measured rotational
constants of S_0 2HP and 2DP, which makes possible the determination of the COM coordinates of
the isotopically substituted atom using Kraitchman's equations. Changes in these coordinates,
revealed by applying the same strategy to the two S_1 ZPL's, show that electronic excitation
produces two different non-planar equilibrium geometries of the lactam form of 2HP that have
different energies. Thus, the two lower energy 0_0^0 bands in 2HP originate in a single conformer
but terminate in two different conformers of the lactam form of 2HP. A comparison of the
measured inertial defects of the two S_1 conformers provides considerable information about
their structural differences. Similar experiments on the highest energy 0_0^0 band of 2HP are in
progress.

[2]M. R. Nimlos, D. F. Kelley, and E. R. Bernstein, J. Phys. Chem. 93, 643 (1989).

Address of Held, Plusquellic, and Pratt: Department of Chemistry, University of Pittsburgh,
Pittsburgh, PA 15260.

WH2 (2:32)

ROTATIONALLY RESOLVED FLUORESCENCE EXCITATION SPECTRA OF 4-DIMETHYLAMINOBENZONITRILE ALONG TWO
LOW FREQUENCY COORDINATES.[1]

J. L. TOMER, A. HELD, J. F. PFANSTIEL, AND D. W. PRATT

Rotationally resolved spectra of eight bands within 200 cm^{-1} of the S_1 origin of
4-dimethylaminobenzonitrile (DMABN) have been obtained. These bands have previously been
assigned, at vibrational resolution, as progressions involving the inversion and torsional
coordinates of the dimethylamino group.[2] At rotational resolution each band exhibits
perpendicular-type structure, principally b type. All bands have been fit with a near-prolate
symmetric top Hamiltonian, yielding the inertial parameters of the connected vibrational levels
accurate to $\pm$ 0.1 MHz. This information, together with the results of theoretical
calculations, is then used to speculate about the geometry of DMABN in its S_0 and S_1 states,
and how it changes along the two low frequency coordinates. Implications of these results for
the presumed twisted internal charge transfer character of S_1 DMABN[3] also will be discussed.

[2]V. H. Grassian, J. A. Warren, E. R. Bernstein, and H. V. Secor, J. Chem. Phys. 90,
3994 (1988).

[3]Z. Grabowski, K. Rotkiewicz, A. Siemiarczuk, and D. Crowley, Nouveau Journal de
Chimie 3, 443 (1979).

Address of Tomer, Held, Plusquellic, and Pratt: Department of Chemistry, University of
Pittsburgh, Pittsburgh, PA 15260.

WH3 (2:49)

OBSERVATION OF THE ARYLMETHYL RADICALS

CRISTINO P. DAMO, TAI-YUAN DAVID LIN, JAMES R. DUNLOP, AND TERRY A. MILLER

Of all the arylmethyl radicals, only the prototype, benzyl or phenylmethyl, has been observed by laser-induced fluorescence in the gas phase. The diphenyl- and triphenylmethyl radicals have been studied only in condensed phase by visible absorption and electron paramagnetic resonance. Further phenyl substitution of the benzyl radical raises several questions abr 'he structures of the arylmethyl radicals. As a step toward the understanding u :se radicals, we report for the first time the observation of vibrationally-resolved electron \ectra of cold diphenylmethyl, chlorodiphenylmethyl, diphenylethyl, and triphenylmethyl rauicals in a free jet expansion. Convincing arguments as to the nature of the spectral carriers along with precise origin frequencies and fluorescence lifetimes will be presented.

Address of Damo, Lin, Dunlop, and Miller: The Ohio State University, Department of Chemistry, Laser Spectroscopy Facility, 120 West 18th Avenue, Columbus, Ohio 43210.

WH4 (3:01)

THE TORSIONAL ANALYSIS OF JET-COOLED ARYLMETHYL RADICALS

TAI-YUAN DAVID LIN, CRISTINO P. DAMO, JAMES R. DUNLOP, AND TERRY A. MILLER

Low frequency vibrational modes (typically less than 80 cm^{-1}) are ·vident in the laser-induced fluorescence excitation and resolved emission spectra of several arylmethyl radicals. Based upon the analysis of the experimental results, the low frequency modes are attributed to the hindered twisting motions of the phenyl rings and/or the methyl group. Work is proceeding to obtain information about the potential surface relevant to ring twisting and methyl rotation.

Address of Lin, Damo, Dunlop, and Miller: The Ohio State University, Department of Chemistry, Laser Spectroscopy Facility, 120 West 18th Avenue, Columbus, Ohio 43210.

WH5 (3:18)

INFRARED SPECTROSCOPY OF THE CO_2-D(H)Br COMPLEXES: LOCATION OF THE HYDROGEN ATOM

Y.P. ZENG, S.W. SHARPE, C. WITTIG, AND R.A. BEAUDET

Vib-rotational spectra of CO_2-HBr and its deuterated counterpart have been recorded utilizing the CO_2 asymmetric stretch (2349 cm^{-1}) chromophore. These weakly bonded dimers are created by supersonic expansion of a seeded carrier gas (1% CO_2, 1% HBr in Ar-Ne) through a pulsed slit nozzle (.15 x 38 mm^2). Direct absorption spectra are obtained by passing the output of a tunable diode laser through the expanding effluent and monitoring laser attenuation as a function of laser frequency. Rapid tuning of the diode laser allows a complete spectrum (~.75 cm^{-1}) to be obtained during each pulse of the nozzle. As in our previous work on CO_2-HBr,[1] CO_2-DBr also exhibits spectral features associated with an asymmetric rotor. In all, 68 transitions were assigned (K_a=0, 1 and 2) and fit to a Watson type Hamiltonian Due to efficient rotational cooling, characteristic in supersonic expansions, only transitions up to J=12 and K_a=2 was available; hence only the rotational constants A, B, C, and D_{JK} were determined for both the vibrational ground and excited states. A combination-difference method was used to obtain vibrational ground-state constants, which were then fixed for subsequent fitting of the upper-state constants as well as the band origin, v_0.

Results from the two isotopically different experiments allows us to determine the distance of the H(D) atom from the center of mass of CO_2-H(D)Br. In addition, the angle between the H(D)Br molecular axis and the center-of-mass line is estimated as ~. Substantial differences of the hydrogen location in bent CO_2-H(D)Br vs. linear CO_2-H(D)Cl and linear CO_2-H(D)F have important ramifications for the interpretation of precusor-geometry-limited photoinitiated reactions such as H + CO_2 → CO + OH, which will also be discussed in the following talk.

---

[1] S.W. Sharpe, Y.P. Zeng, C. Wittig, and R.A. Beaudet, J. Chem. Phys. 92, 943(1990).

Address of the authors: Department of Chemistry, University of Southern California, Los Angels, CA 90089-0482

WH6 (3:30)

EVIDENCE FOR STATE DEPENDENT DECAY IN SYM-TRIAZINE

Paul UIJT DE HAAG, Jon T. HOUGEN, W. Leo MEERTS

The molecule sym-triazine ($C_3H_3N_3$) is the most symmetric azabenzene. We have measured the one-photon vibronic transition 6_0^1 $S_1 \leftarrow S_0$ at 317 nm by laser induced fluorescence. The combination of a cw intracavity doubled ring dye laser with a molecular beam allowed the observation of completely resolved rotational lines. A complete rotational assignment could be given up to $J=5$.

Like in other azabenzenes, the high resolution spectrum is perturbed by a mixing of singlet and triplet states. The nature of these states is confirmed by a strong dependence of the spectrum on an applied magnetic field. The number of lines clearly proves that sym-triazine is in the small-molecule limit.

The linewidth is not constant, but varies between 12 MHz (the instrumental width) for the strong lines to 50 MHz for the weak lines. This indicates that there is a strong state dependent internal conversion in sym-triazine.

Address of Uijt de Haag and Meerts: Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands
Address of Hougen: Molecular Spectroscopy Division, National Bureau of Standards and Technology, Gaithersburg, MD 20899, USA

WH7 (3:47)

RESONANCE RAMAN SPECTROSCOPY OF FLAMES*

G. BARRALL, M.J. BURMEISTER AND P.B. KELLY

Resonance Raman spectroscopy provides a means of selectively detecting and profiling non-fluorescent species in flames. Selectivity of detection is an important pre-requisite for analytical work in combustion because of the myriad of of potential interfering compounds present in flames. By careful choice of excitation wavelength non-fluorescent compounds present in low concentrations can be detected.

Interference from background fluorescence of polyaromatic hydrocarbons (PAH) is dramatically reduced by exciting in the far ultraviolet. Emission from PAH molecules begins at ~250 nm and extends to longer wavelengths. Excitation at ~216 nm leaves a spectral window in which to observe the Raman spectrum.

The vibrational Raman spectrum of the target molecule, and species present in high concentration (methane, nitrogen, and water) have been obtained. Results for trichloroethylene, tetrachloroethylene, and benzene in methane flames will be presented.

Address of the Authors: Department of Chemistry, University of California, Davis, CA 95616.

WH8 (4:04)

EXCITATION SPECTROSCOPY OF OZONE – THE HARTLEY SYSTEM

C. P. Bewick, M. G. Garripoli, H.-A. Eckel, J. Kreil and W. Demtröder

A high-resolution spectroscopic investigation of rotationally cooled ozone in the high wavelength end of the Hartley band (~300 nm) has recently been performed. In the experiments to be reported the output of a CW single-mode ring dye-laser was pulse amplified in an excimer-laser-pumped, three stage amplification chain. The pulsed output (~3mJ, 100MHz FWHM), frequency doubled in a BBO crystal, was crossed perpendicularly to an uncollimated supersonic argon beam seeded with 5 % ozone utilizing LIF detection. Preliminary survey spectra (~5 GHz FWHM) show a series of strong emission features, separated by about 230 cm^{-1}, which appear to have a discrete rotational structure. These features bear similarity to that observed in the absorption cross-section data of Freeman and coworkers [1], for which a theoretical discussion has recently been given [2]. Sub-doppler resolution (~100 MHz FWHM) spectra are currently being recorded for presentation.

[1] D.E.Freeman, K.Yoshino, J.R.Esmond, and W.H.Parkinson, Planet Space Sci. 32, 239 (1989)
[2] Bruce R. Johnson and James L. Kinsey, J. Chem. Phys. 91, 7638 (1989).

Fachbereich Physik, Universität Kaiserslautern. Erwin-Schrödinger-Straße,
D–6750 Kaiserslautern, Federal Republic of Germany.

WH9 (4:21)

PREDISSOCIATON DYNAMICS OF THE METHYL RADICAL $\tilde{B}$ STATE

S.G. WESTRE AND P.B. KELLY

Quantum level specific dynamics that occur on a subpicosecond timescale have been probed using resonance Raman spectroscopy. Excited state dissociation rates and lifetimes have been determined for the [0000] vibrational level of the $\tilde{B}$ state of CH_3. The mean lifetimes varied from 69 femtoseconds for $J' = 4$ to 84 femtoseconds for $J' = 11$. The role of rotational forces in the unimolecular dissociation dynamics of CH_3 has been examined by modeling the observed dissociation rates assuming a centrifugally modified potential energy function. Estimates for the height and curvature of the barrier to dissociation were compared to Ziegler's results for ammonia.[1] The results were consistent with predissociation of the excited states of the methyl radical and ammonia by hydrogen tunneling through a potential barrier. The CH_3 barrier was found to be approximately the same height rates the barrier for NH_3, but was considerably narrower. The distance from the inner minimum, r_0, to the barrier, r_b was also found to be smaller for CH_3. The theoretical work[2] of Yu et al. was in qualitative agreement with our work, however their calculations predicted $r_b = 1.55$ Å, which was much larger than that found by our value of $r_b = 1.35$ Å. Experiments to examine the predissociation dynamics of the $\tilde{B}$ state of CD_3 are in progress. The combined analysis of CH_3 and CD_3 dissociation rates will provide a more accurate characterization of the $\tilde{B}$ state potential surface.

[1] L.D. Ziegler, Y.C. Chung, P. Wang and Y.P. Zhang, in Time Resolved Spectroscopy, edited by R.J.H. Clark and R.E. Hester (Wiley, New York, 1989) and references therein.

[2] H.T. Yu, A Sevin, E. Kassab and E.M. Evleth, J. Chem. Phys. 80, 2049 (1984).

Address of the Authors: Department of Chemistry, University of California, Davis, CA 95616

WH10 (4:38)

INVESTIGATION OF THE HYPERFINE SPLITTING OF IODINE MOLECULAR LINES IN THE RED SPECTRAL REGION

S. Rakowsky, D. Zimmermann

By means of Doppler-free polarization spectroscopy using a tunable single-mode dye laser we have investigated the hyperfine splitting of various absorption lines of molecular iodine with wavenumbers between 12620 and 13890 cm^{-1} due to the transition $B\ ^3\Pi_u \leftarrow X\ ^1\Sigma_g^+$. In order to get a sufficient population of vibrational levels $v'' = 10...13$ of the X state the iodine absorption cell was heated to about 430°C the iodine vapor pressure being fixed to about 0.7 Torr by a cold side-finger of the cell. 15 and 21 hfs components have been observed for even and odd rotational quantum number of the X state resp. The linewidth of a single hfs component was about 15 MHz. Despite of a partial overlapping of hfs components in most line patterns we were able to determine the center frequencies of all 15 or 21 hfs components with an accuracy of typically 2 MHz.

The observed hfs patterns could fully be explained by a simple model with the two parameters $\Delta(eQq)$ of the difference in electrical quadrupole coupling and ΔC of the difference between effective magnetic dipole interaction. Values of $\Delta(eQq)$ and ΔC have been determined for vibrational transitions $v'-v''$ with $v'=0, 1, 2$ and $v''=10...15$. As an example we have obtained the following result for the transition $v'=2-v''=10$ as a mean value over 14 rotational lines: $\Delta(eQq)=(1958\pm2)$ MHz and $\Delta C=(24\pm3)$ KHz. In addition, the absolute wavenumbers of the o-component of 17 rotational transitions with even rotational quantum number have been determined with an accuracy of 0.001 cm^{-1} /1/.

/1/ S. Rakowsky, D. Zimmermann, W. E. Ernst: Appl. Phys. B 48 (1989) 463

Institut für Strahlungs- und Kernphysik, Technische Universität Berlin, Hardenbergstr. 36, D-1000 Berlin 12

WH11 (4:50)

MOLECULAR BEAM RADIO FREQUENCY-OPTICALN DOUBLE-RESONANCE STUDY
OF ^{87}SrF IN ITS $X^2\Sigma^+$ STATE

Y. AZUMA, W.J. CHILDS, G.L. GOODMAN AND T.C. STEIMLE

A molecular beam rf-optical double resonance experiment was performed on ^{87} in its naturally occurring abundance ratio. Numerous magnetic dipole allowed transitions between p-doublets in the $X^2\Sigma^+$ state were measured to an accuracy of ~ 3 kHz. The observed spectra were analyzed in terms of an effective Hamiltonian which includes the magnetic hyperfine and electric quadrupole interactions arising from the ^{87}Sr(I = 9/2) and ^{19}F(I = 1/2) nuclei. The extracted spectroscopic hyperfine parameters were interpreted in terms of a simple molecular-orbital picture for the electronic nature of the $X^2\Sigma^+$ state. A comaprision is made to previous results for the more abundant ^{86}SrF and ^{88}SrF isotopic forms.

Address of Azuma, Childs, and Goodman: Physics Division, Argonne National Laboratory, Argonne, IL 60439.

Address of Steimle: Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604.

WH12 (5:02)

LASERSPECTROSCOPIC INVESTIGATION OF THE VAN DER WAALS MOLECULE NaXe

P. Baumann, D. Zimmermann

This work reports on a first successful spectroscopic investigation of the van der Waals molecule NaXe. The molecules were produced by supersonic expansion of a mixture of sodium vapor and xenon gas through a nozzle into a vacuum. The absorption spectrum due to the transition $A\Pi \leftarrow X\Sigma$ of NaXe has been recorded with high resolution for wavenumbers between 16800 and 16900 cm^{-1} using a tunable single-mode dye laser. In addition, a low resolution scan has been performed between 16470 and 16950 cm^{-1}.

Due to the presence of 5 stable Xe isotopes with relative abundance of more than 5% in natural mixture of isotopes the observed absorption spectrum of NaXe is highly congested. An assignment of rotational quantum numbers was only possible by extensive application of the method of optical-optical double resonance which produces isotope-selective signals. Up to now, four vibrational transitions from the $X\Sigma$ v''=0 level to the $A\Pi_{3/2}$ v' and v'+2 level and to the $A\Pi_{1/2}$(v'+1) and v'+2 level have been analysed for the 3 Xe isotopes 129, 131 and 132 with relative abundance of 26.4, 21.2 and 26.9% resp. From about 70 rotational lines per isotope and per vibrational transition we have determined preliminary values for the parameters of molecular rotation. As an example the rotational constants of NaXe^{132} turn out to be B(v''=0)=1.038(1) GHz and B(v')=1.614(1) GHz. A vibrational assignment has not been possible up to now. However, from the results of previous model potential calculations we expect v' to be around 13. As a result of our low-resolution scan we could estimate the fine structure splitting between the $A\Pi_{1/2}$ v' and the $A\Pi_{3/2}$ v' state of NaXe to be about 480 GHz.

Institut für Strahlungs- und Kernphysik, Technische Universität Berlin, Hardenbergstr. 36, D-1000 Berlin 12, Germany

RA1 (8:30)

THE IR SPECTRUM OF ACETYLENE: APPLICATION TO MOLECULAR ASTRONOMY

J. J. HILLMAN

Acetylene is known to be a constitutent in planetary atmospheres and in the atmospheres of cool carbon stars based on spectra in the 12- to 14-micron region. From ground-based heterodyne observations of the carbon star IRC+10216 one can determine mass loss and velocity structure from these high resolution data (5 MHz, 0.3 Km/sec). A systematic laboratory study has been undertaken to interpret these astrophysical data on a quantitative basis. Spectra have been recorded with the one-meter FTS located at the McMath Solar telescope at the National Solar Observatory. The FTS was used in the double-pass mode to produce an unapodized spectral resolution of 0.0025 cm^{-1}.

We will present our current interpretation of these data. GSCD analysis has resulted in refinement of the ground state, the fundamental bending modes, and the associated hot and hot-hot bands. We have also begun an analysis of the regional intensity and will discuss progress.

Address of Hillman: NASA/Goddard Space Flight Center, Laboratory for Extraterrestrial Physics, Code 690, Greenbelt, MD 20771

RA2 (9:00)

The Dissociation Energy of Acetylene

Peter G. Green, James L. Kinsey, and Robert W. Field

Recently we reported [J. Chem. Phys. 91, 5160 (1989)] an *upper bound* measurement of D_0^0 (HCC-H) $\leq$ 126.65 kcal/mol, based on observations of Stark-induced *increases* in radiative decay rates of *securely assigned* rovibronic levels of the HCCH $\tilde{A}^1A_u$ state. The lowest level to show a significant zero-pressure-extrapolated lifetime decrease (from 667(5)ns at ε=0 volts/cm to 514(4)ns at ε=113kV/cm) is v_3'=2, K_a=1, J=1 at 44295.65(10) cm^{-1} above v"=0, J"=0 of the $\tilde{X}$-state. Our interpretation of this Stark-induced lifetime decrease as predissociation has been the subject of considerable controversy, owing to the importance of D_0^0(HCC-H) and ΔH_f^0(HCC) in models of combustion kinetics and to recent reports of experimental and *ab initio* values 5-7 *kcal/mol larger than our upper bound value.*

Alternative interpretations of our Stark effect result and other conflicting experimental results will be discussed.

Address of Green: Division of Geology and Planetary Sciences, CalTech 170-25, Pasadena, CA 91125

Address of Kinsey: Wiess School of Natural Sciences, Rice University, Houston, TX 77251

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

RA3 (9:25)

STARK AND ZEEMAN SPECTROSCOPY OF ACETYLENE:
LOCATING A TRIPLET ISOMERIZATION BARRIER

P. G. Green, P.Dupré, M.Lombardi, R.Jost, J.L.Kinsey and R.W.Field

Anticrossing and quantum beat spectroscopies (employing magnetic fields from zero to 8 Tesla = 80 kGauss, or electric fields of up to 113 kV/cm) have been used to study intramolecular interactions in the acetylene molecule. Both Zeeman and Stark activity occurs among the low-lying rovibrational levels of the first excited singlet electronic state S_1 ($\tilde{A}\,^1A_u$). These properties, as well as the quantity and strength of interactions between the selected levels and those nearby levels belonging to the lower-lying triplet electronic states T_i (i=1-3) — and highly vibrationally excited levels of the ground electronic state S_0 ($\tilde{X}\,^1\Sigma_g^+$) — change rapidly with small changes of total energy in the molecule. The variety of observations are best explained by the surmounting of a triplet isomerization barrier between the *trans-* and *cis*-bent minima on the T_1 potential energy surface. This barrier would be located near or below the v_3'=2 level, thus at about 44,000 cm^{-1} above the zero point level of S_0

Address of Green: Mail Stop 170-25, Caltech, Pasadena, CA 91125 USA
Address of Dupré, Lombardi and Jost: Service National des
Champs Intenses, C.N.R.S., BP 166X, 38042 GRENOBLE Cedex France
Address of Kinsey: Weiss School of Natural Sciences, Rice University,
Box 1892, Houston, TX 77251 USA
Address of Field: Department of Chemistry, Massachusetts
Institute of Technology, Cambridge, MA 02139 USA

RA4 (9:42)

STATISTICAL SPECTROSCOPY OF VIBRATIONALLY EXCITED ACETYLENE

D. M. Jonas, Y. Chen, R. J. Silbey, and R. W. Field

Stimulated Emission Pumping spectra of HCCH above 14,000 cm^{-1} indicate that the rotation - vibration separation has partially broken down. In addition, the large amplitude isomerization of acetylene to vinylidene has been demonstrated to occur near 15,600 cm^{-1}. Throughout this region, the density of states observed by SEP exceeds the total calculated by an anharmonic direct count by up to a factor of two. To test for the quantum analog of classical chaos, SEP spectra obtained by PUMPing two different vibrational levels of the $\tilde{A}$ state were pooled and sorted into *complete, pure sequences* of all levels having the same values of the rigorously good quantum numbers J and parity. Complete, pure sequences of energy levels exhibit a "level repulsion" and "spectral rigidity" in the semiclassical limit for certain extreme forms of classical chaos. Analysis of the level spacing statistics for these pure sequences indicates that the spectrum of acetylene at 15,000 cm^{-1} is not as rigid as predicted for strongly chaotic dynamics.

Address of Jonas, Silbey, and Field: Department of Chemistry and George R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Address of Chen: Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482.

RA5 (9:59)

VIBRATIONALLY HIGHLY EXCITED ACETYLENE AS STUDIED BY DISPERSED
FLUORESCENCE AND STIMULATED EMISSION PUMPING SPECTROSCOPY

K. Yamanouchi, N. Ikeda, S. Tsuchiya, D. M. Jonas, J. K. Lundberg, and R. W. Field

Dispersed Fluorescence (DF) spectra of C_2H_2 in the $\tilde{X}$ state were measured at ~30 cm^{-1} resolution by exciting single rovibronic levels of the $\tilde{A}$ state. The DF spectra are mainly composed of progressions in the v_2 and v_4 modes. The Franck-Condon bright features have vibrational quantum numbers of $v_1=0,1$, $v_2=0-5$, $v_3=0$, $v_4=0-30$, $v_5=0-4$. A total of 117 vibrational bright states, distributed between 5700 and 23,400 cm^{-1} were identified. The vibrational term values of the assigned features are represented by a third order anharmonic expansion to within experimental error. The determined expansion coefficients are consistent with literature values.

The vibrationally highly excited region between 16,500 and 21,000 cm^{-1} was also investigated with higher resolution (0.4 cm^{-1}) by Stimulated Emission Pumping spectroscopy. A comparison of the SEP and DF spectra having the same upper rovibronic levels reveals that a single feature assigned to one bright state in the DF spectrum is composed of >10-40 peaks. The considerable couplings revealed in the vibrationally highly excited region are evidenced by the splittings resolved under high resolution.

Address of Yamanouchi, Ikeda, and Tsuchiya: Department of Pure and Applied Sciences, The University of Tokyo, Komaba, Megoro-ku, Tokyo 153, Japan.
Address of Jonas, Lundberg, and Field: Department of Chemistry and George R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Intermission (10:16 -10:30)

RA6 (10:30)

Ab initio study of vibrational resonances in polyatomic molecules.

F. CULOT and J. LIEVIN

An ab initio method for the study of vibrational resonances in polyatomic molecules is presented. It is based on a variational resolution of the vibrational motion within an electronic potential fitted from a grid of ab initio calculated points. An original multiconfigurational self-consistent field approach (VMCSCF) has been developed in order to eliminate the problem of basis set dependency occuring with usual methods, like configuration interaction (VSCF-CI), when strong vibrational resonances exist. The method is expected to provide configuration mixing coefficients directly useful to the interpretation of energy and intensity redistribution in spectra. Preliminary results on H_2O, CH_2O and C_2H_2 are discussed.

Address: Laboratoire de Chimie Physique Moléculaire, CP.160, Université Libre de Bruxelles, Ave. Roosevelt 50, 1050, Brussels, Belgium.

RA7 (10:42)

Ab initio study of the ^1A_g valence states of acetylene.

J. LIEVIN

Ab initio calculations (SCF, CASSCF and CI) on the valence excited states of ^1A_g symmetry of the acetylene molecule are presented. Term energy values, equilibrium geometries, rotational and vibrational constants have been derived from. The results concerning the $\tilde{C}$ ^1A_g state arising from the ...$(3b_u)^2 (4a_g)^2$ configuration are in close agreement with a recent experimental study[1] by UV double resonance technique. An ab initio interpretation of the Walsh diagrams is used to illustrate the important electron rearrangements that occur along the bending coordinate, explaining the stabilization to strongly bent trans structures.

[1] J.K. Lundberg, J.P. Pique, Y. Chen, R.W. Field. "44th Symposium on Molecular Spectroscopy". The Ohio State University, Colombus (1989).

Address: Laboratoire de Chimie Physique Moléculaire, CP.160, Université Libre de Bruxelles, Ave. Roosevelt 50, 1050, Brussels, Belgium.

RA8 (10:54)

THE RAMAN SCATTERING INTENSITY PARAMETERS OF ACETYLENE

K. M. GOUGH AND W. F. MURPHY

The Raman trace scattering cross sections for CH stretching vibrations may be described in terms of derivatives of the mean molecular polarizability with respect to the CH stretching internal coordinate. There is, in general, good agreement between values for these parameters obtained from experimental absolute intensity studies and those calculated by *ab initio* quantum mechanical techniques. In particular, this has been verified for the cases of methane, ethane, n-propane, cyclohexane and ethylene. One apparent exception to this result is acetylene, for which this derivative is calculated to be significantly smaller than the experimental value, when compared with the results for other molecules.[1,2]

We have remeasured the Raman trace and quadrupole scattering cross sections for acetylene and re-analysed the experimental results within the double harmonic approximation. The obtained parameters fit the experimental results to a high degree of accuracy, and both the measured cross sections and derived intensity parameters agree well with the previous results.

We have also considered the contribution of various approximations made in the *ab initio* calculations. When we examined the effect of electron correlation on the calculated ethane, ethylene and acetylene intensity parameters, we found that the acetylene results were affected differently than those for ethane and ethylene. For these three cases, the *ab initio* calculations with electron correlation yield CH stretching intensity parameters that more closely parallel those obtained from experiment.

[1] E. N. Svendsen and T. Stroyer-Hansen, Molec. Phys. 56, 1025 (1985).
[2] K. M. Gough, J. Chem. Phys. 91, 2424 (1989).

Address: Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6.
Current address of Gough. Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

RA9 (11:11)

RAMAN-ULTRAVIOLET DOUBLE RESONANCE SPECTROSCOPY OF THE ACETYLENE MOLECULE

B. L. CHADWICK AND B. J. ORR

We report optical double resonance (ODR) experiments in which selective preparation of gas-phase acetylene (C_2H_2) in discrete rotational states of the $v_2 = 1$ (C≡C stretch, 1974 cm^{-1}) vibrational level is achieved by pulsed coherent Raman excitation, with laser-induced fluorescence (LIF) detection.[1] The quality of these LIF-detected Raman-ODR spectra is superior to that attained in our previous work on larger polyatomic molecules.[2]

The method depends on a careful choice of the vibronic bands used to monitor the v_2-mode Raman excitation, since the $\tilde{A} \leftarrow \tilde{X}$ absorption system of C_2H_2 involves a bent ← linear geometric transition and the Franck-Condon principle favors quanta of the symmetric bending modes (v_3' in the $\tilde{A}$ state and v_4 in the $\tilde{X}$ state). Several previously unreported $\tilde{A} \leftarrow \tilde{X}$ vibronic bands have been recorded with the intensity-enhancement of v_2-mode Raman excitation : $2^0_1 3^1_0$ (242 nm), $2^0_1 3^2_0$ (236 nm), $2^0_1 3^3_0$ (231 nm), $2^0_1 3^1_0 4^0_1$ (246 nm) and $2^0_1 3^2_0 4^0_1$ (240 nm). Our Raman-ODR spectra clearly demonstrate the effect on rovibronic intensities of "axis-switching",[3] resolved one rotational state at a time. Variation of the delay between the Raman pump pulses and the LIF probe also provides a view of collision-induced state-to-state rotational energy transfer. Another Raman-ODR spectroscopic approach yields highly resolved state-specific Raman spectra, recorded by fixing the LIF probe wavelength on a single rovibronic transition and scanning the Raman-excitation frequency through O-, Q- and S-branch rovibrational transitions. Parallel infrared-ultraviolet double resonance and Raman-ODR studies of C_2D_2 and C_2HD are also in progress.

[1] B. L. Chadwick, D. A. King, L. Berzins, and B. J. Orr, J. Chem. Phys. 91, 7994 (1989).
[2] A. B. Duval, D. A. King, R. Haines, N. R. Isenor, and B. J. Orr, J. Opt. Soc. Amer. B 2, 1570 (1985).
[3] J. T. Hougen and J. K. G. Watson, Canad. J. Phys. 43, 298 (1965).

Address of Chadwick and Orr : School of Chemistry, Macquarie University, N.S.W. 2109, Australia

Chemical structures cited :

H-C≡C-H
H-C≡C-D
D-C≡C-D

RA10 (11:28)

INTERMOLECULAR POTENTIAL FUNCTIONS FOR ACETYLENE

J. S. Muenter

Intermolecular potential functions based on the properties of isolated molecules provide an efficient means of describing small molecular systems. The challenge is to construct a function which is complex enough to be realistic, and yet have a small enough number of parameters to be useful. The relatively large number of high resolution spectroscopic studies of acetylene containing van der Waals molecules provides a data base to test different analytic forms for intermolecular potential functions. A model, which contains no adjustable parameters, has been developed to calculate intermolecular interactions in small molecular clusters containing acetylene. Dispersion and repulsion interactions are described with atom centered Lennard-Jones C_6 and C_{12} terms. The C_6 coefficients are obtained by subdividing known long range dispersion interactions over the atoms of the molecule in question. The repulsion terms are based on conventional van der Waals radii. Electrostatic interactions are calculated from published distributed multipole descriptions of the monomer charge distributions. The absence of induction terms is justified by the small electric fields generated by the charge distributions of the nonpolar molecules considered here. The van der Waals molecules considered include the dimer, trimer, and tetramer of acetylene, $HCCH\text{-}CO_2$, $HCCH\text{-}N_2O$, $HCCH\text{-}CO$, and $HCCH\text{-}N_2$. Good agreement between predicted and observed geometry is found in each case. Where experimental estimates exist for either harmonic frequencies or vibrational amplitudes, agreement is also very satisfactory.

Address of Muenter: Dept. of Chemistry, University of Rochester, Rochester, N.Y. 14627.

RA11 (11:45)

PHOTOELECTRON-INDUCED DISSOCIATIVE ATTACHMENT IN C_2H_2: D_0 (HCC-H)

B. RUSCIC AND J. BERKOWITZ
Argonne National Laboratory, Argonne, IL 60439

Photoelectrons generated in the photoionization of acetylene are observed to produce C_2H^- upon collision with other C_2H_2 molecules. The photoelectron energy can be continously tuned from 0 - 8eV by varying the incident photon energy from 11.40 eV (the ionization potential of C_2H_2) to higher energy. The dissociative attachment process $e + C_2H_2 \rightarrow C_2H^- + H$ has a threshold at 877 ± 2 Å, corresponding to a photoelectron energy of 2.74 ± 0.03 eV. The same threshold value has been obtained at $298°K$ and $\sim150°K$, and hence the temperature dependence, if any, is slight. When this threshold is combined with E.A. $(C_2H) = 2.969 \pm 0.010$ eV, one obtains D_0 $(HC_2 - H) \leq 5.71 \pm 0.03$ eV $\equiv 131.6 \pm 0.7$ kcal/mol.

RA12 (11:57)

TUNABLE FAR INFRARED LASER SPECTROSCOPY OF JET-COOLED CARBON CLUSTERS: THE ν_2 BENDING VIBRATION OF C_3

C.A. SCHMUTTENMAER, R.C. COHEN, N. PUGLIANO, J.R. HEATH, A.L. COOKSY, K.L. BUSAROW and R.J. SAYKALLY

Seven rovibrational transitions of the $(01^10) \leftarrow (00^00)$ fundamental bending band of C_3 have been measured with high precision using a tunable far-infrared laser spectrometer. The C_3 molecules were produced by laser vaporization of a graphite rod and cooled in a supersonic expansion. This is the first determination of the astronomically important ν_2 fundamental frequency near 63 cm^{-1}. These measurements provide the basis for studies of C_3 in the interstellar medium with far-infrared astronomy.

Address: Department of Chemistry, University of California, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

RB1 (8:30)

PERTURBATIONS IN THE ν_7 STATE OF CD_3CCH

R. J. KSIRSAGAR, C. MEDHEKAR, V. A. JOB, V. B. KARTHA, A. WEBER, AND W. B. OLSON

Rotational line assignments of the 1048 cm^{-1} (ν_7) perpendicular band of the CD_3CCH molecule have been made and molecular parameters derived, taking into account various vibration-rotation interactions. The dominant perturbation is an xy Coriolis interaction with a non-degenerate state at 1111 cm^{-1} which is most probably ν_4. Transitions to the latter state are weak and could not be identified. The crossover of the K(+ℓ) component of the degenerate state and the K-1 level of the non-degenerate state takes place after K=9 of the degenerate state. It was possible to derive approximate molecular parameters of the unseen level from the magnitude of the perturbations. The A_1A_2 splittings of K=2 (-ℓ) component of the degenerate level have been observed for J>32 and accurately measured with a diode laser spectrometer. These splittings originate mainly from K-type doubling interaction between 0° and 2^{-1} levels. XY Coriolis interactions between 0° and 1^1 levels and ℓ-type "+2,-1" resonance between 1^1 and 2^{-1} levels also contribute to the splittings.

Address of Ksirsagar, Medhekar, Job, and Kartha: Spectroscopy Division, Bhabha Atomic Research Centre, Bombay 400085, India.

Address of Weber and Olson: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899.

RB2 (8:47)

HIGH RESOLUTION FT SPECTROSCOPY OF THE $2\nu_9$ BAND OF CD_3CCH

K. SINGH, G. RAJAPPAN, V. A. JOB, V. B. KARTHA, A. WEBER, AND W. B. OLSON

A high resolution Fourier transform spectrum of CD_3CCH recorded at an apodized resolution of 0.004 cm^{-4} in the region of the $2\nu_9$ band has been analyzed. The spectrum is heavily overlapped with strong hot bands as a result of which many lines are blended. More than 600 lines of the parallel component of the $2\nu_9$ band up to J=50 and K=9 were fitted with a standard deviation of 0.0025 cm^{-1} to derive molecular parameters. The J-structure of the three hot band transitions arising from the parallel components of $2\nu_9 + \nu_{10} - \nu_{10}$, $2\nu_9 + 2\nu_{10} - 2\nu_{10}$, and $3\nu_9 - \nu_9$ was analyzed.

Address of Singh, Rajappan, Job, and Kartha: Spectroscopy Division, Bhabha Atomic Research Centre, Bombay 400085, India.

Address of Weber and Olson: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899.

RB3 (9:04)

IR SIDEBAND SPECTRA OF NF_3 AND PF_5

H. PRINZ, W.A. KREINER, G. MAGERL, N. ROHRINGER, AND
W. SCHUPITA

The technique of IR laser sidebands has been applied to both molecules. On NF_3, a saturation spectrum of the ν_1 fundamental has been recorded. On PF_5, the ν_3 fundamental ($\sim$ 946 cm^{-1}) has been investigated up to J" = 76. As a result, 11 parameters have been determined, yielding an overall standard deviation of 207 kHz. Around 1020 cm^{-1}, in the range of the ν_5 / $2\nu_8$ vibrations, a large number of saturation dips has been recorded with a resolution of about 100 kHz, but the spectrum has not been assigned so far.

Address of Prinz and Kreiner: Abt. Physikalische Chemie, University of Ulm, Ulm, W.-Germany

Address of Magerl, Rohringer, and Schupita:
Institut für Nachrichtentechnik, Technical University of Vienna, Vienna, Austria

RB4 (9:21)

VIBRATIONALLY INDUCED DIPOLE MOMENT OF TRIFLUOROSILANE

KENSUKE HARADA, KEIICHI TANAKA, AND TAKEHIKO TANAKA

CO_2 laser Stark spectroscopy has been applied to the ν_4 (SiF_3 degenarate stretch) fundamental band of trifluorosilane. For $SiHF_3$ and $SiDF_3$[1], the vibrationally induced dipole moments in the ν_4 state (μ_r) are $\pm0.03438(17)$ and $\pm0.03516(13)$ D, respectively, while the vibrational changes of the dipole moments on excitation of the ν_4 mode ($\delta\mu_4$) are $0.02673(10)$ and $0.02649(10)$ D, respectively. These μ_r and $\delta\mu_4$ values are satisfactorily explained by a simple model, in which we only take account of the first and second derivatives of the SiF bond moment ($(\partial\mu/\partial R)_e$, $(\partial^2\mu/\partial R^2)_e$) and the mechanical anharmonicity of the SiF bond (f_{RRR}). The same model also well reproduces the vibrationally induced dipole moment in the ν_3 state of SiF_4, if $(\partial\mu/\partial R)_e$, $(\partial^2\mu/\partial R^2)_e$, and f_{RRR}/f_{RR} are transferable. The dipole moment derivatives, $(\partial\mu/\partial R)_e = 3.78(76)$ D/Å and $(\partial^2\mu/\partial R^2)_e = 23.8(70)$ D/Å^2, are derived, where $(\partial\mu/\partial R)_e$ is estimated from the ν_3 band intensity of SiF_4. We also discuss extension of the present model to the $\delta\mu$ and μ_r values associated with the SiF and CF stretching vibrations in various molecules.

[1] K. Harada, I. Nagano, S. Kimura, K. Tanaka, and T. Tanaka, *J. Mol. Spectrosc.* 138, 230 (1989).

Adress: Department of Chemistry, Faculty of Science, Kyusyu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan.

RB5 (9:38)

INFRARED DIODE LASER SPECTROSCOPY OF THE ν_3 FUNDAMENTAL AND $\nu_2+\nu_3 \leftarrow \nu_2$ BANDS OF THE CD_3 RADICAL.

WAFAA M. FAWZY, TREVOR J. SEARS AND PAUL B. DAVIES

The observation and a preliminary analysis of about twenty ro-vibrational transitions of the ν_3 fundamental of the CD_3 radical was reported at this meeting last year[1]. We present here analysis of sixty two infrared absorption lines in the ν_3 fundamental band. The main molecular parameters determined in the present work are the band origin $\nu_0 = 2381.0886(84)$, $B' = 4.758737(40)$, $C' = 2.373297(34)$, $(\zeta C)_3 = 0.476278(72)$, $q_3 = 0.00376(59)$, all in cm^{-1} with one standard deviation in parenthesis. The derived molecular parameters were compared with those for the CH_3 radical $\nu_3 = 1$ level determined previously[2]. A relatively weak set of transitions were also observed in the vicinity of the ν_3 fundamental. These transitions were tentatively assigned to the $\nu_2+\nu_3 \leftarrow \nu_2$ infrared transition. Results for both the ν_3 and $\nu_2+\nu_3 \leftarrow \nu_2$ bands will be discussed.

[1] W. M. Fawzy and T. J. Sears, Forty-Fourth Symposium on Molecular Spectroscopy at Ohio State, Columbus, paper MF9.
[2] T. Amano, P. Bernath, C. Yamada, Y. Endo, and E. Hirota, J. Chem. Phys. 77, 5284(1982).

Address of FAWZY and SEARS: Department of Chemistry, Brookhaven National Laboratory, Upton, N.Y. 11973.

Address of DAVIES: Department of Chemistry, University of Cambridge, Cambridge, CB21EP, UK.

RB6 (9:55)

HIGH RESOLUTION FTIR AND DIODE LASER SPECTRA OF PROPYNE-D IN THE 9-11 μm REGION

S. B. KARTHA, V. A. JOB, V. B. KARTHA, A. WEBER, AND W. B. OLSON

Methyl acetylene (propyne) is of interest because of its presence in planetary atmospheres, application in optically pumped lasers, and possible isotope enrichment. Almost all the energy levels of the isotopic propynes interact strongly giving a variety of perturbation effects, which make their vibration-rotation spectra very complex. An understanding of the spectra is possible only by a detailed study of the various transitions in the different isotopomers. In this paper we present the results of our high resolution Fourier transform and diode laser spectral studies on CH_3CCD in the 9-11 μm region. The $2\nu_9$ and ν_6 bands fall in this region. It has been conjectured by earlier workers (1,2) from indirect evidence that the K-numbering of Thomas and Thompson (3) for the ν_6 band of CH_3CCH requires a revision by 3 units. Our studies give direct evidence for such a renumbering in CH_3CCD also. This and other interesting features of the $2\nu_9$ and ν_9 bands, together with detailed assignments and analysis of the lines in the 9-11 μm region will be presented and discussed.

1. J. I. Duncan, I. J. Wright, and D. Ellis, J. Mol. Spectrosc. 37, 394 (1971).
2. T. Al Adlouni, F. Meyer, C. Meyer, J. G. Layahe, and A. Fayt, Int. J. Infrared and Millimeter Waves 7, 405 (1986).
3. R. K. Thomas and H. W. Thompson, Spectrochim. Acta. 24A, 1353 (1968).

Address of Kartha, Job, and Kartha: Spectroscopy Division, Bhabha Atomic Research Centre, Bombay 300085, India.

Address of Weber and Olson: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Intermission

RB7 (10:30)

ANALYSIS OF THE HIGH-RESOLUTION INFRARED SPECTRUM OF METHYL ISOCYANIDE

MOHAMMAD ELSHAKRE, L. PETER GOLD, AND ROBERT A. BERNHEIM

The infrared spectrum of methyl isocyanide, CH_3NC, has been measured in the region 2120 - 2190 cm^{-1} at a resolution of 0.002 cm^{-1} using a Bomem DA3 Fourier-transform spectrometer. The ν_2 fundamental band and two combination bands, $\nu_2+\nu_8-\nu_8$ and $\nu_2+2\nu_8-2\nu_8$, have been assigned. Molecular constants for the upper states of the three bands have been derived using the ground state constants determined by microwave spectroscopy[1,2] and fitting procedures and programs developed by Plíva[3].

1 A. Bauer, M. Bogey, and M. A. Kastler, C. R. Acad. Sci. Ser. B 271, 892 (1970).
2 A. Bauer, M. Bogey, and S. Maes, J. Phys. (Paris) 32, 763 (1971).
3 J. Plíva, personal communication.

Address of Elshakre, Gold, and Bernheim: Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802.

RB8 (10:47)

INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF ETHYL AT 19 µm

T. J. SEARS, P. M. JOHNSON, J. M. FRYE AND W. M. FAWZY

We discuss progress in the analysis of the infrared spectrum of the ethyl radical (C_2H_5) first reported at this meeting last year. We have succeeded in modelling the gross features of part of the observed spectrum close to 530 cm^{-1}. The model used assumes nearly free internal rotation about the C-C bond and we find that the inertial constants derived from one of the few calculations on this species do not have to be very much altered. The model makes predictions and there are regions of the spectrum that need to be searched but were not covered previously. We hope to report on the results of these additional experiments at the meeting.

Address of Sears and Fawzy: Department of Chemistry, Brookhaven National Laboratory, Upton, N.Y. 11973.
Address of Johnson: Department of Chemistry, SUNY Stony Brook, Stony Brook, N.Y. 11790.
Address of Frye: Department of Chemistry, Howard University, Washington, D.C. 20059.

RB9 (11:04)

INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF HOCO AND DOCO RADICALS.

WAFAA M. FAWZY AND TREVOR J. SEARS

Several infrared bands of the HOCO and DOCO radicals were previously observed in CO matrices[1]. The band origin of the C=O vibrational stretching mode was determined to be 1833 and 1825 cm^{-1} for trans-HOCO and DOCO, respectively[1]. We report what is believed to be the first gas phase observation of these reactive radicals. The HOCO and DOCO were produced by excimer laser photolysis of CH_3COOH, CH_3COOD, and CD_3COOD at 193nm. Relatively strong and congested ro-vibrational spectra were detected by diode laser absorption around 1860 cm^{-1}. We assigned these transitions to the C=O stretch of HOCO and DOCO. This assignment was supported by chemical evidence and effects of H/D exchange on the observed spectrum. We are currently searching for more transitions. Experimental results and preliminary analysis of the observed spectra will be presented.

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

Address of FAWZY and SEARS: Department of Chemistry, Brookhaven National Laboratory, Upton, N.Y. 11973.

RB10 (11:21)

GAS COMPOSITION CONTROL FOR A PULSED NOZZLE FT MICROWAVE SPECTROMETER AND APPLICATIONS

TRYGGVI EMILSSON, T. C. GERMANN, AND H. S. GUTOWSKY

Pulsed supersonic jets of inert carrier gases seeded with more reactive species are used to generate small clusters for a variety of experiments. In our case, it is the sample source for a Balle/Flygare Fourier transform microwave spectrometer[1] used to observe rotational transitions of the clusters and determine their structure. In such experiments, accurate control of the small concentrations of reactive species is both important and can be difficult.

A system has been built which permits rapid (5 sec) and reproducible control of the composition and pressure of gas mixtures supplied to the nozzle. Typical samples consist of an arbitrary mixture of two inert gases seeded with one or two other substances at concentrations between several ppm to several percent. The concentration of each ingredient can be controlled to about 1% of its value. The system is comprised of four mass flow controllers (MKS Instruments, Model 1259) and a microprocessor based programmer (MKS, Model 147), as well as a handful of small bore valves and miscellaneous plumbing.

The gas control system is being used to explore kinetic features of the supersonic expansion in the spectrometer. For example, one may inquire whether the first step in the formation of an Ar_2-HCN trimer is the formation of Ar_2 or of Ar-HCN, or both. The intensity observed for the $1_{11} \rightarrow 2_{02}$ transition of the trimer at 4312.38 MHz, using first run neon (70% Ne, 30% He) as the carrier gas, shows it to be first order in [Ar] and in [HCN]. This suggests that Ar_2-HCN is formed primarily from Ar-HCN and Ar. The details of this and related experiments will be described.

[1] T. J. Balle and W. H. Flygare, Rev. Sci. Instr. $\underline{52}$, 33 (1981).

Address: Noyes Chemical Laboratory, University of Illinois, Urbana. Illinois, 61801.

RB11 (11:38)

ROTATIONAL SPECTRUM OF Ar_2-HCN, A VERY FLOPPY T

T. D. KLOTS, C. E. DYKSTRA, AND H. S. GUTOWSKY

The rotational spectrum of Ar_2-HCN has been observed between 2.5 and 11.5 GHz with a pulsed nozzle, Fourier transform, Balle/Flygare microwave spectrometer. The ground-state rotational constants were determined to be 1769.366, 1743.854, and 857.600 MHz, with b-dipole transitions. The centrifugal distortion, fitted by a Watson Hamiltonian, is extremely large with values for τ_1, τ_2, τ_{aaaa}, τ_{bbbb}, and τ_{cccc} of -6.54, -1.199, -0.68, -0.360, and -0.052 MHz and for H_J and H_{JK} of 0.077 and -1.7 kHz. Even with the two 6th order terms the fit has a large rms deviation of 160 kHz.

The equilibrium geometry is found to be T-shaped with C_{2v} symmetry and ostensibly planar; however, the inertial defect is 13.9 μA^2, extremely large for a planar structure. The ^{14}N hyperfine interaction depends somewhat on J and K and shows that bending vibrations of the HCN are large and highly anisotropic, averaging 34° in the plane of the cluster (θ_{ab}) and 25° out of-plane (θ_{bc}). The Ar to HCN center of mass distance is significantly shorter than in Ar-HCN dimer, 4.16 versus 4.34 A.

The unusual properties of the trimer are a more extreme version of those found for the Ar-HCN dimer.[1] As in the case of the latter, they are attributed to the shape of the potential function as calculated with a largely classical electrical model using low-order moments and multipole polarizabilities.[2] The potential surface for Ar_2-HCN, as a function of θ_{ab} and θ_{bc}, has a broad elliptical minimum while that for Ar_2-HF is steep and more circular. There are similar differences in the dependence on the Ar_2 c.m. to HX c.m. distance.

[1] T. D. Klots, C. E. Dykstra, and H. S. Gutowsky, J. Chem. Phys. $\underline{90}$, 30 (1989).
[2] C. E. Dykstra, J. Am. Chem. Soc. $\underline{111}$, 6168 (1989).

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.

RB12 (11:55)

Vibrations in Small Be_n and Mg_n Clusters ($n = 3,4$)

Timothy J. Lee, Alistair P. Rendell, and Peter R. Taylor

Equilibrium structures, binding energies and harmonic vibrational frequencies of the Be_3, Be_4, Mg_3 and Mg_4 clusters have been determined using large Gaussian basis sets in conjunction with highly correlated wave functions. The electron correlation methods used include singles and doubles coupled-cluster [CCSD] theory and the extension including the effects of connected triple excitations [CCSD(T)] along with the multireference configuration interaction [MRCI] approach. In addition, full cubic and quartic force fields have been determined (with the CCSD(T) method) and used in evaluating anharmonic constants, vibration-rotation interaction constants and quartic and sextic centrifugal distortion constants. Infrared absorption intensities have been determined using the double harmonic approximation. The anharmonic analyses display some very interesting features which will be discussed.

Address of Lee and Rendell: NASA Ames Research Center, Mail Stop 230-3, Moffett Field, California 94035.
Address of Taylor: ELORET Institute, NASA Ames Research Center, Mail Stop 230-3, Moffett Field, California 94035.

RC1 (8:30)

IMPROVED NONADIABATIC CALCULATION OF EXCITED SINGLET STATES OF THE HYDROGEN MOLECULE

SHILIANG YU AND KURT DRESSLER

Avoided crossings of the electronic energy curves of the $1\sigma_u^2$ state and of the Rydberg series ns, $nd\sigma$ (n=3,4...) of hydrogen give rise to the double minima in the EF and GK $^1\Sigma_g^+$ states and to strong coupling between the vibrations of the adiabatic $^1\Sigma_g^+$ states. From the analysis of *ab initio* calculations of the five rovibronically coupled states $(2s)EF$ + $(3d\sigma)GK$ + $(3s)H$ $^1\Sigma_g^+$ + $(3d\pi)I$ $^1\Pi_g$ + $(3d\delta)J$ $^1\Delta_g$,[1] we know that still higher states contribute to the nonadiabatic energy shifts. We have included the three states $(4d\sigma)P$ $^1\Sigma_g^+$ + $(4d\pi)R$ $^1\Pi_g$ + $(4d\delta)S$ $^1\Delta_g$ in the eight-state coupled equations which describe the simultaneous vibronic and L-uncoupling interactions. The remaining deviations between calculated and experimental term values in H_2 and D_2 depend systematically on electronic state, on vibrational energy, and on isotopic mass; they are between two to ten times smaller than in the previous five-state calculation.[1]

---

[1] P. Quadrelli, K. Dressler, and L. Wolniewicz, J. Chem. Phys. (in press).

Adress: Physical Chemistry Laboratory, ETH-Zentrum, CH-8092, Zurich, Switzerland.

RC2 (8:42)

ROVIBRATIONAL INTENSITIES OF THE ELECTRIC QUADRUPOLE AND MAGNETIC DIPOLE TRANSITIONS IN OXYGEN

T.K. BALASUBRAMANIAN, ROMOLA O'CUNHA, V.P. BELLARY AND K. NARAHARI RAO.

The oxygen molecule is known to display an extremely weak rotation-vibration spectrum which is mainly attributable to an electric quadrupole (EQ) transition[1]. Due to the unpaired electronic spin in the ground state $(X^3\Sigma_g^-)$ a magnetic dipole (MD) contribution to the intensities of branches with $\Delta J=0,\pm1$ is conceivable. But this must necessarily arise through indirect mechanisms[2,3] since the magnetic moment is largely independent of the internuclear separation. Nevertheless, because of the intrinsically higher strength of MD transitions, the small intensities which do result may yet be comparable to the EQ contribution.

In the talk a rigorous theoretical approach to line intensities in the O_2 fundamental band will be presented which (i) evaluates the EQ and MD contributions, (ii) includes refinements due to vibration-rotation interaction and (iii) incorporates in the calculation the intermediate nature of the coupling in the $X^3\Sigma_g^-$ state.

---

[1] J.Reid, R.L. Sinclair, A.M. Robinson and A.R.W. McKellar, Phys.Rev. A 24, 1944 (1981).

[2] V.P. Bellary, Ph.D. Dissertation, University of Bombay, (1989).

[3] D. Papousek, Collect Czech. Commun. 54, 2555 (1989).

Address of Balasubramanian, O'Cunha and Bellary. Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085, India.

Address of Narahari Rao: Department of Physics, Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210.

RC3 (9:10)

VISIBLE-LASER SPECTROSCOPY OF NbN: NEW ELECTRONIC STATES AND HYPERFINE EFFECTS

A.G. ADAM, Y. AZUMA, G. HUANG, M.P.J. LYNE, A.J. MERER AND V.I. SRDANOV

Measurements of the hyperfine parameters of four excited electronic states of NbN have been carried out. Including previous work on the $B^3\Phi$ - $X^3\Delta$ system[1], hyperfine parameters have now bn measured for a total of six electronic states, namely $\delta\pi$ $^{1,3}\Pi$, Φ, $\sigma\delta$ $a^1\Delta$ and $X^3\Delta$. It is not simple to interpret these parameters without considering higher order spin-orbit effects. For example, the $\delta\tau$ $^1\Pi$ state lies within the spin-orbit structure of the $\delta\pi$ $^3\Pi$ state in zero order, and so strong is the interaction between them that the energy order of the two lowest spin components of the $^3\Pi$ state is reversed. Extensive wavelength-resolved fluorescence studies were needed to understand these interactions.

These wavelength-resolved fluorescence studies have also led to the discovery of three new low-lying electronic states, δ^2 $^3\Sigma^-$, δ^2 $^1\Gamma$ and σ^2 $^1\Sigma^+$, and to the location of $\sigma\delta$ $^1\Delta$. Above 19,000 cm^{-1} the energy level patterns are severely distorted by the onset of charge transfer transitions, the spectra become very perturbed and complicated in this region. The pattern of states found in NbN is likely to be typical of the early diatomic 4d metal compounds, fairly well-behaved low-lying states can be associated with unpaired electrons in the metal orbitals, but the regularity of the structure will break down totally when a ligand electron is promoted to the metal orbitals.

[1] Y. Azuma, J.A. Barry, M.P.J. Lyne, A.J. Merer, J.O. Schröder and J.L. Féménias, J. Chem. Phys. 91, 1 (1989).

Address of Adam, Huang, Lyne and Merer Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C V6T 1Y6, Canada.
Address of Azuma: Physics Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439.
Address of Srdanov: 926 W. Campus Lane, Goleta, California 93117.

RC4 (9:27)

ROTATIONAL AND HYPERFINE ANALYSIS OF THE $B^4\Pi$ - $X^4\Sigma^-$ (0,0) BAND OF NbO

A.G. ADAM, Y. AZUMA, J.A. BARRY, G. CHEVAL, J.L. FÉMÉNIAS, A.J. MERER, U. SASSENBERG AND J.O. SCHRÖDER

Over 6000 hyperfine-rotational lines have been assigned in the (0,0) band of the $B^4\Pi$ - $X^4\Sigma^-$ system of NbO near 6500 Å. The $B^4\Pi$ state is almost unperturbed rotationally, though its spin-orbit structure is severely distorted by spin-orbit interactions with nearby states. A global least squares fit (to the complete data set) has been attempted. The hyperfine parameters in the ground state are close to those obtained from matrix e s r work[1], but the unusual structure of the upper state requires higher order extensions to the conventional magnetic hyperfine and rotational Hamiltonians. Asymmetric hyperfine patterns in the $^4\Pi_{-1/2}$ - $^4\Sigma_{3/2}$ sub-band give evidence for a large value of the off-diagonal quadrupole parameter e^2Qq_2 in the $^4\Pi$ state.

The negative value for the Fermi contact parameter in the $B^4\Pi$ state suggests that its electron configuration is $\delta^2\pi$, like the upper state of the 7900 Å system of VO.

[1] J.M. Brom, C.H. Durham and W. Weltner, Jr. J. Chem. Phys. 61, 970 (1974).

Address of Adam and Merer Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Y6, Canada.
Address of Azuma: Department of Physics, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439.
Address of Barry: Department of Chemistry, University of Arizona, Tucson, Arizona 85721.
Address of Cheval and Féménias Laboratoire d'Optique Atomique et Moléculaire, Faculté des Sciences et des Techniques, Université de Nice, Parc Valrose, Nice 06034, France.
Address of Sassenberg Department of Physics, University of Stockholm, Vanadisvägen 9, Stockholm, S-113 46, Sweden.
Address of Schröder: Drägerwerk Aktiengesellschaft, Moislinger Allee 53/55, P.O. Box 13 39, D-2400 Lübeck 1, Germany.

RC5 (9:44)

HYPERFINE STRUCTURE IN THE $B^3\Pi_0{}^+{}_u \leftarrow X^1\Sigma_g{}^+$ TRANSITION OF $^{79}Br_2$.

J. E. MAYHUGH, T. J. SLOTTERBACK, AND K. C. JANDA

The $B^3\Pi_0{}^+{}_u \leftarrow X^1\Sigma_g{}^+$ transition of jet cooled $^{79}Br_2$ recorded with a narrow bandwidth ring dye laser will be analyzed using a hyperfine hamiltonian containing an electric quadrupole term, a spin-rotation term, and scalar and tensor spin-spin terms. Accurate fits of lines associated with low J levels yield the reduced matrix elements for both the upper and lower electronic states. These reduced matrix elements contain information on how the atomic orbitals contribute to the molecular orbitals in bromine and how their contributions change along the vibrational ladder. A study of how these reduced matrix elements are perturbed by the presence of a van der Waals' bond to neon and how they can be used to obtain additional information about the atom-molecule potential will be introduced.

Address of Mayhugh, Slotterback, and Janda: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

RC6 (10:01)

HYPERFINE STRUCTURE MEASUREMENTS IN THE $A^3\Pi(1) \leftarrow X^1\Sigma^+$ ELECTRONIC TRANSITION OF $I^{35}Cl$ NEAR THE DISSOCIATION LIMIT.

J. R. JOHNSON, T. J. SLOTTERBACK, K. C. JANDA, D. W. PRATT AND C. M. WESTERN

Vibrational levels near the dissociation limit of the $A^3\Pi(1)$ electronic state of $I^{35}Cl$ have been studied using fluorescence excitation techniques. By using a single mode ultra high resolution ring laser and a collimated molecular beam, the hyperfine structure due to both Iodine ($I = 5/2$) and Chlorine ($I = 3/2$) nuclei has been resolved. The hyperfine structure for the $v' = 19$, 24 and 29 vibrational levels will be discussed along with changes in the rotational (B), electric quadrupole (eQq_0, eQq_2 for both I and Cl), and magnetic hyperfine (a) constants as the molecule approaches dissociation. In addition, observed heterogeneous (state mixing) perturbations in the spectra of these high vibrational levels wil be discussed.

Address of Slotterback, Janda and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

Address of Western: Department of Chemistry, University cf Bristol, UNITED KINGDOM.

Address or Johnson: Texas Instrument, Dallas, TX.

Intermission

RC7 (10:30)

NEW ELECTRONIC STATES OF NH

R. D. Johnson III, J. W. Hudgens

Three new electronic states of NH and ND (imidogen radical) have been observed by REMPI (Resonance Enhanced Multiphoton Ionization) Spectroscopy in the region of 258 through 288 nm and assigned. The NH (ND) was produced by the photolysis of HN_3 (DN_3) (hydrazoic acid) in the same wavelength region. The observed two-photon transitions are from the $a\,^1\Delta$ state to 3p Rydberg states. Transitions were also observed from the $a\,^1\Delta$ state to the $d\,^1\Sigma^+$ state. The assignments for the new states are: $f\,^1\Pi$ $(3p\sigma)$ at 86378 cm^{-1}, $g\,^1\Delta$ $(3p\pi)$ at 88140 cm^{-1}, and $h\,^1\Sigma$ $(3p\pi)$ at 89531 cm^{-1}. Rotational constants (B and D) and, where possible, vibrational spacings for the thirteen observed bands are also determined.

Address: Chemical Kinetics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

RC8 (10:47)

EXAMINATION OF THE STRUCTURE, Λ-DOUBLING AND PERTURBATIONS IN THE $1^1\Pi_g$ STATE OF Li_2

C. LINTON[1], F MARTIN AND R. BACIS

Fluorescence in the $C^1\Pi_u - 1^1\Pi_g$, $2^1\Sigma_u^* - 1^1\Pi_g$ and $2^1\Sigma_u^* - 2^1\Sigma_g^*$ transitions of $^7Li_2$ and $^6Li_2$, excited by ultraviolet lines of argon and krypton ion lasers, has been studied in the region 7000 - 12000 cm^{-1} using a Fourier Transform spectrometer.

The rotational analysis concentrates on $^6Li_2$. In $C^1\Pi_u - 1^1\Pi_g$ fluorescence, long progressions, up to v=34, are observed in the $1^1\Pi_g$ state. The Dunham coefficients obtained from the analysis are in good agreement with ab-initio calculations. From the data, an RKR potential curve has been constructed for the $1^1\Pi_g$ state. The dissociation energy has been calculated by several independent methods giving a 'best value' of 1422.03 ± 0.05 cm^{-1}.

The Λ-doubling in both isotopomers is found to be irregular, both with respect to vibration and rotation. The interaction between the $1^1\Pi_g$ and $2^1\Sigma_g^*$ states has been studied in detail and is shown to account for the observed irregularities. The same interaction also accounts for some very strong perturbations observed in the $1^1\Pi_g$ and $2^1\Sigma_g^*$ states of $^6Li_2$. Some of these perturbations show very clear intensity interference effects. From an examination of intensity anomalies, ratios of transition moments of $2^1\Sigma_u^* - 1^1\Pi_g$ and $2^1\Sigma_u^* - 2^1\Sigma_g^*$ transitions have been determined.

Details of the above studies will be presented and the results discussed and compared with ab-initio predictions.

Address: Laboratoire de Spectrométrie Ionique et Moléculaire, Université Claude Bernard-Lyon I, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France.

[1]On leave from Physics Department, University of New Brunswick, Box 4400, Fredericton, N.B., Canada, E3B 5A3

RC9 (11:04)

Rydberg States of CaF observed by Optical-Optical Double Resonance

J. E. Murphy, J.M. Berg, N. Harris, A. J. Merer and R.W. Field

There have been many spectroscopic studies of the low-lying or valence states of the alkaline earth monohalides (MX) in recent years. These states are well represented by a simple physical model where there is a lone non-bonding electron centered on the metal ion. These M^+ states are perturbed by the electrostatic field of X^- acting at a distance R_e. Although this model has succesfully described the X, A, B and C states CaF, where $<r>$ of the Ca^+ 4s, 4p and 3d states is considerably less than R_e, it cannot be used to represent Rydberg states where $<r>$ will be greater than R_e. The core-penetrating ($r<R_e$) s,p and d Rydberg orbitals will however show evidence of their relationship to their core precursors through their quantum defects.

We have observed and assigned according to Λ, v and J, 68 vibronic states of CaF in the region from 40 600 cm^{-1} to 45 905 cm^{-1} using pulsed optical-optical double resonance via the A $^2\Pi_{3/2}$ state. O.O.D.R. transitions are detected by observation of direct UV fluorescence. These states have been organized into 18 Rydberg series (3 Σ series, 2 Π series and 1 Δ series converging to v=0, 1 and 2 levels of the ion) and this has enabled us to make an improved estimate of the CaF ionization potential (v=0 of CaF^+) at 47 005 cm^{-1} ± 20 cm^{-1}. These series are shown to extrapolate to previously observed low Rydberg and valence states, thus allowing assignments of absolute quantum defects. Using this information in conjunction with preliminary measurements of spin-orbit and spin-rotation constants, we have assigned the series according to n and l. We have observed all of the Λ components of the core penetrating s,p, and d Rydberg series in the region from n*=4 to n*=10. This is consistent with exitation out of the $A^2\Pi_{3/2}$ state which has been shown from ligand field calculations to be a mixture of Ca^+ 4p and 3d states. Reasons for the absence of f states in our spectra will be dicussed

Address of Murphy, Berg, Harris and Field: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Address of Merer: Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, V6T 1Y6 Canada

RC10 (11:21)

Rydberg States of CaCl Observed by Optical-Optical Double Resonance

Nicole A. Harris, J.E. Murphy, Z.J. Jakubek, R.W. Field

We have observed s, p, and d Rydberg series of CaF in the region from 40,600 to 45,905 and have recently begun work on the Rydberg series of CaCl. We scanned the region from 40,898 cm^{-1} to 41,860 cm^{-1} and observed only one $^2\Sigma$ state at 41,260 cm^{-1}. Pulsed-pulsed optical-optical double resonance via the intermediate B $^2\Sigma^+$ state is used to excite the Rydberg states. OODR transitions are detected by observation of direct UV fluorescence. The fluorescence from this state is weak compared with that typically observed for CaF Its lifetime appears to be much shorter than those we have observed for CaF Rydberg states. We have also examined the region from 43,527 cm^{-1} to 45,431 cm^{-1} and found no states in this region. We also expected to see more states in the lower energy region where we found one $^2\Sigma$ state. Since both regions examined are above the dissociation limit (32,988 cm^{-1}), the absence of states could be explained by predissociation. The characteristics of the observed $^2\Sigma$ state also suggest predissociation. Future plans include detection of OODR by the fluorescence dip method used previously for CaF.

Address of Harris, Murphy, and Field. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

RC11 (11:38)

What's new on YH

B. Simard, W.J. Balfour, H. Niki and P. A. Hackett

The YH molecule has been generated in a molecular beam apparatus employing laser vaporization, and its visible spectrum has been re-investigated at low and high resolution. Several $^1\Sigma$-$^1\Sigma$ and $^1\Pi$-$^1\Sigma$ transitions, all with the same lower $^1\Sigma$ state, have been observed in the 420-750 nm region. Many of the same bands were observed in the high temperature emission experiment of Bernard and Bacis (Can. J. Phys., 55, 1322 (1977)). They also observed strong transitions in the 550-560 nm region, which they assigned as the (0,0) band of the a$^3\Phi$-X$^3\Delta$ system. No triplet-type transitions have been observed in our low temperature experiment which suggests that the ground state of YH is a $^1\Sigma$ state, in agreement with recent ab initio calculations. Detailed analysis and comparisons will provided at the meeting.

Address of Simard and Hackett: Laser Chemistry Group, National Research Council of Canada, 100 Sussex Dr., Ottawa, Ontario, K1A 0R6
Address of Balfour: Department of Chemistry, University of Victoria, Victoria, B.C., V8W 2Y2
Address of Niki: Institute of Laser Engineering, Osaka University, Osaka, Japan.

RC12 (11:55)

Stark Spectroscopy of Refractory Molecules: The Permanent Dipole Moments of YH and HYN.

B. Simard, H. Niki , W.J. Balfour and P. A. Hackett

The dipole moments of the HY molecule and the recently discovered HYN molecule in some of their electronic states have been measured by Stark spectroscopy in a molecular beam apparatus. Electric fields up to 16 kV/cm have been employed resulting in the complete resolution of Stark patterns even in the molecular states of Σ symmetry of HYN. The dipole moments were extracted by fitting the calculated to the experimental Stark splittings for several electric field strengths using a least-squares procedure. The calculated splittings were generated (when necessary) from the exact diagonalization of the appropriate Hamiltonian matrix. The derived values will be presented, discussed and compared (when available) with recent ab initio results.

Address of Simard and Hackett: Laser Chemistry Group, National Research Council of Canada, 100 Sussex Dr. Ottawa, Ontario, K1A 0R6.
Address of Balfour: Department of Chemistry, University of Victoria, Victoria, B.C. V8W 2Y2
Address of Niki: Institute of Laser Engineering, Osaka University, Osaka, Japan.

RD1 (8:30)   W.C. Ermler

RD2 (9:05)   K. Balasubramanian

RD3 (9:40)

AB INITIO CALCULATIONS OF DIRHENIUM COMPLEXES USING RELATIVISTIC EFFECTIVE CORE POTENTIALS

Jean-Philippe Blaudeau, Richard Ross, Russell Pitzer, Pierre Mougenot and Marc Benard

The complexes $Cl_2(OH)_2ReReCl_2(PH_3)_2$ and $Re_2Cl_8^{-2}$ were studied. Atomic basis sets were optimized for rhenium, chlorine, oxygen, and phosphorus for use with Christiansen effective core potentials. Hartree-Fock calculations for these complexes were performed. The known quadruple rhenium-rhenium bond was investigated and is under analysis in our present and future calculations. Recently the Ohio State graphical unitary group approach multi-configuration self-consistent field (MCSCF) and configuration interaction (CI) programs have been modified to incorporate relativistic effective core potentials. A 252–configuration MCSCF calculation on the ground state of the latter complex showed the quadruple bond. Calculations on some excited states of this complex as well as states of the former complex are proceeding at this level. Final calculations will be at the CI level and will include spin-orbit matrix elements.

Address of Blaudeau, Ross, Pitzer: Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210

Address of Mougenot and Benard: Laboratoire de Chimie Quantique, E.R. 139 du CNRS, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France

RD4 (9:57)

INVESTIGATION OF THE BULK/CLUSTER INTERFACE THROUGH AB INITIO STUDIES OF CLUSTERS OF UP TO 135 BERYLLIUM ATOMS*, R.B. ROSS, W.C. ERMLER,† C.W. KERN, AND R.M. PITZER

The interface between bulk and cluster-like behavior has been investigated via ab initio calculations on large clusters of up to 135 Be atoms. Calculations have been carried out at the Hartree-Fock level of approximation. The largest cluster corresponds to sixteen coordination spheres of a central Be with internuclear separations derived from the lattice constants of the bulk metal. Ab initio effective core potentials are employed to replace the effects of the 1s electrons reducing the complexity of the calculations. In addition, the use of full D_{3h} symmetry results in a substantial reduction in the number of two-electron integrals that must be computed and processed. Properties calculated for selected states include binding energy, electric field gradient, nuclear-electron potential, diamagnetic shielding constant, second moments, quadrupole moment, and Mulliken populations. In addition, density of states and valence-electron density distribution analyses have been performed and are compared to those of bulk Be metal.

---

*Work performed under a grant from The Ohio Supercomputer Center.

Address of authors: Department of Chemistry, The Ohio State University, Columbus, OH 43210.

†Permanent address of Ermler: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030.

Intermission

RD5 (10:30)

ACCURATE DETERMINATION OF THE Na-Kr INTERACTION POTENTIAL FROM LASERSPECTROSCOPIC DATA

R. Brühl and D. Zimmermann

Usually, the well-known RKR method is applied in order to determine the interatomic potential from experimental energy values. Difficulties with the RKR method arise if only a small number of rovibrational levels has experimentally been observed. In addition, the correct long-range behaviour of the interaction potential is not included. A quantum-mechanical recalculation of the molecular energy values from the RKR potential leads to deviations between the input and output values in the order of 0.1 cm^{-1} which is frequently much larger than the experimental error.

For the case of Na-Kr in the $X\Sigma$ and in the $A\Pi$ state we have developed a computer routine which avoids some of the imperfections mentioned above. The program calculates the molecular energy levels by solving the Schrödinger equation for the nuclear motion using an analytical expression for the interatomic potential. By means of a standard least-squares fit procedure the parameters of the analytical expression are varied until the deviation between experimental and calculated energy values is minimal. Several analytical expressions with suitable long-range behaviour have been tried, for example the Thakkar-potential, the Tang-Toennies potential and the HFD potential.

For the case of the $A\Pi$-state our laserspectroscopic data /1/ consist of energy values of rovibrational levels with $v'=7...14$. In order to save computing time only 5 rotational levels with total angular momentum up to 20.5 have been included in our analysis for each vibrational state. In order to give an example, 30 experimental energy values of rovibrational levels of the $A\Pi_{3/2}$ state are reproduced by a 5-parameter Thakkar potential with an accuracy of less than 0.002 cm^{-1} ($p=4$ 30, $R_e=3.059(2)$Å, $D_e=774(10)cm^{-1}$).

For the $X\Sigma$ state 76 rovibrational leve with $v''=0,1$ and 2 and N'' ranging up to about 30 have been measured /1/. The corr ponding energies are all reproduced by a 5-parameter HFD potential to within 0.001 cm^{-1} accuracy yielding $R_e=4.197(1)$Å, $D_e=68.4(1.5)$ cm^{-1} and $C_6=8.65 \cdot 10^6$ cm^{-1}Å^6. In addition, the repulsive part of the $X\Sigma$ potential has been determined from our experimental spectral distribution of the fluorescence light by means of a comparison with calculated spectra.

/1/ E. Zanger, V. Schmatloch, D. Zimmermann: J. Chem. Phys. **88** (1988) 5396
    R. Brühl, I. Kapetanakis, D. Zimmermann: to be published

Institut für Strahlungs- und Kernphysik, Technische Universität Berlin,
Hardenbergstr. 36, D-1000 Berlin 12

RD6 (10:47)

SUBSTITUENT EFFECTS IN TWO- AND THREE-COORDINATE BORON CATIONS

W. F. SCHNEIDER, B. E. BURSTEN, C. K. NARULA, AND H. NÖTH

The importance of substituent effects in determining the structure, stability, and reactivity of organic species has received considerable attention. Mononuclear boron compounds are also subject to substantial substituent effects but these influences have received less consideration. The recently synthesized two- and three-coordinate boron cations, along with the well-known neutral three-coordinate substituted boranes, provide a useful series for comparison of substituent effects as a function of boron charge and coordination number.

We have employed *ab initio* SCF calculations with the 6-31G* basis set to compute the structure of three separate molecular series: R_2B^+, R_2BH, and $R_2B(NH_3)^+$, for R = H, CH_3, NH_2, OH, and F. The selected R groups span a wide range of σ donor/acceptor abilities as well as π donor strengths. The relative importance of these factors in determining the strength of the R - B bonds can be analyzed through variations in molecular structure, charge distribution, and energetics. A spectrum of bonding characteristics exists, with the two-coordinate cations dominated by ligand π donor ability, three-coordinate neutrals preferring good σ acceptors, and the three-coordinate cations occupying a middle ground.

Address of Schneider and Bursten: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

Address of Narula: Department of Chemistry, Ford Motor Company, P. O. Box 2053, Dearborn, Michigan 48121.

Address of Nöth: Institute of Inorganic Chemistry, the University of Munich, Meiserstrasse 1, 8000 Munich 2, West Germany.

RD7 (11:04)　　　　THIS PAPER WILL BE PRESENTED AS TH 8

SPECTROSCOPIC CONSTANTS OF O_2^- ELECTRONIC STATES *IN VACUO* AND IN IONIC SOLIDS

C. S. EWIG AND J. TELLINGHUISEN

MCSCF and MCSCF/CI computations have been carried out for the ground and several excited states of O_2^- both *in vacuo* and in simulated ionic lattices. The potential energy curves are fitted to modified Morse functions. The $a\,^4\Sigma_u^-$ state is unique in representing a stable anionic excited state in the gas phase, while the $A\,^2\Pi_u$ state is metastable. From stability plots the $a\,^4\Sigma_u^-$ state is unstable with respect to electron autodetachment at bond lengths where it lies above the ground state of O_2.

The effect of an ionic host lattice on the spectroscopic parameters is simulated by an array of point charges in which the anion is oriented <100>, <110>, or <111>. All electronic states examined are electronically stable in these lattices. However the spectroscopic constants, particularly of the more highly excited states, differ markedly from those in the gas phase. The $^4\Sigma_u^-$ states exhibit an avoided crossing with no analog in the gas phase. A pronounced crystal-field splitting is found for all Π states in the <110> lattice. The computed spectroscopic properties of the $A \leftrightarrow X$ transition are compared with experimentally known absorption and luminescence spectra that have been attributed to this system in alkali halide hosts.

Address of Authors: Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235

RD8 (11:16)

AB INITIO STUDIES OF THE DIURANIUM MOLECULE

M. PEPPER, B. E. BURSTEN, AND R. M. PITZER

The question of the existence and nature of uranium-uranium multiple bonds has been investigated via *ab initio* self-consistent field (SCF), multiconfiguration SCF (MCSCF) and configuration interaction (CI) calculations on the diuranium molecule. Relativistic effects have been included using effective core potentials. In the LS coupling regime, the potential surface for U_2 shows a double minimum similar to that reported for the dichromium molecule.

At short bond distances (2.2 Å), both 5f and 6d atomic orbitals are involved in the formation of molecular orbitals in U_2. The lowest-energy state is $^5\Sigma_g^+$, with configuration $d\pi_u^4 f\sigma_g^2 f\pi_u^2 d\delta_g^2 7s\sigma_g^2$. At longer bond distances (3.0-3.6 Å), the 5f atomic orbitals remain atom-like, with each atomic f shell containing three electrons. The remaining six valence electrons occupy molecular orbitals formed from 6d and 7s atomic orbitals, resulting in a group of high-spin states which are closely spaced in energy. The bonding in these states is principally through the $7s\sigma_g$ and $6d\pi_u$ molecular orbitals. Considering the 5f core as a pair of ^4S states coupled $^7\Sigma_g^+$, all possible occupancies of the 6d and 7s molecular orbitals have been considered. $^9\Sigma_g^-$, $^9\Sigma_u^+$, $^{11}\Delta_g$, $^{11}\Delta_u$, $^9\Pi_u$, and $^{13}\Delta_u$ states are of roughly equivalent energies, and all display shallow potential minima near 3.0 Å. At the SCF and CAS-MCSCF levels of theory, the 2.2 Å states lie approximately 250 kcal/mol higher in energy than the high-spin 3.0 Å states. Inclusion of correlation effects through single-reference CI calculations reduces the energy difference to approximately 120 kcal/mol, with the high-spin states remaining lower in energy. The relative energies of the two sets of states should be further affected by inclusion of spin-orbit and additional correlation effects, providing an even more accurate description of the U_2 molecule.

Address of Pepper, Bursten, and Pitzer: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

RD9 (11:33)   THIS PAPER WILL BE PRESENTED AS TH 9

LEAST-SQUARES ERROR PROPAGATION: NEGLECTED ASPECTS

J. Tellinghuisen

The usual outcome of a detailed analysis of a body of spectroscopic data is a set of spectroscopic parameters and their associated variances and covariances. While it is standard procedure to report the parameters and their errors (and sometimes the covariances or correlation coefficients), it is much less common to see errors reported for important derived functions of the parameters, even though the calculation of such propagated errors is quite straightforward. For example, in the analysis of diatomic data, one should really be more interested in the propagated error in the rotational constant B_v as a function of v than in the errors in the various expansion coefficients (B_e, α_e, etc.). In the high-order polynomial expansions that are often required to represent B_v or the vibrational energy G_v over a large range of v, the highest-order coefficients are seldom physically significant. Thus the errors in these parameters are not very informative, while the errors in the *functions* they help represent certainly are.

The present talk will illustrate error propagation in a number of examples, ranging from the simple cases mentioned above to more complex applications, such as (1) the calculation of RKR potentials, and (2) the extraction of population distributions from emission spectra.

Address of Tellinghuisen: Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235.

RD10 (11:45)

FLUORESCENT DECAY AND RADIATIVE LIFETIMES OF THE $A^1\Sigma_u^-$ STATE OF C_2N_2.
S. BARTS, K. PINNEX, P. MISRA, AND J. HALPERN

Emission lifetimes have been measured for almost all of the bound vibrational bands of the $A^1\Sigma_u^-$ state of C_2N_2. They range from 1.3μs for the 4_0^1 band to 0.6 μs for the $1_0^1 4_0^1$ band. Self-quenching rate constants range from gas kinetic (4.3 x 10^{-10} cm^3/molecule-s) for the 4_0^1 to 13.0 x 10^{-10} cm^3/molecule-s for the $1_0^1 4_0^1$ band. In addition, foreign quenching rates have been measured for most of the bands. We used He, Ar, N_2 and CH_4. The quenching rates from the foreign gases were less than the respective self-quenching rates and with an increasing trend with respect to increasing molecular structure.

We are currently acquiring dispersed fluorescence spectra and high resolution excitation spectra for some of the strong bands of C_2N_2.

Address of Barts, Pinnex and Halpern: Laboratory of Extraterrestrial Chemistry, Department of Chemistry, Howard University, Washington, D.C. 20059.
Address of Misra: Laboratory of Extraterrestrial Chemistry, Department of Physics and Astronomy, Howard University, Washington, D.C. 20059.

158

RE1 (1:30)

LASER VAPORIZATION-FOURIER TRANSFORM MICROWAVE STUDY OF THE HYPERFINE STRUCTURE OF THE
J = 3/2 ← 1/2 ROTATIONAL TRANSITION OF $X^4\Sigma^-$ NbO.

R. D. SUENRAM, G. T. FRASER, F. J. LOVAS, AND C. W. GILLIES

The NbO radical has a $^4\Sigma^-$ ground electronic state. The ^{93}Nb nucleus has a spin of 9/2 and one of the largest nuclear magnetic moments of any nuclei. All of these factors contribute to make the optical spectrum of NbO extremely complex with large hyperfine effects being observed. Based on results from previous high resolution optical studies[1], several hyperfine components of the J=3/2 ← 1/2 rotational transition were predicted to fall in the 6-26 GHz frequency range of our pulsed Fourier transform microwave spectrometer which is equipped with a laser vaporization source. Spectral searches have led to the observation of four of the five observable hyperfine components of this transition in the v=0 state as well as several satellite transitions that are believed to arise from the v=1 state. From a Stark analysis of two of the hyperfine components a dipole moment of ~3.2D has been determined.

[1]G. Cheval, J. L. Femenias, A. J. Merer and U. Sassenberg, J. Mol. Spectrosc. 131, 113-126 (1988).

Address of Suenram, Fraser, and Lovas: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899.

Address of Gillies: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, 12180.

RE2 (1:47)

THE NUCLEAR QUADRUPOLE COUPLING TENSOR FOR D_2O FROM LOW-J STARK-HYPERFINE SPECTRA: IMPLICATIONS FOR THE STRUCTURE DETERMINATION OF VAN DER WAALS COMPLEXES

MARK D. MARSHALL, RATAN BHATTACHARJEE, AND JOHN S. MUENTER

Stark-hyperfine spectra are obtained for the 1_{10} and 1_{11} rotational states of D_2O using a molecular beam electric resonance spectrometer. Hyperfine constants and the electric dipole moments determined from the data are in general agreement with earlier results with the exception of an apparent confusion in the literature with regard to the axis system in which the components of the nuclear quadrupole coupling tensor are reported. As these components are often used in the structure determination of van der Waals complexes, inconsistencies have sometimes been observed.

The rotational states measured in this study provide directly two of the tensor components in the principal *inertial* axis system of the molecule, namely $eQq_{bb} = 22.436(95)$ kHz and $eQq_{cc} = -175.027(22)$ kHz, with the traceless character of the tensor providing the third. These components may be used to provide structural data for van der Waals complexes containing D_2O and resolve an inconsistency in the N_2 D_2O molecule. Implications for other complexes will be discussed and comparison will be made with the quadrupole coupling tensor for HDO.

Address of Marshall: Department of Chemistry, Amherst College, Amherst, Massachusetts 01002

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

RE3 (2:04)

THE HYPERFINE SPECTRUM OF LIF

J. CEDERBERG, D. OLSON, D. BARTZ, P. SOULEN, T. STEINBACH, H. TON AND K. URBERG[*]

The lineshape fitting procedure described in the previous paper has been used to determine the zero-field frequencies of several pure hyperfine transitions in LiF as observed with our electric resonance molecular beam spectrometer. These are being analyzed to determine the corresponding molecular constants. We have so far observed transitions in rotational states J = 1-2 and vibrational states v = 0-2. Preliminary values of the constants are significantly different from those previously reported.[1]

[*]Work supported by NSF grant #PHY-8617538

[1]A. J. Hebert and C. D. Hollowell, J. Chem. Phys. 65, 4327 (1976).

Address: Physics Department, St. Olaf College, Northfield, Minnesota, 55057.

RE4 (2:16)

THE ROTATIONAL SPECTRUM OF THE T-SHAPED HBr·CO₂ COMPLEX EXAMINED BY FT-MICROWAVE SPECTROSCOPY

J.K. Rice, R.D. Suenram, F.J. Lovas, G.T. Fraser and W.J. Lafferty

The structure of $HBr \cdot CO_2$ has recently been reported to be T-shaped from IR absorption spectroscopy measurements.[1] This geometry differs considerably from the linear or near-linear structures of $CO_2 \cdot HF$ and $CO_2 \cdot HCl$. Presumably, the lower gas-phase acidity of HBr and the higher polarizability of Br results in a stronger bromine-carbon interaction in the $HBr \cdot CO_2$ complex. Here, we report further details of the structure and dynamics of $HBr \cdot CO_2$ from a FT-microwave investigation.

A number of b-type transitions have been measured for $H^{79}Br \cdot CO_2$ and $H^{81}Br \cdot CO_2$. Using an asymmetric rotor, centrifugal distortion Hamiltonian with first order nuclear-electric quadrupole interaction terms, we report the following rotational and hyperfine constants.

	Rotational Constants (MHz)			Hyperfine Constants (MHz)	
	$H^{79}Br \cdot CO_2$	$H^{81}Br \cdot CO_2$		$H^{79}Br \cdot CO_2$	$H^{81}Br \cdot CO_2$
A+A_t	12780.84	12778.24	eqQ_a	-167.20	-138.98
B	1392.65	1378.95	eqQ_b	364.29	364.32
C	1235.98	1225.95	eqQ_c	-197.09	-165.34
			σ	0.35	0.34

Calculations of the geometry of the complex indicate a planar T-shaped structure with a OC·Br angle of $\approx 90°$. The bromine-carbon bond distance is 3.586 Å and the hydrogen is positioned at an angle of $\approx 66°$ (or 114°) from the a axis of the complex. The $K_a = 1-0$ separation observed here differ substantially (≈ 1200 MHz) from that calculated from the constants of Sharpe et al[1], suggesting hydrogen tunneling between the two equivalent C_s structures with a C_{2v} transition state. We are currently searching for $K_a = 1 \rightarrow K_a = 2$ transitions to confirm this assertion.

[1] S.W. Sharpe, Y.P. Zeng, C. Wittig and R.A. Beaudet, J. of Chem. Phys., 92, 943 (1990).

Address of Rice: Chemistry Division, Code 6111, Naval Research Laboratory, Washington, D.C. 20375-5000.
Address of Suenram, Lovas, Fraser and Lafferty: Molecular Physics Division, NIST, Gaithersburg, MD 20899.

RE5 (2:33)

MICROWAVE AND CO₂-SIDEBAND-LASER OPTOTHERMAL SPECTROSCOPY OF Ar-NH₃

G.T. FRASER, A.S. PINE, W.A. KREINER, D.D. NELSON, Jr., AND W. KLEMPERER

Microwave spectra of Ar-NH₃ states correlating to j=1, k=1 NH₃ have been recorded using electric-resonance and pulsed-nozzle Fourier-transform spectrometers. Hyperfine analysis and microwave-microwave double resonance are combined to obtain a definitive rotational assignment for these states, extending the earlier j=0, k=0 Ar-NH₃ results of Nelson et al[1]. As noted previously[1], the j=1, k=1 spectra display complications from the NH₃ inversion and internal rotation, and are not well characterized using standard spectroscopic analyses. Here, we are attempting to model the spectra using various anisotropic potentials to couple the rotational angular momentum of the NH₃ to the orbital angular momentum of the complex. The results of this approach will be discussed.

A microwave-sideband CO₂ laser optothermal spectrometer with a resolution better than 1 MHz has been used to record the infrared spectrum of Ar-NH₃ in the vicinity of the R(0) line of the ν_2 vibration of free NH₃. A Π-Σ type band is observed giving a positive l-type doubling constant of 90.9 MHz for the upper state, consistent with the Σ, j=1, k=0 state being above the Π, j=1, k=0 state. The vibrationally excited complex is found to predissociate in less than the ~ 1 ms transit time between the bolometer detector and laser excitation region. A lower limit to the upper-state lifetime is obtained from the observed linewidths, which are less than 3 MHz. The present results are in excellent agreement with the previous diode-laser measurements of Howard et al[2].

[1] D.D. Nelson, Jr., G.T. Fraser, K.I. Peterson, K. Zhao, W. Klemperer, F.J. Lovas, and R.D. Suenram, J. Chem. Phys. 85, 5512 (1986).
G.T. Fraser, D.D. Nelson, Jr., A. Charo, and W. Klemperer, J. Chem. Phys. 82, 2535 (1985).
[2] B.J. Howard, private communication.

Address of Fraser and Pine: National Institute of Standards and Technology, Molecular Physics Division, Gaithersburg, MD 20899.
Address of Kreiner: Abteilung Fur Physikalische Chemie, Universitat Ulm, Oberer Eselsberg, D-7900 Ulm, West Germany.
Address of Nelson: Aerodyne Research, 45 Manning Road, Billerica, MA 01821.
Address of Klemperer: Department of Chemistry, Harvard University, Cambridge, MA 02138.

RE6 (2:50)

THE MICROWAVE SPECTRUM AND STRUCTURE OF THE $(CH_3)_2NH \cdot SO_2$ COMPLEX

J. J. OH, K. W. HILLIG II, AND R. L. KUCZKOWSKI

The microwave spectra of $(CH_3)_2NH$ SO_2 have been observed with a pulsed beam, Fourier transform microwave spectrometer. In addition to the normal isotopic form, we have observed the spectra of $(CH_3)_2NH$ $^{34}SO_2$, $(CH_3)_2ND$ SO_2, $(CH_3)_2NH$ $SO^{18}O(H)$, $(CH_3)_2NH$ $SO^{18}O(C)$, and $(CH_3)_2{}^{15}NH$ SO_2. The transitions are characterized by both a- and c-type selection rules. The rotational constants (in MHz) for $(CH_3)_2NH$ SO_2 are A = 4445.495(3), B = 2063.031(1) and C = 1752.470(1). Stark effect measurements give electric dipole components of μ_a = 4.030(4) and μ_c = 1.752(4) Debye. The structure of this complex, based on the isotopic substitution data, has no symmetry plane even though μ_b is 0 within experimental uncertainty. The N-S distance (2.35 Å) is a little longer than for the trimethylamine SO_2 complex (2.27 Å) and reflects the strength of the complex ($\Delta H_{diss} \approx 10$ kcal/mole). There is no evidence for any internal motion in this complex.

Address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

RE7 (3:02)

THE MICROWAVE SPECTRUM AND STRUCTURE OF THE $(CH_3)_2O \cdot SO_2$ COMPLEX

J. J. OH, K. W. HILLIG II, AND R. L. KUCZKOWSKI

The microwave spectra of $(CH_3)_2O$ SO_2 have been observed with a pulsed beam, Fourier transform microwave spectrometer. In addition to the normal isotopic form, we have observed the spectra of $(CH_3)_2O$ $^{34}SO_2$, $^{13}CH_3OCH_3$ SO_2, $(CH_3)_2O$ $S^{16}O^{18}O$, and $(CH_3)_2O$ $S^{18}O_2$. The transitions are characterized by both a- and c-type selection rules. The rotational constants (in MHz) for $(CH_3)_2O$ SO_2 are A = 4536.869(23), B = 1865.145(1) and C = 1457.854(1). Stark effect measurements give electric dipole components of μ_a = 1.860(1) and μ_c = 0.591(1) Debye. The dipole components and moment of inertia data show that the complex belongs to the C_s point group. The two monomers are separated by 3.05 Å (R_{cm}). The structure of this complex, after fitting the derived moments of inertia, has the planes of the two monomer units in an approximately parallel stacked configuration with the oxygen atom of the ether closest to the sulfur atom of SO_2. There is no evidence for methyl group internal rotation splittings.

Address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

Intermission

RE8 (3:30)

THE MICROWAVE ROTATION-INVERSION SPECTRUM AND STRUCTURE OF THE SO_2 DIMER

A. TALEB-BENDIAB, K. W. HILLIG II, AND R. L. KUCZKOWSKI

The radio frequency and microwave spectrum of $(SO_2)_2$ was first reported by Nelson et al.[1] They showed that this dimer undergoes a low frequency inversion tunneling and determined the center-of-mass distance (R_{cm}) and the μ_a dipole moment. However, it was not possible to determine the relative orientation of each subunit and the inversion motion was not very well understood.

We have reinvestigated the microwave spectrum of $(SO_2)_2$ using the FTMW technique. New transitions for the normal species arising from the $K_a \leq 3$ states and the spectra of 8 isotopically substituted species were measured. The tunneling motion treatment[2] used for $(H_2O)_2$, has been applied to $(SO_2)_2$. The latter undergoes an inversion motion similar to the water dimer. From analysis of the moments of inertia of the various isotopic species, an ac plane of symmetry is established for the dimer and the tilt angles of the C_2 axis of each subunit relative to the distance joining their centers of mass were determined. From Stark effect measurements, μ_a was remeasured and μ_c shown to be nearly zero. These components are consistent with the structure determined for $(SO_2)_2$.

1. D. D. Nelson, Jr., G. T. Fraser, and W. Klemperer, J. Chem. Phys. 83, 945 (1985).
2. L. H. Coudert and J. T. Hougen, J. Mol. Spectrosc. 130, 86 (1988).

Address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

RE9 (3:47)

ROTATIONAL SPECTRA OF THE H₂O-HCCCCH AND HCCCCH-NH₃ COMPLEXES

K. MATSUMURA, F. J. LOVAS, AND R. D. SUENRAM

A pulsed-beam Fabry-Perot cavity Fourier transform microwave spectrometer has been employed in the measurement of the rotational spectra of the hydrogen-bonded complexes of diacetylene with water and ammonia. The molecular beam was produced from Ar seeded with about 1% of diacetylene and 1% of either water or ammonia.

For the H₂O-HCCCCH species an a-type spectrum was observed which was characteristic of a planar prolate C_{2v} species. Transitions from J = 4-3 to J = 11-10 were observed for K_a = 0 and 1 states of the H₂O and D₂O species. For the HDO isotopic form only the K_a = 0 state was detected due to cooling of the higher K_a states in the supersonic expansion. Spectral analysis provided the molecular constants B = 1065.4515(2) MHz and C = 1062.0299(2) MHz and a dipole moment μ_a = 2.2971(12) D for H₂O-HCCCCH.

For the HCCCCH-NH₃ complex a symmetric-top a-type spectrum was observed for the ¹⁴NH₃, ¹⁵NH₃ and ND₃ isotopic species of the complex. Rotational analysis of HCCCCH-¹⁴NH₃ yielded B = 1067.8309(1) MHz, D_J = 0.3678(8) kHz and D_{JK} = 132.94 kHz. The ¹⁴N nuclear electric quadrupole structure was resolved for the lowest frequency transitions of HCCCCH-¹⁴NH₃ providing eQq_a = -3.198(5) MHz. The molecular electric dipole moment was determined for HCCCCH-¹⁵NH₃ to be μ_a = 2.3188(13) D.

The derived molecular structures will be described and comparisons with the closely related complexes H₂O-HCCH[1] and HCCH-NH₃[2] will be made.

[1] K. I. Peterson and W. Klemperer, J. Chem. Phys. 81, 3842 (1984).
[2] G. T. Fraser, K. R. Leopold, and W. Klemperer, J. Chem. Phys. 80, 1423 (1984).

Address of Matsumura: Seinan Gakuin University, Nishijin, Sawaraku, Fukuoka 814, JAPAN
Address of Lovas and Suenram: Molecular Physics Division ,National Institute of Standards and Technology, Gaithersburg, MD, 20899

RE10 (4:04)

MICROWAVE SPECTRA AND MOLECULAR STRUCTURE OF THE KETENE-ACETYLENE COMPLEX

J. Z. GILLIES, C. W. GILLIES, B. PATRIARCA, F. J. LOVAS, AND R. D. SUENRAM

Rotational spectra of CH₂=C=O•HC≡CH and CD₂=C=O•HC≡CH were observed with a pulsed beam Fourier transform microwave spectrometer employing the dual flow pulsed solenoid valve described previously.[1] Four states for each isotopic species were identified and fit separately to a quartic Watson Hamiltonian. Relative intensities and nuclear spin weights observed for these states show the splitting arises from internal rotation about the C₂ axis in ketene and the axis perpendicular to the molecular axis of acetylene. These motions exchange the two pairs of hydrogen atoms in the monomer units. The rotational constants (in MHz) of the I_R=0 ground state are A=8389.969(16), B=2372.179(29) and C=1846.535(25). A planar structure is found with an inertial defect of Δ= +0.41023 u•Å². The geometry obtained from the moment of inertia data corresponds to the molecular symmetry axes of the monomers tilted by ~25° from parallel alignment with a center of mass distance of 3.60(1) Å and an acetylenic hydrogen to oxygen distance of 2.96 Å. These results will be compared to the related formaldehyde-acetylene complex.[2]

[1] J. Z. Gillies, C. W. Gillies, F. J. Lovas, K. Matsumura, and R. D. Suenram, 44th Symposium on Molecular Spectroscopy, paper TF3, (1989).
[2] N. W. Howard and A. C. Legon, J. Chem. Phys. 88, 6793 (1988).

Address of J. Z. Gillies: Department of Chemistry, Union College, Schenectady, NY, 12308.

Address of C. W. Gillies and Patriarca: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY, 12180.

Address of Lovas and Suenram: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899.

RE11 (4:21)

THE STRUCTURE OF ArCH₃CN DETERMINED BY MICROWAVE SPECTROSCOPY

THE STRUCTURE OF $ArCH_3CN$ DETERMINED BY MICROWAVE SPECTROSCOPY

R.S. Ford, R.D. Suenram, F.J. Lovas, G.T. Fraser, and K.R. Leopold

The microwave spectrum of the van der Waals dimer $ArCH_3CN$ has been observed using a pulsed-nozzle Fourier transform microwave spectrometer. The ^{14}N nuclear hyperfine structure has been analyzed in the ground (m=0) and excited (m=1) internal rotor states. Spectroscopic constants for the m=0 state, in megahertz, are

$$eqQ_{aa} = 2.060 \qquad eqQ_{bb} = -4.168 \qquad eqQ_{cc} = 2.108$$

$$A = 9323.4 \qquad B = 1886.3 \qquad C = 1556.1$$

The structure is T-shaped, with a center of mass separation of 3.43 Å.

Address of Ford and Leopold: Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455.
Address of Suenram, Lovas, and Fraser: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899.

RE12 (4:38)

MOLECULAR BEAM LINESHAPE ANALYSIS

D. OLSON, J. CEDERBERG, D. BARTZ, P. SOULEN, T. STEINBACH, H. TON AND K. URBERG[*]

In earlier work[1,2] we have described a statistical technique for locating the centers of spectral lines obtained with a molecular beam spectrometer. That technique is of value for isolated lines because it does not require knowledge of a specific lineshape. We were reluctant to try fitting a specific lineshape function for two main reasons: 1. Velocity averaging produces subtle effects on the lineshape that are difficult to account for because detailed velocity distributions are not known, and 2. One of the experimental parameters, namely the amplitude of the radio frequency field, is difficult to measure, and may vary significantly over the length of the transition region.

With LiF the hyperfine coupling constants are small enough that, even with our 200 Hz linewidth, most of the lines overlap. We therefore had an incentive to pursue the possibility of fitting the specific lineshape in order to deconvolute the overlapping lines. We have found that the effects of velocity averaging can be accommodated in a very simple way by using a two-point velocity distribution, while the rf amplitude can be treated as a variable determined by the fitting process. The result is an excellent fit of the Rabi lineshape to our experimental data which not only provides center frequencies, but also gives us meaningful values for other experimental parameters including the rf amplitude.

[1]J. Cederberg, et al, Symposium on Molecular Spectroscopy, Ohio State University, 1985.

[2]J. Cederberg, et al, J. Mol. Spect. 122, 171-181 (1987).

Address: Physics Department, St. Olaf College, Northfield, Minnesota, 55057.

RE13 (4:55)

THE ACETYLENE-SULFUR DIOXIDE VAN DER WAALS COMPLEX

A. M. ANDREWS, K. W. HILLIG II, R. L. KUCZKOWSKI, N. W. HOWARD AND A. C. LEGON

Thirty-three a- and c-dipole transitions of the acetylene SO_2 van der Waals complex have been observed by Fourier transform microwave spectroscopy. They are fit with a Watson S-reduced Hamiltonian to rotational constants A = 7176.804(2) MHz, B = 2234.962(1) MHz, C = 1796.160(1) MHz. The structure of the complex has the C_2H_2 and SO_2 straddling an ac symmetry plane (i.e. only the S atom lies in the plane). The two subunits are separated by a distance R_{cm} = 3.431(1) Å and the C_2 axis of the SO_2 is tilted 14.1(1)° from the perpendicular to the R_{cm} vector with the S atom closer to the acetylene. The dipole moment of the complex is 1.683(5) D. The deuterium nuclear quadrupole hyperfine splitting was resolved and assigned for both the C_2HD SO_2 and C_2D_2 SO_2 species. Although the C_2H_4 SO_2, C_2H_4 O_3 and C_2H_2 O_3 complexes all exhibit tunneling doublets from an internal rotation of the hydrocarbon subunit, no doubling was observed for the $C_2H_2 \cdot SO_2$ complex.

Address of Andrews, Hillig, Kuczkowski. Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

Address of Legon. Department of Chemistry, University College London, 20 Gordon St., London, WCIH OAJ, Great Britain.

Address of Howard. Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, Great Britain.

RE14 (5:12)

MICROWAVE SPECTRA OF THE NONLINEAR NNO-H^{35}Cl COMPLEX

M. A. ROEHRIG, D. J. PAULEY, J. C. SHEA, AND S. G. KUKOLICH

Microwave spectra were obtained for the bimolecular gas phase complex of NNO-H^{35}Cl using a pulse-beam Fourier transform microwave spectrometer. Rotational constants (A - D_K), B, C, and the distortion constants D_J, D_{JK}, and the chlorine nuclear quadrupole coupling constants eQq_{aa} and eQq_{bb} were obtained by fitting the spectra to a distortable rotor Hamiltonian including first-order quadrupole coupling. The structure can be described with R_{CM}, θ, the angle between the NNO monomer unit and R_{CM}, ϕ, the angle between HCl and R_{CM}. The structure appears to be planar with a large inertial defect which is characteristic for this type of complex.

Address of Roehrig, Pauley, Shea, and Kukolich: Department of Chemistry, University of Arizona, Tucson, Arizona 85721

RE15 (5:24)

ROTATIONAL ANALYSIS OF THE EXCITED STATES OF METHYL CYANIDE AND METHYL CYANIDE-D3.

J. COSLEOU, J. DEMAISON, D. BOUCHER and G. WLODARCZAK.

The rotational spectrum of CD3CN has been measured up to 1500 GHz for the ground state and up to 400 GHz for several excited vibrational states : v_8=1, 2, 3, v_4=1, v_7=1, v_3=1 and v_6=1. Many of these states are located between 700 and 1100 cm^{-1} and some of them are involved in the submillimeter emissions of CD3CN. The different types of interactions between these levels are discussed. A comparison is made with CH3CN, which shows a similar diagram of energy levels.

Address : Laboratoire de Spectroscopie Hertzienne, UA CNRS 249, Bat. P5, Université de Lille 1, 59655 Villeneuve d'Ascq , France.

RF1 (1:30)

THE OBSERVATION OF THE ν_1 AND $\nu_1 + \nu_7 - \nu_7$ BANDS OF HNCCN$^+$

H. E. WARNER AND T. AMANO

The ν_1 (N-H stretch) fundamental band of HNCCN$^+$ has been observed at around 3450 cm^{-1} by employing the difference-frequency laser system. In addition, a few hot bands are also observed and one of them is assigned to $\nu_1 + \nu_7 - \nu_7$ (C-C-N bend) hot band. The specta were observed in a hollow cathode discharge, consisting of approximately 20 mTorr of cyanogen in a buffer of H_2, with approximately 10 kHz discharge modulation, and dry-ice cooling. The molecular constants have been determined for both the upper and lower states of both bands. There is good agreement between our constants, and those calculated by Botschwina and Sebald.[1]

[1] P. Botschwina and P. Sebald, private communication.

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

RF2 (1:47)

INFRARED-MICROWAVE DOUBLE RESONANCE SPECTROSCOPY OF COLLISION-INDUCED TRANSITIONS BETWEEN ROTATIONAL ENERGY LEVELS IN THE ISOELECTRONIC SPECIES HN$_2^+$ AND HCN

C.J. Pursell, D.P. Weliky, K. Takagi, and T. Oka

The extremely high sensitivity of infrared-microwave double resonance spectroscopy has allowed us to observe collision-induced transitions between rotational levels[1] in the isoelectronic species HN$_2^+$ and HCN.

A color center laser with 2~20 mWatts of power provided the infrared signal radiation, and a millimeter wave klystron with ~400 mWatts of power provided the microwave pump radiation. The frequency of the microwave radiation was swept through the J=1←0 rotational transition in the ground state and the double resonance signal was detected through variation of the ν_1 infrared transition R(J), where J=2, 3, 4, . . . The HN$_2^+$ molecular ion was produced in a hollow cathode discharge cell at low pressures (20-200 mTorr). The hollow cathode (a) produces relatively large concentrations of ions at low pressures and (b) serves as a waveguide for the propagation of the microwave radiation.

We have studied the collisions of HN$_2^+$ and HCN with N_2, He and Ar. The ion-neutral collision is qualitatively different from the neutral-neutral collision because of the presence of the $1/R^4$ Langevin potential[2]. This long range potential is independent of the ion's angular coordinates and therefore does not cause collision-induced transitions in the molecular ion. Its effect is to exert an intermolecular force which is always attractive and reduces the ion-neutral distance. Our results indicate the existence of "selection rules" for the Langevin potential dominated ion-neutral interaction.

We will report the results from this study of rotational energy transfer in a molecular ion, along with a comparison between the isoelectronic species HN$_2^+$ and HCN.

1. T. Oka, _Advan. At. Mol. Phys._, 9, pp.127-206 (Academic Press, New York, 1973).
2. P. Langevin, _Ann. Chim. Phys._, 5, 245 (1905).

Address of Pursell,Weliky, and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637
Address of Takagi: Department of Physics, Toyama University, Gofuku, Toyama 930, JAPAN

RF3 (2:04)

OBSERVATION OF *l*-TYPE DOUBLING TRANSITIONS IN HN_2^+ USING INFRARED-MICROWAVE DOUBLE RESONANCE SPECTROSCOPY

D.P. Weliky, C.J. Pursell, K. Takagi, and T. Oka

The *l*-type doubling in the v_2 and $v_1 + v_2$ states of the HN_2^+ molecular ion has been studied using infrared-microwave double resonance spectroscopy. The molecular constants q and q_J were determined for both states from our observed transition frequencies. This work is a continuation of our application of this sensitive technique to molecular ions and represents the first observation of centimeter wave transitions of a molecular ion.

The HN_2^+ ion was produced in a hollow cathode discharge at a pressure of 50 mTorr. Microwave transitions for J=6, 7, and 8 in the v_2 state and J=6 and 7 in the $v_1 + v_2$ state were pumped with 6 Watts of radiation produced by a centimeter wave synthesizer and amplified by a traveling wave tube amplifier. This radiaiton was introduced into the hollow cathode cell via an X-band waveguide soldered to the hollow cathode. A color center laser served both to saturate the infrared transition and as a probe of the microwave transition.

Similar *l*-type doubling transition were first observed for the isoelectronic neutral HCN. In addition, many collision-induced transitions were observed for HCN.

Address of Weliky, Pursell, and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637
Address of Takagi: Department of Physics, Toyama University, Gofuku, Toyama 930, JAPAN

RF4 (2:21)

MICROWAVE SPECTRUM OF SO^+.

TAKAYOSHI AMANO, TAKAKO AMANO, AND H. E. WARNER

Warner, Carballo, and Woods[1] observed the microwave spectrum of SO^+ using a magnetically confined glow discharge, and, based on this laboratory observation, Woods et al detected this ion in the interstellar clouds. However, Warner et al were unable to observe tne lines in the $^2\Pi_{3/2}$ state. We have generated SO^+ in a hollow cathode discharge in SO_2, and the lines in both $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states have been recorded with better signal to noise ratios. The more complete and better molecular constants have been determined from a least-squares analysis.

[1] H. E. Warner, N. Carballo, and R. C. Woods, The 40th Symposium on Molecular spectroscopy, paper TE 11, 1985 (Columbus, Ohio)

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

RF5 (2:33)

Infrared Diode Laser Spectroscopy of SiF and SiF*

Keiichi Tanaka, Yasunobu Akiyama, Masahiro Tamura, and Takehiko Tanaka

The SiF radical was observed in the positive column of a glow discharge of SiF_4 and Ar mixture. The SiF lines were discriminated from much stronger SiF_2 lines by the discharge current modulation and Zeeman modulation techniques. Totally 209 lines belonging to the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin states were identified for the fundamental band and hot bands up to $v = 9 - 8$ in the ground electronic state. Most of the lines in the $^2\Pi_{1/2}$ state were observed with splitting due to the Λ-type doubling. The harmonic frequency obtained is 857.3251 ± 0.0007 cm^{-1}, where the uncertainty corresponds to three standard deviations. The equilibrium bond length r_e is derived as $1.600\,997 \pm 0.000\,002$ Å from the rotational constant, $B_e = 0\,581\,257 \pm 0.000\,001$ cm^{-1}.

The SiF* ion was observed in the hollow cathode discharge of pure SiF_4. Twenty-one and ten lines in the R and P branches, respectively, of the fundamental band and some lines in the $v = 2 - 1$ hot band were recorded using the discharge modulation technique. A sharp decrease of the intensity caused by the magnetic field, which is characteristic to ion lines, was observed. From the band origins for the fundamental and hot bands, the harmonic frequency $\omega_e = 1050.3757 \pm 0.0013$ cm^{-1} and the anharmonic constant $\omega_e x_e = 4.9462 \pm 0.0004$ cm^{-1} are derived. The equilibrium bond length $r_e - 1.526\,52 \pm 0.000\,08$ Å derived from the rotational constant is considerably shorter than the value of the SiF radical.

Address: Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan.

RF6 (2:50)

Infrared Diode Laser and Millimeterwave Spectra of the GeF⁻ Ion

Keiichi Tanaka, Yasunobu Akiyama, Takehiko Tanaka
Chikashi Yamada, and Eizi Hirota

The GeF⁻ ion was generated in the hollow cathode discharge of GeF₄ mixed with He More than 30 absorption lines belonging to the fundamental band were observed by infrared diode laser spectroscopy and identified for five Ge isotopes. The spectroscopic constants derived for the ^{74}GeF⁻ species are ω_e = 815.60(12), $\omega_e x_e$ = 3.223(62), B_e = 0.40212 14, and α_e = 0.0025060(53) cm⁻¹. The equilibrium bond length r_e = 1.66549 29 Å was calculated from the equilibrium rotational constant. A sharp decrease of the signal intensity caused by the magnetic field also confirmed that the observed spectrum was due to a charged species.

Based on the results by the infrared spectroscopy, four millimeterwave lines for the J = 9 − 8 ~ 12 − 11 rotational transitions were observed for each Ge isotope. The millimeterwave spectrum was consistent with the infrared results and much improved the molecular constants.

Address of Tanaka, Akiyama, and Tanaka: Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan.
Address of Yamada and hirota: Institute for Molecular Science Okazaki 444, Japan.

Intermission

RF7 (3:20)

INFRARED STUDIES OF THE v_1 BAND OF HCCD⁺

M. RÖSSLEIN, M.-F. JAGOD, C. GABRYS, and T. OKA

In our attempt to obtain the complete structure of $C_2H_2^+$,[1] we are studying the v_1 fundamental vibration-rotation band of HCCD⁺ ($^2\Pi_u$). The monodeuterated acetylene cation is produced in a liquid nitrogen-cooled AC-glow discharge with a gas mixture of He : H_2 : CD_4 : CH_4 (700 : 4 : 4 : 1) with a total pressure of ≈ 7 torr. The spectra around the assumed band origin of the monodeuterated species were recorded using a difference frequency spectrometer and velocity modulation. The monodeuterated cation is of special interest for radioastronomical search of the acetylene ion in interstellar space and planetary ionospheres because of the presence of an effective permanent dipole moment. The spectroscopic study of CH_2D^+ is also underway for the same purpose.

[1]M. W. Crofton, M.-F. Jagod, B. D. Rehfuss, and T. Oka, *J. Chem. Phys.* 86, 3755 (1987).

Address: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637-1403.

RF8 (3:37)

QUADRATIC HERMAN-WALLIS CORRECTION FACTORS FOR SYMMETRIC-TOP MOLECULES. APPLICATION TO THE H_3^+ ION.

J. K. G. WATSON

The Herman-Wallis correction factors to the intensities of allowed rovibronic transitions of symmetric-top molecules can be written in the form

$$F = \left\{1 + A_1^J m_J + A_1^K m_K + A_2^{JJ(Q)}[\overline{J(J+1)} - m_J^2] + A_2^{JJ(PR)} m_J^2 + A_2^{KK}\overline{K^2} + A_2^{JK} m_J m_K\right\}^2,$$

where $m_J = \frac{1}{2}[J'(J'+1) - J''(J''+1)]$, $m_K = \frac{1}{2}[K'^2 - K''^2]$, $\overline{J(J+1)} = \frac{1}{2}[J'(J'+1) + J''(J''+1)]$, and $\overline{K^2} = \frac{1}{2}[K'^2 + K''^2]$. When different $(J', K') - (J'', K'')$ transitions mix together, the square root of the above factor can be applied to each transition moment. For parallel bands the terms in m_K are absent. In fundamental bands the A_1 and A_2 coefficients are related to the parameters $\Theta_k^{\alpha,\gamma}$ and $\Theta_k^{\alpha\beta,\gamma}$ in the effective dipole moment operator[1]. Values of the A_1 and A_2 coefficients obtained by fitting the ab initio line strengths of H_3^+ calculated by Miller and Tennyson[2,3] will be compared with the results of perturbation calculations. The correction factors are important at the high rotational temperatures observed in emission spectra in the laboratory[3,4] and from Jupiter[5].

1. M. R. Aliev and J. K. G. Watson, in *Molecular Spectroscopy: Modern Research*, Vol. III (ed. K. Narahari Rao), pp. 1–67 (1985).
2. S. Miller and J. Tennyson, *Astrophys. J.* **335**, 486–490 (1988).
3. W. A. Majewski, P. A. Feldman, J. K. G. Watson, S. Miller, and J. Tennyson, *Astrophys. J.* **347**, L51–L54 (1989).
4. W. A. Majewski, M. D. Marshall, A. R. W. McKellar, J. W. C. Johns, and J. K. G. Watson, *J. Mol. Spectrosc.* **122**, 341–355 (1987).
5. P. Drossart, J.-P. Maillard, J. Caldwell, S. J. Kim, J. K. G. Watson, W. A. Majewski, J. Tennyson, S. Miller, S. K. Atreya, J. T. Clarke, J. H. Waite, Jr., and R. Wagener, *Nature* **340**, 539–541 (1989).

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

RF9 (3:54)

INFRARED EMISSION SPECTRA OF H_3^+ AND ITS ISOTOPES

W.A. MAJEWSKI, A.R.W. MCKELLAR, AND J.K.G. WATSON

Recently, there have been remarkable observations of H_3^+ infrared emission in the 4 and 2.1 μm regions from auroral "hot spots" on Jupiter.[1] This has encouraged us to extend earlier[2,3] laboratory observations of H_3^+ emission spectra. The spectra are obtained using a Bomem Fourier transform spectrometer and a small hollow cathode discharge cell featuring high current density and high pressure operation.

In the present series of measurements, we are improving the signal to noise ratio and extending the spectral range of the earlier H_3^+ spectra, and also running spectra of D_2 and H_2 + D_2 mixtures in order to study the isotopes D_3^+, D_2H^+, and H_2D^+. The goal is to extend the current laboratory data on this fundamental molecular ion to higher rotational and vibrational states. We also hope to obtain improved data on neutral H_3 and its isotopes.

[1] P. Drossart, J.-P. Maillard, J. Caldwell, S.J. Kim, J.K.G. Watson, W.A. Majewski, J. Tennyson, S. Miller, S.K. Atreya, J.T. Clarke, J.H. Waite, and R. Wagener, Nature **340**, 539-541 (1989).
[2] W.A. Majewski, M.D. Marshall, A.R.W. McKellar, J.W.C. Johns, and J.K.G. Watson, J. Mol. Spectrosc. **122**, 341 (1987).
[3] W.A. Majewski, P.A. Feldman, J.K.G. Watson, S. Miller, and J. Tennyson, Astrophys. J. (Letters) **347**, L51-L54 (1989).

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

RF10 (4:11)

OBSERVATION OF THE 4 μm FUNDAMENTAL v_2 BAND OF H_3^+ IN JUPITER

TAKESHI OKA AND T.R. GEBALLE

The recent detection of the H_3^+ molecular ion in the Jovian auroral region[1,2,3] via its 2 μm $2v_2 \leftarrow 0$ overtone band is the first instance that this hydrogenic species, which is thought to be basic to the production of many complex molecules in the interstellar medium, has been detected by astronomical observation.

In this paper we report our detection of 10 lines belonging to the 4 μm fundamental v_2 band of H_3^+ in emission in the northern and southern polar ionosphere of Jupiter. The previously observed 2 μm overtone band emission was absent as were lines of other hot bands of H_3^+ and the 2 μm lines of H_2 indicating a drastic temporal dependence of physical conditions in Jovian ionosphere.[4]

[1] J.P. Maillard and P. Drossart, *CFHT Bull.* 20, 13 (1989).

[2] L. Trafton, D.F. Lester and K.L. Thompson, *Ap. J.* 343, L73 (1989).

[3] P. Drossart, J.-P. Maillard, J. Caldwell, S.J. Kim, J.K.G. Watson, W.A. Majewski, J. Tennyson, S. Miller, S.K. Atreya, J.T. Clarke, J.H. Waite, Jr. and R. Wagener, *Nature* 340, 539 (1989).

[4] T. Oka and T.R. Geballe, *Ap. J.* March 15 (1990), in press.

Address of Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637.

Address of Geballe: Joint Astronomy Center, Hilo, HI.

RF11 (4:28)

THE TUNNELING ROTATIONAL ENERGY LEVELS OF H_5^+

L. H. COUDERT

The molecular ion H_5^+ can be thought of as an H_2 molecule weakly bound to an H_3^+ ion. However, ab initio calculations have shown that this picture is inaccurate and that this ion is fairly non-rigid. It exhibits at least three tunneling motions; the most feasible one, involving intramolecular proton transfer, corresponds to the isomerization $H_3^+ \cdot H_2 \rightleftharpoons H_2 \cdot H_3^+$. This along with the fact that this ion has 60 equilibrium configurations leads to a complicated energy level diagram. Determining this energy pattern in order to understand the infrared spectrum of this ion[1] is one of the motivations of the present investigation.

In this work the formalism developed for the water dimer has been applied to the determination of the splitting pattern of the H_5^+ ion. Although applying this formalism is fairly straightforward, it is worthwhile mentioning that the large number of equilibrium configurations leads to a very large tunneling Hamiltonian matrix. It is also worhtwhile pointing out that we were led to use the permutation group S_5 to label the tunneling sublevels. This group, because it contains operations equivalent to rotation about a 5-fold axis of symmetry, has only been used in a small number of cases, for instance, in the Berry pseudo rotation of phosphorus pentafluoride.

The validity of the present approach has not yet been demonstrated. The theoretical formalism was originally designed for hindered tunneling motions, and it may not apply to a light molecule like the H_5^+ ion, but certainly to the heavier species D_5^+.

[1] M. W. Crofton, G. Niedner-Shatteburg, J. M. Price and Y. T. Lee, 44 Symposium on Molecular Spectroscopy, Paper RF13, OSU, (1989)

Address: Laboratoire de Physique Moléculaire et Atmosphérique, Tour 13, Université Pierre et Marie Curie et CNRS, 4 Place Jussieu, 75252 Paris Cedex 05, France

Time required 15 minutes.
Session in which paper is recommanded for presentation: (5) High resolution IR & THEORY

RF12 (4:45)

ROTATIONAL SPECTRUM AND INTERNAL ROTATION OF THE METHANE-HCL COMPLEX

Yasuhiro OHSHIMA and Yasuki ENDO

Rotational spectra of CH_4.HCl and CD_4.HCl have been studied using a pulsed-nozzle Fourier-transform microwave spectrometer newly constructed in our laboratory.[1] The K = 0 and K = 1 components of the J = 1-0, 2-1, and 3-2 transitions have been detected in 4-18 GHz and assigned through the Cl-nuclear quadrupole hyperfine structure characteristic for a symmetric top. The Cl-isotopic dependence of the determined rotational constants is consistent with the methane...HCl geometry, i.e. methane acts as a proton acceptor, as in the case of the CH_4.HCN complex.[2] The K = 0 transitions were observed to be split into doublet while only one component was detected for K = 1. We attribute this anomaly to the two-dimensional internal-rotation of methane. An analysis considering the angular momentum coupling between the internal rotation and over-all rotation of the complex reveals the correlation between a free-internal rotor and a rigid symmetric top. The observed two K = 0 and one K = 1 components correspond to the three lowest states with different symmetries, A, F, and E, which correlate respectively to the j = 0, 1, and 2 states of the freely-rotating methane.

[1] Y. Ohshima, M. Iida, and Y. Endo, Chem. Phys. Lett. 161, 202 (1989).
[2] A.C. Legon and A.L. Wallwork, J. Chem. Soc., Chem. Comm. 1989, 588 (1989).

Address   Ohshima and Endo: Department of Pure and Applied Sciences, The College of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153, Japan.
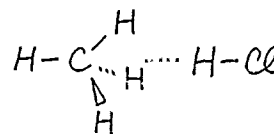
RF13 (4:57)

PULSED LASER-MICROWAVE DOUBLE RESONANCE STUDY OF SO_2 $\tilde{C}$-$\tilde{X}$ BAND

Y. Endo and Y. Ohshima

The $\tilde{C}^1B_2$-$\tilde{X}^1A_1$ system of SO_2 has been studied by the pulsed laser-microwave double resonance technique around the region 220nm. The present method, which detects changes of the ground state microwave absorption caused by the electronic transition induced by a pulsed tunable laser, provides rotationally selected and simplified spectra for the otherwise complicated electronic transition. By combining data of several microwave transitions used to monitor, we were able to determine rotational energy levels of many vibronic bands of the $\tilde{C}$ state unambiguously even when they were severely perturbed; in some cases, rotational lines were found to be split into doublet.

It is expected that systematic double resonance study of the vibronic bands is of great help to reveal the nature of the perturbations, whether they are due to highly excited vibrational levels of the ground electronic state or triplet states, and of the predissociation found below 218nm.

Address of Endo and Ohshima: Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Komaba, Meguroku, Tokyo 153, Japan.

170

RG1 (1:30)

DEVELOPMENT OF FT SPECTROMETER FOR HIGH-RESOLUTION EMISSION SPECTRA OF
UNSTABLE SPECIES
SANG. K. LEE, M. H. SUH, T. A. MILLER, AND V. E. BONDYBEY

We have improved a technique for obtaining high-resolution emission spectra of unstable species in the visible and u.v. range. For this purpose, the Bruker FT-IR Model #120 at OSU has been employed with a PMT detector, and the unstable species have been produced with an electric DC discharge in a supersonic nozzle system. The accuracy of the frequencies obtained, and the resolution in the visible region will be discussed. However, the rotational temperature of the species is relatively higher compared to that obtained with laser photolysis. The spectra of CH_3S and benzyl radicals will be presented as examples as well as the details of the development of the system.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

RG2 (1:47)

SPECTRA OF COLD FLUOROBENZENE IONS WITH AN FT SPECTROMETER

M. H. SUH, S. K. LEE, T. A. MILLER, AND V. E. BONDYBEY

The spectra of several fluorobenzene cations have been generated by a corona discharge in a supersonic expansion. Rotational temperatures have been determined by computer simulation to be ~30°K. The band origin of $C_6F_6^+$ determined with high precision compares well with that obtained by laser excitation studies. 1,2,3 trifluorobenzene cation spectra have been taken by the same technique and have been compared with matrix spectra. The rotational contour in the FT spectra are analyzed to identify the type of electronic transition.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

RG3 (2:04)

INTERNAL ROTATION, LOW FREQUENCY VIBRATIONS AND THEIR INTERACTIONS IN p-FLUOROTOLUENE AND ITS $-d_3$ DERIVATIVE

Z.Q. ZHAO and C.S. Parmenter

In a continuing study of interactions between methyl group internal rotation and ring vibrations[1,2] we have revisited the S_1-S_0 fluorescence spectroscopy. Improved resolution has yielded the rotational contours of low energy bands in the excitation spectra as well as many new features in the dispersed fluorescence spectra. The $-d_3$ spectra allow secure distinction between bands involving ring vibrations and those involving methyl group internal rotation. Franck-Condon intensities are abnormal. More than four types of rotational contours occur in the excitation bands.

Several assignments by Ito et al.[3] in the excitation spectrum have been revised and additional assignments have been made. Franck-Condon activities and band contours are explained by interactions among electronic motion, vibration, internal rotation and overall rotation. Abnormal Franck-Condon activities in the dispersed fluorescence spectra tell us which internal rotation states couple with which vibrational states and whether this coupling is turned on by overall rotation and nuclear spin.

[1]. C.S. Parmenter and B.M. Stone, J. Chem. Phys., 84, 4710 (1986).
[2]. D.B. Moss, C.S. Parmenter and G.E. Ewing, J. Chem. Phys., 86, 51 (1987).
[3]. K. Okuyama, N. Mikami, and M. Ito, J. Phys. Chem., 89, 5617 (1985).

Address of Zhao and Parmenter: Department of Chemistry, Indiana University, Bloomington, IN 47405

RG4 (2:21)

SINGLE VIBRONIC LEVEL FLUORESCENCE SPECTRA FROM THE S_1 ($^1B_{2u}$) STATE OF
DEUTERATED p-DIFLUOROBENZENE [p-DFB(d_4)] VAPOR.

F. Todd, and C.S. Parmenter

$^1B_{2u} \rightarrow ^1A_{1g}$ fluorescence spectra have been obtained after pumping each of 6
absorption bands in pDFB(d_4). Transitions in these spectra can be assigned based on
assignments of ground state vibrational frequencies of pDFB(d_4) [1], previous work
on SVLF of pDFB(h_4) [2], and a simple qualitative picture of normal mode vibrations.
Assignments of the low energy end of $^1B_{2u} \rightarrow ^1A_{1g}$ absorption spectrum are secured by
SVL fluorescence spectroscopy. Two low frequency S_1 modes undergo large frequency
changes upon deuteration. The out-of-plane ring distortion ν_8' drops from 175 cm^{-1}
in -h_4 to 151 cm^{-1} in -d_4. As a result the level of the lowest frequency S_1 mode
$\nu_{30}' - 118$ cm^{-1} in -d_4 is very near that of ν_8'. The mode ν_4' drops from 1015 to
819 cm^{-1} where it almost matches the frequency of the most prominent progression
forming mode ν_5'. As a consequence the -d_4 spectra in absorption and (as Dunn et
al. [1] showed) in emission as well contain and extra set of progressions not present
in the -h_4 molecule. These changes open new opportunities for S_1 energy transfer
studies.

1. A.F. Childs, T.M. Dunn, A.H. Francis, J. Mol. Spectros., 102, 56 (1983).
2. R.A. Coveleskie and C.S. Parmenter, J. Mol. Spectros., 86, 66 (1981).

Address of Todd and Parmenter: Department of Chemistry, Indiana University,
Bloomington, IN 47405

RG5 (2:38)

ROTATIONALLY RESOLVED FLUORESCENCE EXCITATION SPECTRA OF 1-NAPHTHALDEHYDE.[1]

S. JAGANNATHAN, B. B. CHAMPAGNE, A. HELD, J. L. TCHER AND D. W. PRATT

Several vibronic bands in the $S_1 \leftarrow S_0$ fluorescence excitation spectrum of 1-naphthaldehyde
(1NA) have been rotationally resolved using the new molecular beam laser spectrometer operating
in the ultraviolet.[2] Typical linewidths are of order 30-50 MHz, making possible the
determination of the band origins, the inertial parameters, and the transition moment
orientations to high accuracy. Hartree-Fock calculations on the S_0 state with a 3-21G basis
set also have been performed. The experimental results suggest that 1NA has a nonplanar
equilibrium geometry in its ground electronic state, with a twisted formyl group. Structural
changes along this and other coordinates on electronic excitation are revealed by comparisons
of the rotational constants of different S_1 vibronic levels of 1NA, isotopically labelled
1NA's, and other 1-substituted naphthalenes.[2,3]

[1] Work supported by NSF.

[2] W. A. Majewski, D. F. Plusquellic, and D. W. Pratt, J. Chem. Phys. 90, 1362 (1989).

[3] X.-Q. Tan, W. A. Majewski, D. F. Plusquellic, D. W. Pratt, and W. L. Meerts, J. Chem.
Phys. 90, 2521 (1989); J. R. Johnson, K. D. Jordan, D. F. Plusquellic, and D. W. Pratt,
submitted; D. F. Plusquellic and D. W. Pratt, work in progress.

Address for Jagannathan, Champagne, Held, Tomer and Pratt: Department of Chemistry, University
of Pittsburgh, Pittsburgh, PA 15260.

RG6 (2:55)

HIGH RESOLUTION FLUORESCENCE EXCITATION SPECTRA OF THE 1- AND 2-AMINONAPHTHALENES.[1]

D. F. PLUSQUELLIC AND D. W. PRATT

Continuing our study of internal motions of isoelectronic species attached to the naphthalene chromophore, we report here the observation and analysis of the $S_1 \leftarrow S_0$ fluorescence excitation spectra of 1- and 2-aminonaphthalene as well as many isotopically substituted derivatives at a resolution of ~ 10 MHz in the UV. Deuterium has been used to label both the amino hydrogen positions and selected ring hydrogen positions. The rotational constants obtained from analyses of these spectra, in conjunction with Kraitchman's equations, has allowed us to define geometric features of the protonated molecule in both states. We also find the 0^0_0 band of 1-aminonaphthalene (1AN) to be primarily b-axis polarized, contrary to earlier obervations on 1AN and related species.[2] We also obtain information about the magnitudes of the barriers to inversion of the amino group in both states. These results will be summarized and discussed in the framework of molecular orbital theory. A brief overview of the software developed to record and analyze the high resolution spectra of large polyatomic molecules also will be given.

[2] J. M. Hollas and S. N. Thakur, Mol. Phys. 27, 1001 (1974).

Address of Plusquellic and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

Intermission

RG7 (3:30)

Photoacoustic Absorption Spectrum Of The 1426 Cm[-1] Band Of The $^3B_{3u}$ -^1A_g System of s-Tetrazine.

A.Meenakshi and K.K.Innes

The $^3B_{3u}$- ^1A_g (π^*·n) band system of s-tetrazine with its origin at 13608 cm^{-1} is known [1-3] to be dominated by a progression built on the $6a^1_0$ in-plane ring breathing vibrational mode. A high resolution room temperature vapor phase intracavity absorption spectrum of the $6a^2_0$ band of s-tetrazine was recorded using photoacoustic detection The band origin is located at 15043.8 cm^{-1} and the band is violet degraded. The sharp and extensive rovibronic features of this band are subjected to rotational analyses , the results of which will be presented along with a few interesting dynamic properties of the spin sublevels of this triplet state.

1. K.K.Innes, I.G.Ross & W.R.Moomaw J. Mol. Spectrosc. 132, 492 (1988).
2. R.Hochstrasser and D.S.King Chem. Phys. 5, 439 (1974).
3. D.T.Livak and K.K.Innes J. Mol. Spectrosc. 39, 115 (1971).

Address of A.Meenakshi and K.K.Innes: Department of Chemistry, S.U.N.Y. Binghamton, N.Y. 13901, U.S.A.

RG8 (3:42)

OBSERVATION OF LARGE VIBRATIONAL ℓ-TYPE RESONANCES IN THE S_1 STATE OF BENZENE

E. RIEDLE AND J. PLIVA

Improved experimental methods have recently allowed us to analyze the structure of the fundamental bands in both the IR and UV spectrum of benzene with rotational resolution. Deviations from regular behavior could be well accounted for by anharmonic, Coriolis, and rotational ℓ-type interactions. However, the spectra of multiply degenerate states are still incompletely understood. Large splittings of the various vibrational angular momentum components and the observed relative intensities remain to be explained.

With sub-Doppler spectroscopy in a collimated beam, rotationally resolved spectra of the two vibronic bands which were previously assigned to the $6_0^1(\ell_0^{\pm 1})10_0^2(\ell_0^0)$ and $6_0^1(\ell_0^{\pm 1})10_0^2(\ell_0^{\pm 2})$ transitions (Wilson numbering) were measured in the Munich laboratory. Each band could be separately described in terms of effective rotational and Coriolis ζ-constants. However, the values of these effective band constants would imply unrealistically large deviations from planarity C'_v-$B'_v/2$ of -5.46×10^{-4} and 6.72×10^{-4} cm^{-1} respectively for the two bands), and effective ζ's of -0.0083 and $+0.0656$ instead of the expected values $\sim \mp \zeta_6 = \mp 0.578$. We have therefore carried out a simultaneous analysis of the two bands with inclusion of a vibrational ℓ-type interaction of the form $\langle \ell_t, \ell_{t'} | h_2^+ | \ell_t + 2, \ell_{t'} + 2 \rangle = C \{ (v_t + \ell_t + 2)(v_t - \ell_t)(v_{t'} - \ell_{t'} + 2)(v_{t'} - \ell_{t'}) \}^{1/2}$ in the Hamiltonian. The resulting constants, C'_v-B'_v of 1.6×10^{-5} cm^{-1}, and ζ_{eff} of -0.5248 and $+0.5822$, appear very reasonable; the coupling parameter C has the value 1.575 cm^{-1}.

This result, and a similar one for the $6_0^1 16_0^2$ bands, shows the importance of vibrational ℓ-type resonances in the multiply degenerate combination states of benzene. The vibrational angular momentum character of such states, which comprise the majority of all vibrational states of benzene at higher excess energies, is therefore not well defined. Important implications for the intramolecular vibrational redistribution and for the nonradiative decay of benzene states are expected to arise.

Address of Riedle: Institut für Physikalische Chemie, TU München, Lichtenbergstrasse 4, D-8046 Garching, West Germany.

Address of Pliva: Department of Physics, The Pennsylvania State University, University Park, PA 16802, USA.

RG9 (3:59)

EFFECTIVE ROTATION AND FINE-STRUCTURE HAMILTONIANS OF SYMMETRIC TOP MOLECULES IN DEGENERATE VIBRONIC STATES

XIANMING LIU AND TERRY A. MILLER

Effective Hamiltonians, both first and second order, for rotation, spin-rotation and electron dipolar spin-spin interactions of a symmetric top molecule in a doubly degenerate vibronic state have been obtained group theoretically by the irreducible tensor method. It has further been shown that both first and second order Hamiltonians obey the same symmetry selection rules and thus have identical forms. A systematic procedure for obtaining the complete effective Hamiltonian as well as detailed results for the most frequently encountered symmetric top molecule point groups will be presented. Application of the theory to specific cases will be discussed.

Address of Liu and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210.

RG10 (4:16)

TRANS-STILBENE AND ITS ARGON VAN DER WAALS COMPLEXES: ROTATIONALLY RESOLVED FLUORESCENCE EXCITATION SPECTRA OF THE ONE-PHOTON $S_1 \leftarrow S_0$ OPTICAL TRANSITION.[1]

B. B. CHAMPAGNE, J. F. PFANSTIEL, D. F. PLUSQUELLIC, AND D. W. PRATT

We have obtained numerous rotationally resolved trans-stilbene fluorescence excitation spectra in a range of excess energies from ~ 0 to ~ 1200 cm^{-1} above the S_1 origin using the high resolution spectrometer operating in the ultraviolet. An analysis of the 0_0^0 band has recently been reported.[2] Higher energy bands exhibit diffuse structure long before the experimentally observed rapid decrease in fluorescence lifetime[3] thought to be associated with light-induced trans-cis isomerization. We report some results and ongoing progress in our rotational spectroscopic analysis yielding molecular geometry information which is clearly relevant to understanding trans-stilbene and its dynamic behavior following the absorption of light. We also report recent elucidation of the structure of argon-stilbene complexes and some possible strategies for obtaining 'dynamical' information directly from studies in the frequency domain.

Addresses for Champagne, Pfanstiel, Plusquellic and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

RG11 (4:33)

INFRARED EMISSION SPECTRA OF POLYCYCLIC AROMATIC HYDROCARBONS

JOE KURTZ

Infrared fluorescence and thermal emission spectra were collected from gaseous samples of several polycyclic aromatic hydrocarbons (PAHs) including naphthalene, perylene, and coronene. The samples were heated to temperatures ranging from 200 to 500 C under helium atmospheres. The sample cell used was similar to that described in reference [1]. The heated cell was used as the IR source of a Mattson Polaris FTIR spectrometer. For collecting flourescence spectra, the samples were exposed to UV-visible light from a Xe discharge source, while for thermal emission spectra, the Xe lamp was turned off. Background emission was obtained under the same conditions with no PAH present.

[1] D. W. Salisbury et al. in Experiments on Cosmic Dust Analogues, E. Bussoletti et al. (eds.), pp. 129-135 (1988).

Naphthalene   Perylene   Coronene
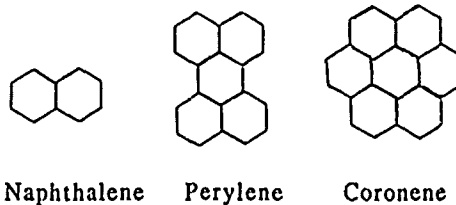
Address of Joe Kurtz: Code 691, Goddard Space Flight Center, Greenbelt, Maryland, 20771.

RG12 (4:50)

PHOTO-EXCITATION AND PHOTOLUMINESCENCE STUDY OF COORDINATION COMPLEXES OF LEAD DIIODIDE WITH PYRIDINE

L. C. YU AND A. H. FRANCIS

PbI_2 exhibits a lamellar CdI_2 crystal structure, similar to that of the transition metal dichalcogenides (MX_2) and transition metal phosphorus trichalcogenides (MPX_3). When PbI_2 is exposed to any of a variety of organic Lewis bases, it undergoes a solid-state reaction that produces a material with a substantially altered electronic spectrum. Because the reaction is similar to the intercalation reactions of the lamellar chalcogenide lattices with Lewis bases, the reaction of PbI_2 has also been described as an intercalation reaction. Examination of the liquid helium temperature photo-excitation and photo-luminescence spectra of the reaction product with pyridine suggests that there are important differences between the reaction products of the lamellar chalcogenide lattices and PbI_2 with organic Lewis bases. The latter may be described better as coordination compounds resulting from a reversible, heterogeneous reaction between solid PbI_2 and the vapor or liquid phase of the organic ligand.

Address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

RG13 (5:07)

THE STRUCTURE AND PHOTOPHYSICS OF CLUSTERS OF IMMISCIBLE LIQUIDS:
$C_6H_6\text{-}(H_2O)_n$

Albert J. Gotch, Aaron W. Garrett, Ralph E. Bandy, and Timothy S. Zwier.

We have carried out a detailed study of mixed clusters of benzene and water formed in a supersonic expansion. These clusters are intriguing because they offer a microscopic view of the interactions between two compounds which form immiscible liquid solutions. The structure and dynamics of these clusters are probed using resonance-enhanced multiphoton ionization coupled with time-of-flight mass spectroscopy. Fluorescence lifetimes for the complexes are also recorded where possible.

One of the unique features of these complexes is their extremely efficient fragmentation upon photoionization which has led past studies to misassign the spectra. We have determined geometries for the $C_6H_6\text{-}H_2O$ (1:1) and $C_6H_6\text{-}(H_2O)_2$ (1:2) complexes using a combination of rotational band contour analysis and vibronic selection rules. The 1:1 complex has a structure in which the oxygen atom of the water molecule is above the plane of the benzene ring near the six-fold axis. It is configured in a hydrogen-bonding geometry with the benzene π cloud. The current best-fit geometry of the 1:2 complex retains the 1:1 geometry but places a second H_2O molecule at a position where it can hydrogen bond with the first H_2O molecule much as it would in the free H_2O dimer.
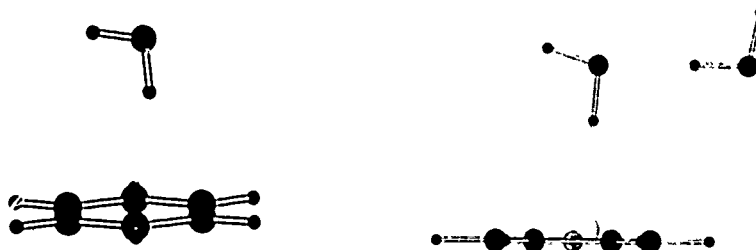
The hydrogen bonding geometries are responsible for the efficient fragmentation of the ion since upon photoionization of the benzene molecule, the hydrogen-bonded H_2O molecule finds itself in a geometry in which its positive H atom is pointing in toward the positively charged benzene cation. The Franck-Condon factors to the ionization continuum are thus strongly weighted toward energies well above the adiabatic ionization threshold for the complex, where fragmentation is energetically feasible.

The absorption features for the 1:3 and 1:4 complexes are remarkably similar to the 1:2 complex both in appearance and in frequency shift relative to free benzene. We conjecture that these higher-order complexes are in fact mimicking an immiscible liquid in which the additional water molecules are clumping together on one side of the ring rather than solvating the benzene ring.

Contribution from the Department of Chemistry, Purdue University, West Lafayette, IN 47907

RH1 (1:30)

PICOSECOND TRANSIENT RAMAN INVESTIGATION OF THE ROLE OF VIBRATIONAL ENERGY IN THE ULTRAFAST PHOTODISSOCIATION OF CHROMIUM HEXACARBONYL IN SOLUTION

Sou-Chang Yu, Xiaobing Xu, R.L. Lingle,Jr., and J.B. Hopkins

The ultrafast photochemistry of $Cr(CO)_6$ has been the subject of recent controversy. Picosecond transient Raman spectroscopy has been used to study the photodissociation of $Cr(CO)_6$ at 266nm. It is found that the appearance time of the vibrationally cold hexacarbonyl photoproduct is rate limited by vibrational relaxation. The dynamics of the Stokes and anti-Stokes Raman spectrum indicate that vibrational cooling occurs on a remarkably long time scale requiring over 100ps for complete thermalization.

Solvent coordination of the photoproducts is directly observed in the Raman spectrum and is found to occur in $\leq$5ps for hydrocarbon solvents.

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

RH2 (1:47)

ACETIC ACID DECOMPOSITION DYNAMICS FOLLOWING ^{1}(n,π*) EXCITATION

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

Acetic acid has been photolyzed at 200nm at low pressure. The nascent OH $X^2\Pi$(v"=0) photo-fragment has been probed using laser fluorescence excitation to determine its scalar and vector quantities. Only a few percent of the available energy is partitioned into OH rotational energy, and fragment OH is produced in v"=0 only. The OH Λ-doublet levels are equally populated, and the $F_1(^2\Pi_{3/2})$ and $F_2(^2\Pi_{1/2})$ spin orbit levels are non-statistically populated. The OH fragment is not rotationally aligned. Fragment OH translational energy was determined using Doppler spectroscopy and compared to OH translational energy from acetic acid photolysis at lower energy (218nm) in the same absorption band[1]. Nearly the same total amount of translational energy is imparted to OH for 200nm and 218nm photolysis, indicating the presence of a barrier to product formation in the decomposition exit channel.

Energy partitioning shows that the primary reaction path vay for OH production is

$$CH_3COOH \longrightarrow CH_3CO + OH$$

for 200 nm acetic acid photolysis. Sufficient energy is channeled into internal energy modes of the acetyl fragment for it to decompose subsequently. RRKM calculations will be presented to indicate whether the acetyl fragment decomposes on the time scale of the experiment. Phase space calculations will also be presented to predict the nascent energy partitioning into the fragments' translational, rotational and vibrational degrees of freedom. Experimental exploration of photochemical reaction mechanisms, such as the formation of an enol intermediate, will also be discussed.

1. Hunnicutt, S. S.; Waits, L. D.; Guest, J. A. J. Phys. Chem. 1989, 93, 5188-5195.

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

RH3 (2:04)

ROTATIONALLY-MEDIATED IVR IN JET-COOLED TRANS-ETHANOL AT 2990 CM^{-1}

JUNGSUG GO, G. A. BETHARDY, AND DAVID S. PERRY

Rotationally-resolved infrared absorption spectra of jet cooled ethanol are reported which reveal extensive mixing of the zero-order methyl C-H stretch vibration with bath rotational-vibrational states. The resulting fragmentation of single rotational lines into multiplet of molecular eigenstates is the spectroscopic signature of the kinetic phenomenon of intramolecular vibrational redistribution (IVR). The spectra are assigned to trans-ethanol by ground state combination differences. The number of molecular eigenstates resolved in our spectrum increases from about 4 at J'=0 to about 20 at J'=4 but is independent of K_a'. The observed density of spectral features implies that the IVR explores both the gauche and the trans forms of ethanol and that K_a' is not a good quantum number. The rotational dependence is the apparent signature of Coriolis type-b and/or -c coupling. Centrifugal coupling is expected to be smaller but could also explain the data.

Address of Go: 1-402 Dongjin-Manston, Sansu-2-Dong, Kwangju-jikhalsi, South Korea 501-092

Address of Bethardy and Perry: Department of Chemistry, The University of Akron, Akron OH 44325-3601

CH_3CH_2OH.

RH4 (2:21)

PULSED LASER HEATING AND SPECTROSCOPIC STUDIES OF ORGANIC AMORPHOUS/GLASSY SYSTEMS I. EXPERIMENTS WITH ANTHRACENE

DANIEL J. GRAHAM AND DWAYNE L. LABRAKE

Organic amorphous/glassy solids are characterized by structural disorder and a range of activation energy barriers. In our laboratory, we are investigating these non-equilibrium systems using pulsed laser heating, cryogenic, and optical spectroscopic techniques. We introduce this subject here by way of experiments with amorphous/glassy anthracene. We discuss three important components of our experiments: (1) preparation of amorphous/glassy anthracene at 15 K, (2) transformations activated by heat generated by an infrared laser pulse, and (3) use of laser induced fluorescence as a spectroscopic probe. Experimental results are discussed which help formulate a better understanding of solid anthracene's reaction profile.

Address of Graham and LaBrake: Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

RH5 (2:38)

PULSED LASER HEATING AND SPECTROSCOPIC STUDIES OF ORGANIC AMORPHOUS/GLASSY SYSTEMS II. EXPERIMENTS WITH BENZOPHENONE

DANIEL J. GRAHAM AND DWAYNE L. LABRAKE

Low temperature conditions preserve the non-equilibrium states of organic amorphous/ glassy materials and allow them to be investigated by optical spectroscopy. Structural changes in such materials may be induced by pulsed laser heating. We continue our discussion of this subject by way of experiments with amorphous/glassy benzophenone and naphthalene/benzophenone. In particular we describe how laser induced phosphorescence spectroscopy is a sensitive probe of amorphous/glassy structure and solid phase transformations. To that end, we develop a model which facilitates understanding of our phosphorescence decay measurements. Our model points toward structural features intrinsic to amorphous/glassy benzophenone and the changes resulting from pulsed laser heating. These results help formulate a better understanding of solid benzophenone's reaction profile.

Address of Graham and LaBrake: Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

RH6 (2:55)

PICOSECOND RAMAN INVESTIGATION OF ELECTRONIC CURVE CROSSING IN SOLUTION

Huiping Zhu, Xiaobing Xu, Soo-Chang Yu, Robert Lingle, Jr. and J.B. Hopkins

The physics of solvent effects on electronic curve crossing processes are currently of great interest due to the importance of these mechanisms in condensed phase reaction dynamics. Picosecond Raman spectroscopy has been used to measure the dynamics of electronic state decay in simple diatomic molecules. It has been found that electronic decay occurs by formation of transient solvent complexes which relax the electronic energy. The rate of energy relaxation is highly dependent on the detailed vibrational structure of the solvent accepting modes. The ability of different solvents to promote electronic curve crossing is correlated with a simple theory.

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

RH7 (3:12)

A "KEYHOLE" MODEL OF IVR TO ACCOUNT FOR THE CONTRASTING EIGENSTATE-RESOLVED INFRARED SPECTRA OF 1-BUTYNE AND ETHANOL

DAVID S. PERRY

Recent molecular eigenstate-resolved infrared spectra 1-butyne[1,2] and ethanol have given insight into the nature of the couplings responsible for intramolecular vibrational redistribution (IVR) at low energies. In the alkynyl C-H band of 1-butyne, the pattern of the coupling is independent of molecular rotation and is therefore attributed to anharmonic vibrational interactions. In contrast, strong rotational effects are observed in the methyl stretching region of ethanol indicating a Coriolis and/or centrifugal coupling mechanism. The present data on the methyl region of 1-butyne does not exhibit this kind of dramatic rotational effect. Despite the apparent difference in coupling mechanism, the interaction widths and average matrix elements are of similar size in both molecules.

A "keyhole" model of IVR will be presented in order to account for the similarities and differences between the two molecules. According to the model, the primary coupling between the zero-order C-H stretch and the bath is similar for both molecules, i. e., anharmonic in nature. The difference between the molecules lies in way bath states couple to each other. In 1-butyne, the bath-bath coupling is mainly anharmonic in nature but in ethanol Coriolis and/or anharmonic coupling among the bath states is also active. Therefore in ethanol, K_a' and K_c' are no longer good quantum numbers and it is possible for IVR to explore the whole of rotational-vibrational phase space.

[1]A. M. de Souza, D. Kaur, and D. S. Perry, J. Chem. Phys. **88**, 4659 (1988).
[2]A. McIlroy, and D. J. Nesbitt, J. Chem. Phys. **92**, 2229 (1990).

$$CH_3CH_2C \equiv CH, \quad CH_3CH_2OH$$

Address: Department of Chemistry, University of Akron, Akron, OH 44325-3601.

Intermission

RH8 (3:35)

DIRECT OBSERVATION OF TIME DEPENDENT IVR IN THE EXCITED ELECTRONIC STATE $^1B_2$
OF ALKYLANILINE MOLECULES

Xinbei Song, Charles W. Wilkerson, John F. Lucia, Steve W. Pauls
and James P. Reilly

Time dependent intramolecular vibrational relaxation (IVR) in the excited

electronic state $^1B_2$ of alkylaniline molecules was directly monitored by

employing a two-photon ionization process. Photoelectrons were produced by

pump-probe picosecond laser pulses impinging on a jet-cooled molecular beam.

The kinetic energies of photoelectrons were measured by a time of flight

method. With the picosecond pump laser tuned to different vibrational modes

in the excited electronic state of alkylaniline molecules and the probe laser

adjusted to the different delay times, photoelectron spectra were recorded.

The extended chain conformation [p-n-(trans)-alkylaniline] and the coiled

chain conformation [p-n-(gauche)-alkylaniline] exhibit remarkably different

IVR behavior. The effect of the chain length on IVR will be also discussed.

Address: Department of Chemistry, University of Indiana, Bloomington, IN 47405

RH9 (3:52)

DETERMINATION OF RATE CONSTANTS FOR $^1\Delta O_2$ ELECTRONIC QUENCHING IN A FLOW TUBE REACTOR

ROBERT R. CRANNAGE, DANIEL E. JOHNSON, AND ERNEST A. DORKO

A flow tube reactor was built to provide an experimental device to measure electronic quenching rate constants for singlet delta oxygen ($^1\Delta O_2$) in the gas phase and at the wall of the tube. Experiments with a cylindrical Pyrex tube have been completed. The source of $^1\Delta O_2$ was a microwave cavity operated at 2.45 GHz. The detection system for the $^1\Delta O_2$ consisted of an intrinsic germanium infrared detector, filters, fiber optics, and associated electronics. The emission from the O_2 (a-X) transition at 1.268μ was transmitted from observation stations at the flow tube reactor by means of a fiber optic cable through a band pass filter to the detector. The chopped signal from the detector was passed into a lock-in amplifier system. The digitized signal was then passed into an IBM PC AT computer for storage and subsequent analysis. A thorough error analysis was performed on the data. The room temperature quenching coefficient for the Pyrex surface was determined to be $\gamma = 2.5 \pm 0.5 \times 10^{-5}$ and the gas phase electronic quenching rate constant for quenching with ground state oxygen was determined to be $k = 3.1 \pm 1.8 \times 10^{-18}$ cc/sec. The kinetic and mathematical models which were used to determine the values for the rate constants will be discussed.

ADDRESS: WL/ARDJ, WEAPONS LABORATORY, KIRTLAND AF BASE, NM 87117-6008

RH10 (4:09)

VISIBLE/ULTRAVIOLET SPECTROSCOPY OF VIBRATION-VIBRATION (V-V) PUMPED CARBON MONOXIDE EXCITED BY A Q-SWITCHED CO LASER

J.W. RICH, J.P. MARTIN, M.Y. PERRIN, V. SUBRAMANIAM, K. MEISTER, D. STRAUB

An electric discharge CO laser, wall-cooled by liquid nitrogen, is Q-switched by an intracavity chopper. Pulsed output on the CO $\Delta V=1$ fundamental band of 3 watts average power is obtained, with > 100 mW on the V=1→0 component forced by laser-induced cascade. This technique is an extension of the method previously reported by Urban et al[1]. The laser is used to excite pure CO, as well as CO/Ar and CO/H_2 mixtures, in a flowing-gas absorption cell. Molecular vibrational modes are thereby maintained in a state of extreme V-V pumped disequilibrium. Electronic state emission from CO and various reaction products is being used to infer V-V and V-E energy transfer channels, as well as chemical reaction mechanisms.

Further developments of a kinetic model previously used for experiments of this type[1] will also be discussed.

[1]W. Urban, J.-X. Lin, V.V. Subramaniam, M. Havenith, and J.W. Rich, Chem. Phys. 130. 389 (1989).

Address of Rich, Subramaniam, Meister, and Straub: Department of Mechanical Engineering, The Ohio State University, 206 W. 18th Ave., Columbus, Ohio 43210.
Address of Martin and Perrin: Laboratoire E.M2.C., UPR 288 C.R.N.S. at Ecole Centrale Paris, 92295 Chatenay-Malabry, FRANCE.

RH11 (4:26)

SPECTROSCOPIC STUDIES OF ELECTRONIC ENERGY TRANSFER BETWEEN TRIPLET STATE N_2 AND ARGON

DANIEL J. GRAHAM AND SCOTT M. HURST

A spectroscopic study of electronic energy transfer between triplet state N_2 and argon is presented. In our experiments, triplet state N_2 is produced by an adiabatic expansion of nitrogen gas in an electrical discharge. We introduce argon downstream from the discharge nozzle by a second adiabatic expansion. High resolution, UV-visible emission spectroscopy is used to interrogate the interaction region of our expansion chamber. Our spectra demonstrate argon-induced perturbations of the second positive system of triplet state N_2. Our spectra thereby provide information about the collision events and relaxation processes involving metastable N_2 and ground state argon.

Address of Graham and Hurst: Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

RH12 (4:43)

DIRECT MEASUREMENT OF GEMINATE RECOMBINATION AND VIBRATIONAL RELAXATION IN I_2 USING PICOSECOND RAMAN SPECTROSCOPY.

Xiaobing Xu, Soo-Chang Yu, Robert Lingle, Jr. and J.B. Hopkins

The chemical dynamics of simple photodissociation reactions in solution are currently of great interest as probes of condensed phase behavior. Picosecond Raman spectroscopy has been used to investigate the photodissociation and geminate recombination of I_2 in a variety of solvents. The dynamics of vibrational cooling in the ground $I_2(X)$ electronic state have been observed with up to $8000 \, cm^{-1}$ of vibrational energy. These results are compared to molecular dynamics simulations of the energy dependence of V-T and V-V energy transfer mechanisms.

Solvent cage dynamics have been investigated by monitoring transient vibrational bands arising from solvent molecules immediately surrounding the I_2 solute. Transient heating in the solvent cage is observed to both appear and decay on the time scale of the 8ps laser pulse. This spectral technique provides a new method for obtaining detailed insight into the solvent environment immediately surrounding a reacting solute molecule.

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

RH13 (5:00)

Infrared-Optical Double Resonance Spectroscopy of High Vibrational Overtones of H_2O_2.
X. Luo and T. R. Rizzo

Room temperature vibrational overtone spectra of polyatomic molecules are typically complicated by severe vibrational and rotational congestion. We have investigated the high-overtone vibrational spectroscopy of hydrogen peroxide using an infrared-optical double resonance technique to eliminate thermal congestion. A pulse from an optical parametric oscillator excites the v_5, v_3+v_5, or v_2+v_5 transitions of H_2O_2 and selects a particular rotational state. A dye laser pulse then promotes the molecule above the threshold for dissociation at the O-O bond by a vibrational overtone excitation of the OH stretch. A third laser probes the OH dissociation fragment via laser induced fluorescence of the A-X band. Scanning the vibrational overtone laser while exciting a particular OH product transition produces a vibrational overtone excitation spectrum of single rotational state of the parent molecule.

The results of these experiments will be presented, and the v, J, K dependence of the vibrational overtone linewidths and their imlications for the unimolecular dissociation dynamics will be discussed.

Address of authors: Department of Chemistry, University of Rochester, Rochester NY 14627

FA4 (9:21)

TUNABLE FAR-INFRARED LASER SPECTROSCOPY OF WATER-CO

R. E. Bumgarner, P. G. Green, and G. A. Blake

The $K = 0 - 1$ rotation-tunneling bands for $O^{12}C-H_2O$ and $O^{13}C-H_2O$ have been measured by direct absorption in the far-infrared using the Caltech tunable-FIR laser spectrometer[1] and a planar supersonic jet. The region studied is from 400 to 600 GHz, that is, 13 to 20 cm^{-1}. Two bands for each isotopomer were observed corresponding to $K=0$ to $K=1$ rotational transitions in the A and B tunneling states of water. In addition, the single $K=0-1$ rotation-tunneling band expected for HOD-^{12}CO in the same region has been measured. All bands have been fit using a Watson type Hamiltonian yielding precise spectroscopic constants.

[1] G. A. Blake and R. E. Bumgarner, J. Chem. Phys. 91, 7300-2 (1989)

Address of Bumgarner, Green, and Blake: Division of Geological and Planetary Sciences, Mail Stop 170-25, Caltech, Pasadena, CA 91125 USA

FA5 (9:38)

RESONANCE RAMAN SCATTERING OF CH₃I IN A SUPERSONIC JET

Y. P. Zhang, P. G. Wang and L. D. Ziegler

This work demonstrates the resonance Raman scattering(RRS) of methyl iodide cooled in neat and seeded supersonic jets. This is the first reported observation of spontaneous RRS in a supersonic jet. Incident excitation is resonant with the predissociative Rydberg B state of CH_3I (201 - 190 nm). Depolarization ratio measurements determine the rotational temperature of the molecular beam to be 10K (4% CH_3I / 2 atm He). The only observed spectral evidence of $(CH_3I)_n$ species (n≥2) in the cooled molecular beam is the appearance of the resonance Raman spectra of I_2 produced by the photodecomposition of methyl iodide clusters. The nascent I_2 is born with an extremely hot ($\sim$ 1000K) vibrational distribution. As determined by the RRS of I_2, the Raman excitation profile (REP) of the I_2 fundamental indicates that the CH_3I clusters have an X→B absorption spectrum which is severly broadened as compared to that of monomer. The I_2 REP is flat over a 125 cm^{-1} region ($\sim$201 nm) whereas the monomer CH_3I absorption band[1] is sharply peaked in this region. The excitation frequency dependence of the I_2 RR scattering illustrates that the effect of dimerization dramatically decreases the excited state lifetime in the clusters by providing a new efficient dissociation channel leading to the formation of I_2. Semiempirical calculations(AM1) predict a CH_3I dimer structure with a bent "head to head" ground equilibrium configuration consistent with efficient I_2 production.

(1) L.D.Ziegler, Y.C.Chung, P.Wang and Y.P.Zhang, J.Chem.Phys. 90, 4125(1989)

Address of Zhang, Wang and Ziegler: Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

FA6 (9:55)

Dynamics of Methyl Iodide B State Photodissociation Probed with Resonance Raman Scattering

P. G. Wang and L. D. Ziegler

The Spontaneous rovibrational resonance Raman scattering of methyl iodide is examined using excitation wavelengths resonant with the predissociative, electronically degenerate B-state absorption band(201–190 nm). The observed intensity wavelength dependence and depolarization ratio dispersion are analysed with an irreducible two phonon tensor approach to determine the mode-dependence of B-state subpicosecond lifetimes. The CH_3I photodissociation rate is found to be same for the B-state origin, ν_3, ν_6, and ν_2 levels but increases by nearly an order of magnitude when one quantum of ν_1 is initially excited on the quasi-bound surface. A similar trend is observed for CD_3I. Lifetimes upon deuteration increase by a factor of 2, except for ν_1 which increases by a factor of 10. Photodissociation rate are also observed to be K-independent.

Contrary to chemical intuition, only excitation of ν_1 (totally symmetric stretch) increases the photodissociation rate, suggesting that the most favorable reaction pathway to methyl iodide dissociation following excitation to the B-state surface involves a small barrier along the C-H stretch coordinate.

[1] P.G. Wang, and L.D Ziegler, J. Chem. Phys. 90 (8), 4125 (1989).

Address of Wang and Ziegler: Department of Chemistry, Northeastern University, Boston, MA 02115, USA

FA7 (10:12)

TUNABLE FAR INFRARED LASER SPECTROSCOPY OF ULTRACOLD FREE RADICALS

R.C. COHEN, C.A. SCHMUTTENMAER, K.L. BUSAROW, Y.T. LEE, AND R.J. SAYKALLY

We report a new high resolution spectroscopic technique designed for the study of short lived free radicals and clusters containing free radicals.[1] Excimer laser photolysis of a suitable precursor during the initial stages of a planar supersonic expansion is used to generate ultracold free radicals, which are subsequently probed by a tunable far infrared laser. In initial experiments we have detected the $1_{11} \leftarrow 0_{00}$ transition of $\cdot NH_2$ with a S/N in excess of 1000. Prospects for 2-3 orders of magnitude improvement in this figure will be presented.

[1] R.C. Cohen, K.L. Busarow, C.A. Schmuttenmaer, Y.T. Lee, and R.J. Saykally, Chem. Phys. Lett. 164,321 (1989).

Address:Department of Chemistry, University of California and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

Intermission

FA8 (10:45)

MEASUREMENT OF THE HYPERFINE STRUCTURE OF $(DCCD)_2$ DIMER

L. H. Coudert, Ratan Bhattacharjee, and J. S. Muenter

Last year, in a theoretical study of the hyperfine structure of $(DCCD)_2$, the effects of nonrigidity of this dimer on the form of the quadrupole hyperfine Hamiltonian were described. It was shown that, for nondegenerate A or B-type tunneling sublevels, the hyperfine Hamiltonian is the sum of four single deuterium Hamiltonians with the same effective coupling constant; while, for doubly degenerate E-type tunneling sublevels, the hyperfine Hamiltonian is less symmetrical and two effective coupling constants arise.

This year we present measurements of the hyperfine structure of several transitions of $(DCCD)_2$ in the radio frequency region. One of the three components of the $1_{10} \rightarrow 1_{11}$ rotational transition, the $B_2^+ \rightarrow B_2^-$, has already been measured with instrumental linewidth of 1.5 kHz. Using the theoretical formalism, it was possible to analyze the frequency of the 11 transitions of the hyperfine pattern with an R.M.S. deviation smaller than 0.1 kHz, and to determine the effective coupling constants of the upper and the lower tunneling states. The results of this analysis will be discussed and an interpretation of these constants in terms of the components of the effective quadrupole tensor will be given.

Measurements are in progress for the $1_{10} A_2^+ \rightarrow 1_{11} A_2^-$, and the $1_{01} E^- \rightarrow 0_{00} E^+$ transitions. The first of these two transitions should be a test for the theoretical formalism since the effective coupling constants should be the same as for the transition already analyzed. The second of these two transitions, involving doubly degenerate sublevels, is of special interest since it will allow us to determine the change in quadrupole coupling for the deuterium atom involved in the hydrogen bond.

Address of Coudert: Laboratoire de Physique Moléculaire et Atmosphérique, Tour 13, Université Pierre et Marie Curie et CNRS, 4 Place Jussieu, 75252 Paris Cedex 05, FRANCE.
Address of Bhattacharjee and Muenter: Dept. of Chemistry, University of Rochester, Rochester, N.Y. 14627.

FA9 (11:02)

An Efficient Approximate Method for Calculating Pressure Shifting Coefficients.

Claudio Chuaqui and *Robert J. Le Roy*

While high quality spectroscopic data of Van der Waals complexes remain the best single source of information about intermolecular potential energy surfaces, those data are most sensitive to the region near the intermolecular potential energy minima. Thus, while they provide detailed information regarding the dependence of an atom-molecule *inter*molecular potential on the *intra*molecular vibrational coordinate, this behaviour is most accurately determined for *inter*molecular distances significantly larger than those associated with vibrational inelasticity or vibrational predissociation.

A better probe of the *intra*molecular stretching dependence of the potential at those relatively small *inter*molecular distances is provided by infrared or Raman pressure shifting coefficients.[1-2] For example, Green's recent close-coupling calculations of the Raman Q-branch lineshape parameters for the H_2-Ar system[3] uncovered inadequacies of the "TT3" surface of Hutson and Le Roy.[4] Unfortunately, the cost of performing such accurate calculations makes their use in an iterative potential fitting procedure prohibitive.[3] However, they still provide a reliable benchmark with which to compare approximate schemes for the calculation of this property.

This paper presents an approximate and computationally inexpensive method for calculating pressure-shifting coefficients which permits their use in iterative fits to determine *intra*molecular-stretching dependent potential energy surfaces.

[1] J.M. Hutson and F.R. McCourt, *J. Chem. Phys.* **80**, 1135 (1984).

[2] R. Blackmore, S. Green and L. Monchick, *J. Chem. Phys.* **88**, 4113 (1988); *ibid* **91**, 3846 (1989).

[3] Sheldon Green, *private communication* (1990).

[4] R.J. Le Roy and J.M. Hutson, *J. Chem. Phys.* **86**, 837 (1986).

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

FA10 (11:14)

PREDICTING THE IR SPECTRA OF ATOM-MOLECULE VAN DER WAALS COMPLEXES: HELIUM-ACETYLENE.

Tom Slee and *Robert J. Le Roy*

The Secular Equation/Perturbation Theory (SEPT) method for calculating infrared spectra of Van der Waals complexes [1] has enabled the most accurate atom-molecule potential surfaces currently known to be determined, for the H_2-rare gas complexes. [2] The present paper explores application of the SEPT method to less isotropic potentials, with He-C_2H_2 as prototype. Kiel *et al.* have obtained a potential surface for He-C_2H_2 from scattering experiments.[3] The spectral properties implied by this potential surface are calculated and compared with nascent experimental observations.[4] The efficiency and range of applicability of the SEPT method are discussed in the light of these calculations.

[1] J. M. Hutson and R. J. Le Roy, *J. Chem. Phys.* **83**, 1197 (1985).

[2] R. J. Le Roy and J. M. Hutson, *J. Chem. Phys.* **86**, 837 (1987).

[3] L. J. Danielson, K. M. McLeod, M. Keil, *J. Chem. Phys.* **87**, 239 (1987).

[4] P. Block, R. E. Miller, unpublished work, (1990).

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

FA11 (11:26)

SOLUTE FREQUENCY SHIFTS AS A PROBE OF STRUCTURE AND DYNAMICS IN HETEROGENEOUS VAN DER WAALS CLUSTERS

Darryl J. Chartrand, Mary Ann Kmetic, and Robert J. Le Roy

Molecular dynamics simulations of SF_6-$(Rg)_n$ clusters (n =5-12), where Rg = Ar and Kr, have been used to determine the minimum energy structures and study dynamical properties, such as transitions between liquid- and solid-like structures. A model, developed by Eichenauer and Le Roy,[1] which predicts the frequency shifts of the v_3 band of the infrared-active SF_6 chromophore, has been used to characterize these clusters. The magnitude of the frequency shift has proved to be a sensitive probe of the distinct "catchment regions" on the potential energy surface which are accessed in the course of a trajectory. Abrupt changes in the frequency shift have been found to be associated with spontaneous iso-energetic isomerizations between structures consisting of a liquid-like monolayer of Ar atoms coating the SF_6, and others in which a solid-like "cap" of $(Ar)_n$ forms on one face of the SF_6 molecule. It has been observed that "melting" is accompanied by a broadening of the simulated v_3 band, behaviour similar to that observed experimentally by Hahn and Whetten[2] in studies of a benzene chromophore in Ar clusters. Illustrative examples of the use of the infrared-active v_3 band of the SF_6 chromophore in probing the structure and dynamical properties of some impure rare gas clusters will be presented and discussed.

[1]D. Eichenauer and R.J. Le Roy, *J. Chem. Phys.* 83, 2898 (1988).

[2]M.Y. Hahn and R.L. Whetten, *Phys. Rev. Lett.* 61, 1190 (1988).

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

FA12 (11:38)

LINE STRENGTHS AND LINE MIXING IN THE 791 cm^{-1} Q BRANCH OF CO_2

L. Strow and S. Hannon

The 791 cm^{-1} Q branch of CO_2 will be used by the CLAES (Cryogenic Limb Array Etalon Spectrometer) instrument on UARS (Upper Atmosphere Research Satellite) for stratospheric temperature sounding. We have measured the strengths of a number of lines in the Q and R branches of this band using a tunable diode laser spectrometer. The line strengths are derived from the spectra using a modified equivalent width method that minimizes uncertainties in the 100% transmission background. Our results are compared to recent measurements of this band by Dana et. al.[1]

Spectra of this Q branch with total pressures between 100 and 740 torr, both self- and N_2-broadened, were also recorded. We find excellent agreement between experiment and calculation for the self-broadened spectra using a simple energy gap scaling law to determine the off-diagonal collisional relaxation matrix. Although our calculations account for most of the line mixing in the N_2-broadened spectra, we systematically underestimate the amount of line mixing by a small amount. This behavior has also been seen in other CO_2 Q branches, both in the laboratory and in atmospheric spectra. The ramification of this disagreement for the energy gap scaling law used in this work will be discussed.

[1]V. Dana, A. Valentin, A. Handouni, and L. Rothman, A.O. 28, 2562 (1989).

Address of Strow and Zheng: Department of Physics, University of Maryland Baltimore County, Baltimore, Maryland 21228.

FA13 (11:50)

TEMPERATURE DEPENDENCE OF SELF-BROADENED LINE MIXING IN A CO_2 Q BRANCH

L. Strow, and L. Zheng

Tunable diode laser spectra of the 2076 cm^{-1} Q branch of CO_2 have been recorded in the 200-350K temperature range between 20 and 720 torr. The self-broadened widths and their dependence on temperature will be compared to measurements in parallel bands of CO_2 and to recent width measurements in another CO_2 Q branch.[1]

The higher pressure spectra exhibit strong line mixing. A simple energy gap scaling law for the collisional rotational relaxation is derived for these transitions using the J-dependence of the pressure-broadening coefficients. This model accurately predicts the line mixing over the complete 200K to 350K temperature range.

---

[1] T. Huet, N. Lacome, and A. Levy, J. Mol. Spectrosc., 128, 206 (1988).

Address of Strow and Zheng: Department of Physics, University of Maryland Baltimore County, Baltimore, Maryland 21228.

FA14 (12:02)

LINE MIXING IN A CO_2 Q BRANCH BROADENED BY Ar AND He

L. Strow and S. Green

Previous studies of Q-branch line mixing in infrared spectra involved self- and N_2-broadened spectra of CO_2 and N_2O. A phenomenological theory of collisional rotational relaxation has been reasonably successful in describing the lineshapes in these systems. Ab-initio calculations have not been tested due to the complexity of the molecule-molecule collision process. Ab-initio calculations are possible for atom-molecule collisions, especially for CO_2-He,Ar collisions, for which good potentials exist. We have recorded Ar- and He-broadened spectra in both CO_2 and N_2O Q branches in order to test the ability of ab-initio calculations to predict line mixing and to determine the general suitability of the presently used phenomenological theory for collisional relaxation. Spectra calculated using ab-initio theory and the phenomenological approach agree very closely for CO2 broadened by He. However, both calculations predict significantly less line mixing than observed.

Address of Strow: Department of Physics, University of Maryland Baltimore County, Baltimore, Maryland 21228.
Address of Greene: NASA Goddard Space Flight Center, Institute for Space Studies, New York, New York 10025.

FB1 (8:30)

VISIBLE OVERTONE SPECTROSCOPY OF ACETYLENE: WHERE DOES ITS OVERTONE INTENSITY COME FROM?

K.K. Lehmann

This talk will start with a review of earlier work on the visible overtone spectrum of acetylene and its isotopomers. Discussion will focus on the overall patterns in the spectrum and the many perturbations. I will then present recent measurements of the intensity of the overtone bands of C_2H_2 and compare them with the intensities of the corresponding bands of HCN.

The talk will finish with a discussion of the source of overtone intensity of the $C\equiv C$-H chromophore. It is found that mechanical anharmonicity plans a much more important role than electrical anharmonicity, although a quantitative prediction of the overtone band strengths is not possible without the latter. It is found that the overtone intensities are extremely sensitive to small changes in the inner wall of the C-H potential function used, but insensitive to the outer wall. The positions of overtone bands are more sensitive to the shape of the outer wall due to its reduced slope. It is proposed that both position and intensity data be used in fitting overtone data to determine the X-H stretching potential.

Address of Lehmann: Department of Chemistry, Princeton University, Princeton NJ 08544

FB2 (8:55)

LASER INDUCED FLUORESCENCE AND ZEEMAN QUANTUM BEAT SPECTROSCOPY OF ELECTRONICAL-LY EXCITED ACETYLENE AND ITS D-SUBSTITUENTS IN SUPERSONIC JETS

N. Ochi, N. Ikeda, and S. Tsuchiya

Laser-induced fluorescence(LIF) spectra of C_2H_2, C_2D_2, and C_2HD were measured with 0.05 cm^{-1} resolution to assign respective rovibronic levels in the $^1\Sigma_u$ state. In C_2H_2, the $3\nu_3$ and $4\nu_3$ vibronic states are perturbed strongly since each rotational level splits into a number of levels, while no level splitting occurs for the $2\nu_3$ state. Most of levels exhibit Zeeman quantum beats(ZQB) in the fluorescence when a weak magnetic field is applied indicating that excited C_2H_2 has large g-values characteristic to respective rovibronic levels which couple with a triplet state. Besides ZQB, quantum beats ascribed to level anticrossing between the A singlet level and a non-fluorescent level were found for a number of excited levels. These anticrossings are due to interaction with its strength of the order of MHz.

In the LIF spectra of C_2D_2 and C_2HD, the observed bands could be assigned to the transitions to the $\ell\nu_2 + m\nu_3 + n\nu_6$ states. Contrary to the case of excited C_2H_2, no level splitting as well as no ZQB were found for respective rovibronic levels which could be assigned unambigiously. This result indicates that the deuteration results in reduction of the coupling strength with triplet states, though the anticrossings observed for C_2H_2 are found also for excited levels of C_2D_2 and C_2HD.

Address of Ochi, Ikeda, and Tsuchiya: Department of Pure and Applied Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

FB3 (9:12)

WHAT DO HIGH TEMPERATURE KINETIC MEASUREMENTS OF ACETYLENE PYROLYSIS TELL US ABOUT THE HEAT OF FORMATION OF C_2H?

R.D KERN, K. XIE, AND J.H. KIEFER

Reaction profiles for C_2H_2, C_4H_2, and C_6H_2 were obtained by dynamic analysis of the reflected shock zone gas by time-of-flight mass spectrometry over the temperature range 1880-2620 K at total reaction pressures of ~ 0.4 atm. The kinetic data were modeled with a new comprehensive mechanism for acetylene pyrolysis[1] which has been applied to experimental results from several laboratories. The reaction scheme features dimerization of acetylene to activated vinylacetylene which then dissociates via both molecular and radical channels. One of the sensitive reactions is $C_2H + H_2 \rightarrow C_2H_2 + H$ the rate of which is affected by the choice of $\Delta_f H$ (C_2H). The value employed herein is 130.4 kcal/mol which is consistent with two recent spectroscopic determinations[2,3]. The use of other proposed values that are considerably higher result in significant deviations between the model calculations and the kinetic data.

[1] J.H. Kiefer and W.A. Von Drasek, Int. J. Chem. Kinetics, in press.
[2] P.G. Green, J.L. Kinsey, and R.W. Field, J. Chem. Phys. 91, 5160 (1989).
[3] J. Segall, R. Lavi, Y. Wen, and C. Wittig, J. Chem. 93, 7287 (1989).

Address of Kern and Xie: Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148.
Address of Kiefer: Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60680.

FB4 (9:24)

Predissociation mechanism of acetylene $\tilde{A}^1A_u$ state[1,2]

M. Fujii, A. Haijima, and M. Ito

The fluorescence excitation spectrum, the MPI spectrum and the absorption spectrum of acetylene were observed for the $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma^+_g$ band system in a static gas cell and in a supersonic jet. A sudden and drastic decrease in fluorescence quantum yield, Φ_f, was found between the V^4K^2 (46339cm^{-1}) and $2^1V^3K^0$ (46673cm^{-1}) sublevels. The decrease in Φ_f is concluded to be due to the predissociation into C_2H+H. J dependence of Φ_f was found for the V^4K^1 vibronic sublevel, while it is absent for the level lying above V^4K^1. From the observed J dependence, the predissociation mechanism was concluded to be vibrational predissociation by tunneling through a potential barrier. Deuterium effect on the predissociation of acetylene is also discussed.

[1] Chem. Phys. Lett., 150, 380 (1988)
[2] J. Chem. Phys., 92, 959 (1990)

Address of Fujii, Haijima and Ito: Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, JAPAN
Bitnet address of Fujii: pba0s6d@JPNTOHOK

FB5 (9:41)

Photodissociation of Acetylene in the 201-216 nm Region: Determination of D_0(HCC-H).

D.P. BALDWIN, M. A. BUNTINE, AND D. W. CHANDLER

Acetylene cooled in a He supersonic expansion was photodissociated by excitation in the 201-216 nm region of the $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g^+$ transition. Subsequent ionization of the H atom fragments by 2+1 (243 nm) REMPI, and mass-selected ion imaging allowed analysis of the velocity distribution of H-atoms from the HCCH + hν → C_2H + H process. Measurement of the maximum H atom velocity produced by photodissociation of acetylene through the $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g^+$ $V_0^5K_0^1$, $V_0^7K_0^1$, and $1_0^1V_0^4K_0^1$ vibronic transitions gave a value for D_0^0(HCC-H) of 131 ± 1 kcal/mol. Other channels producing hydrogen atoms (including $HC_2 \overset{h\nu}{\rightarrow} C_2 + \underline{H}$ and HCCH $\overset{h\nu}{\rightarrow}$ HCCH$^+$ $\overset{h\nu}{\rightarrow}$ $C_2H^+ + \underline{H}$) were detected at all photon fluxes used. These multiphoton channels produce hydrogen atoms with higher translational energy and therefore obscure measurement of the maximum velocity of H atoms produced by single-photon dissociation of acetylene. Reduction of photon flux by more than two orders of magnitude to ~500 J/m^2 gave a background multiphoton signal of ~5% of the peak single-photon signal. Because this multiphoton background limits the detectability of fast H atoms from single-photon dissociation of acetylene, the dissociation energy reported here is an upper limit.

Address of Baldwin, and Chandler: Combustion Research Facility, Sandia National Laboratories, Division 8353, Livermore, CA 94551.
Address of Buntine: Department of Chemistry, Stanford University, Stanford, CA 94305.

FB6 (9:58)

THE $\tilde{A} - \tilde{X}$ BAND SYSTEM IN C_2HD

J. Vander Auwera, T.R. Huet, M.A. Tansamani and M. Herman

The recent vibrational analysis of the $\tilde{A} - \tilde{X}$ band system in C_2HD, performed on the basis of conventional high resolution absorption spectra and of fluorescence excitation jet cooled spectra (1), allows to reinvestigate the rotational analysis of the former ones.

The vibrational assignments are indeed needed to support the rotational investigation, because of strong overlapping mainly with C_2H_2 bands present as impurity, which limits the available information. Several related subbands of this very specific band system (2-5) can be fully rotationally analysed and simultaneously fitted to an appropriate Hamiltonian. Results will be presented, in connection with previous studies on other isotopomers (4,5).

(1) Vander Auwera J., Huet T.R., Herman M., Hamilton C., Kinsey J.L. and Field R.W., J. Mol. Spectrosc. 137, 381-95 (1989).
(2) Ingold C.K. and King G.W., J. Chem. Soc. 2702-55 (1953).
(3) Innes K.K., J. Chem. Phys. 22, 863-76 (1954).
(4) Watson J.K.G., Herman M., Van Craen J.C. and Colin R., J. Mol. Spectrosc. 95, 101-132 (1982).
(5) Huet T.R. and Herman M., J. Mol. Spectrosc. 137, 396-419 (1989).

Address : Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles CP.160, 50 av. F.D. Roosevelt, 1050 Bruxelles, Belgium.

Intermission

FB7 (10:25)

CORRELATION FUNCTION AND SEMICLASSICAL SPECTRAL METHOD
DIAGNOSIS FOR THE ONSET OF CLASSICAL CHAOS IN ACETYLENE.
Young June Cho, Harold H. Harris, Department of Chemistry,
University of Missouri-St. Louis. St. Louis, Missouri 63121
and Frederick G. Haibach, John E. Adams, Department of
Chemistry, University of Missouri-Columbia, Columbia,
Missouri 65211

Instantaneous multiple-mode correlation functions and
the semiclassical spectral method have been investigated as
means of diagnosing the onset of chaotic vibrations in
classical models of acetylene (ethyne)   Correlation
function methods provide an objective, computation ally
efficient, temporally resolving criterion which should be
generaliz able to larger molecules. Trajectories were
performed on the potential energy surface of Halonen,
Carter, and Child 1 , which reproduces experimental bond
lengths, angles, and frequencies, and yields an acceptable
geometry and energy for the metastable vinylidene structure.
Examination of individual trajectories show that there is
participation in chaotic vibrations by flux near the
vinylidene configuration. We have surveyed semiclassical
initial conditions through overtones of all the normal mode
types, and some combinations thereof. Relatively small
differences in thresholds for chaos were observed.

1. L. Halonen, S. Carter, and M. S. Child, Mol. Phys., 41,
191 (1980)

FB8 (10:42)

Photodissociation Processes of Acetylene via Two-Photon Resonant States

M.-S. Lin, Chao-Ping Hsu, Ing-Fang Lee, and Yen-Chu Hsu

The photodissociation processes of acetylene via 9-10 eV two-photon energy levels have been
studied by dispersed emission and the two-color photofragment excitation spectrum. Experimental results
indicate that two dissociation channels have been detected: most (>90%) excited acetylene molecules
undergo sequential bond cleavage to yield vibrationally and rotationally hot $C_2^*(d^3\Pi_g, A^1\Pi_u)$ and
hydrogen atoms, whereas the remaining fraction of molecules undergoes some geometric rearrangement
promptly after the two-photon excitation, in the latter case, subsequent excitation leads to concertive
bond rupture to form $C_2^*(C^1\Pi_g, A^1\Pi_u)$ and H_2. The intermediate state, assigned to be C_2H^*, in the
sequential bond breakage has a lifetime 2.5 ± 0.2 μs.

The geometry of the two-photon resonant states deduced from the photofragment excitation
spectrum will be discussed.

Address: Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166,
           Taipei, Taiwan, R.O.C., and Department of Chemistry, National Taiwan University,
           Taipei, Taiwan, R.O.C.
           fax #: 886-2-3620200, bitnet #: w46a1001@twnmoe01

FB9 (10:59)   C.Y. Robert Wu

FB10 (11:16)

APPLICATIONS OF NEGATIVE ION SPECTROSCOPY TO DETERMINATIONS OF ELECTRON AFFINITIES AND BOND DISSOCIATION ENERGIES

W. C. Lineberger and K. M. Ervin

Negative ion spectroscopy provides a direct method for determination of electron affinities of atoms and small molecules. The photodetachment process also provides direct information on electronic excitation energies of the corresponding neutral species. We present a summary of the vinylidene - acetylene isomerization as studied by this technique. Electron affinities may also be used in a thermochemical cycle involving the gas phase acidity of the corresponding acid to obtain homolytic bond dissociation energies. We will use this cycle to explore bond dissociation energies as acetylene and ethylene are completely dissected to their atomic constituents.

Address of Lineberger and Ervin: Department of Chemistry and Biochemistry, University of Colorado, and Joint Institute for Laboratory Astrophysics, Boulder, Colorado 80309-0440.

FB11 (11:38)

ANOMALOUS BEHAVIOUR OF THE ANTICROSSING DENSITY AS A FUNCTION OF EXCITATION ENERGY IN THE C_2H_2 MOLECULE

P. Dupré, P.G. Green, M. Lombardi, R.W. Field and R. Jost

We have recorded Zeeman Anticrossing (ZAC) spectra of gas phase acetylene (HC≡CH) in the $\tilde{A}$ ^1A_u v_3' = 0 - 3 (v_3' is the trans-bending normal mode of the trans-bent excited electronic state), J = K = 1 = 0, levels. The energy range thus sampled was from 42,200 to 45,300 cm^{-1} above the $\tilde{X}$ $^1\Sigma_g^+$ state. The magnetic field scanned from 0 to 8 Tesla and the ZAC spectra were recorded as variations (decreases) in the intensity of the fluorescence excited by a pulsed, frequency doubled dye laser. The ZAC spectra were unassignably complex. We report a surprisingly rapid increase in the density of anticrossing (AC) over a 3100 cm^{-1} (only 7% of the total excitation energy) energy interval. In the v_3' = 3 level the ZAC spectra are unassignably complex and the anticrossing density is 10^2 times larger than the maximum computed density of triplet vibrational states and quite comparable to the computed density of $\tilde{X}$ $^1\Sigma_g^+$ vibrational states. This constrasts with the AC level density observed in the v_3' = 0 vibrational level where the agreement with the calculated level density is good enough. We suggest three plausible mechanisms to explain this behaviour : the existence of a dissociation limit, the potential curve crossing or the vicinity of a triplet trans- cis-bent isomerization barrier. We prefer this last explanation because this barrier should increase the $S_1 \longleftrightarrow T$ and the $S_0 \longleftrightarrow T$ couplings. Indeed, we suggest that the large level densities are due to $S_1 \longleftrightarrow S_0$ transitions induced by a triplet level[1]. Moreover, the existence of the isomerization barrier is suggested by recent work using the Stark quantum beat technique[2].

[1] P. Dupré, R. Jost, M. Lombardi, P.G. Green, E. Abramson and R.W. Field, in preparation.
[2] P.G. Green, PhD Thesis, MIT (1989), CAMBRIDGE MA (U.S.A.).

Address of P. Dupré, R. Jost and M. Lombardi : Service National des Champs Intenses, CNRS, BP 166X ; 38042 GRENOBLE Cedex (France).
Address of P.G. Green : Mail Stop 170-25, California Institute of Technology ; PASADENA CA 91125 (U.S.A.).
Address of R.W. Field : Department of Chemistry, MIT ; CAMBRIDGE MA 02139 (U.S.A.).

FB12 (11:55)

DOUBLE RESONANCE SPECTROSCOPY OF ACETYLENE: VIBRATIONAL STATE MIXING AND A-STATE VIBRATIONAL FREQUENCIES

A. L. UTZ, J. D. TOBIASON, AND F. F. CRIM

Department of Chemistry, University of Wisconsin-Madison, Madision, WI 53706

Laser induced fluorescence probing of vibrationally excited acetylene molecules created by excitation of the second overtone of the C-H stretching vibration provides a measure of the state mixing in the ground electronic state and directly determines the frequencies of two of the ungerade vibrations in the electronically excited state.

Excitation of the second C-H stretching overtone with light at about 1.0 μ prepares a single angular momentum state of $C_2H_2(3v_{CH})$, and ultraviolet photons at about 2900 Å promote it to its first electronically excited single state (^1A_u). Detecting the emission as a function of the vibrational overtone excitation laser wavelength provides the vibrational spectrum, which clearly shows mixing between zero-order states having largely C-H stretching character and ones having mostly C-C stretching and trans-bending character. We can determine the rotational constants of the perturbing states and identify them as combinations of zero-order stretching and bending vibrations.

The two-photon excitation to the electronically excited state through the B_u vibrational state directly accesses the *ungerade* vibrations in the electronically excited molecule. Using the angular momentum information from the rotational state selection in the first step of the double resonance excitation, we are able to analyze spectra obtained by varying the wavelength of the ultraviolet laser to obtain the wavenumbers of the out-of-plane torsion v_4 (746 cm^{-1}) and the symmetric bend v_6 (768 cm^{-1}).

FC1 (8:30)

HIGH RESOLUTION ELECTRONIC SPECTRA OF JET-COOLED CYCLOPENTADIENYL
RADICAL: OBSERVATION OF JAHN-TELLER INDUCED TRANSITIONS
JAMES M. WILLIAMSON, LIAN YU AND TERRY A. MILLER

The vibrational analysis of the spectrum of the cyclopentadienyl radical (Cp) has not been accomplished, although it was first observed some 40 years ago. The reason lies in the lack of extensive vibrational progressions and the complications due to the Jahn-Teller effect. We have rotationally resolved some of the vibrational bands of the $\tilde{A} \leftrightarrow \tilde{X}$ transition. From its rotational structure, the symmetry of the vibrational mode could be determined. We have thus observed transitions that are conventionally allowed, as well as those induced by the Jahn-Teller effect. One vibrational band that has been assigned to a totally symmetric mode was actually found to be a Jahn-Teller induced transition. These new results and their implications for the Jahn-Teller interaction will be discussed.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210

FC2 (8:47)

ROTATIONAL-TORSIONAL ANALYSIS OF ELECTRONIC SPECTRA OF JET-COOLED
METHYL CYCLOPENTADIENYL RADICAL (CH_3-C_5H_4 AND CD_3-C_5H_4)
LIAN YU, JAMES M. WILLIAMSON, DAVID W. CULLIN AND TERRY A. MILLER

Rotationally resolved electronic spectra of methyl cyclopentadienyl radical (CH_3-C_5H_4 and CD_3-C_5H_4) were recorded in a cold jet (T_{rot} = 0.7 K). The origin band of the $\tilde{B} \leftrightarrow \tilde{X}$ electronic transition consists of two rotational bands with comparable intensity, which are separated by 2 cm^{-1} for CH_3-C_5H_4, and by 1 cm^{-1} for CD_3-C_5H_4. The higher frequency band, which has a simple rigid rotor type-A structure, was assigned to a transition between the ground torsional levels ($\tilde{B}$, $0a_1' \leftrightarrow \tilde{X}$, $0a_1'$). The lower frequency band was assigned to a transition between the first excited torsional levels ($\tilde{B}$, $1e'' \leftrightarrow \tilde{X}$, $1e''$). The two bands were combined in a joint analysis, by diagonalizing the full torsional-rotational matrices, instead of using the more familiar effective Hamiltonian method. In this way, the rotational parameters (A_f, B and C) and torsional parameters (V_6 and B_{top}) were directly determined. Then joint fits for CH_3-C_5H_4 and CD_3-C_5H_4 were performed, realizing that CH_3- and CD_3- are attached to the same framework, hence, $A_f^{H}=A_f^{D}$, and using the isotope relationship $B_{top}^{H} = 2B_{top}^{D}$. The torsional parameters in cm^{-1} are:

	$\tilde{X}$ state	$\tilde{B}$ state
B_{top}^{H}	5.003 (87)	4.879 (100)
V_6^{H}	48.08 (66)	209.1 (2.4)
V_6^{D}	36.01 (63)	145.6 (1.1)

The dramatic change in the torsional barrier V_6 upon electronic excitation and its strong isotope dependence will be discussed. Finally, from the direction of the transition moment, we determined the symmetry of the lowest electronic states to be: $\tilde{X}^2B_2$, $\tilde{A}^2A_2$ and $\tilde{B}^2B_2$.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. .8th Ave., Columbus, Ohio 43210.

FC3 (9:04)

OBSERVATION OF THE SPLITTING OF THE VIBRONIC DEGENERACY UPON
ASYMMETRIC DEUTERATION OF CYCLOPENTADIENYL RADICALS
LIAN YU, DAVID W. CULLIN, JAMES M. WILLIAMSON and TERRY A. MILLER

Rotationally resolved electronic spectra of asymmetrically deuterated cyclopentadienyl radicals (Cp-d_1 -d_2, -d_3 and -d_4) were recorded in a free jet expansion. Upon each deuteration, the origin band is blue-shifted by 50 cm^{-1} (from C_5H_5's $\tilde{A} \leftrightarrow \tilde{X}$ origin at 29 572 cm^{-1}). Asymmetric deuteration reduces the molecular symmetry from D_{5h} to C_{2v}. Correspondingly, the zero point level of the degenerate ground electronic state ($\tilde{X}^2E_1''$) splits into two non-degenerate levels, A_2 and B_2. The order of the split levels are determined from the rotational band type. For Cp-d_1, it is B_2 above A_2, whereas for Cp-d_4, it is A_2 above B_2. In contrast to the symmetric C_5H_5 and C_5D_5, all the rotational constants of the asymmetric molecules could be simultaneously determined. The new information and its implications on the structure and Jahn-Teller effect will be discussed.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210

FC4 (9:21)

ROTATIONAL ENERGY DISTRIBUTIONS IN p-DIFLUOROBENZENE (pDFB) PRODUCED BY
VIBRATIONAL PREDISSOCIATION OF pDFB-Ar VAN DER WAALS COMPLEXES.

H.J. Elston, C.S. Parmenter, K.W. Butz, M.C. Su

Previous experiments[1] have shown interesting, mode selective vibrational predissociation from each of seven initial vibrational levels in the S_1 state of the complex. As an example, V.P. after excitation of the $\overline{5}^1$ complex occurs by two major channels producing the pDFB monomer in the 6^1 and 0^0 states. These monomer states have been recognized by their distinctive vibrational structure in dispersed fluorescence. Now we are using improved fluorescence resolution to learn about the initial rotational distributions in these monomer states, as revealed by rotational band contours.

Rotational contours of the 6_1^1 and 0_0^0 transitions differ from each other markedly; with the 6_1^1 transition having a broader contour. Neither contour matches those calculated for thermal rotational distributions, and that of the 0_0^0 band differs most from an equilibrium contour. Nonetheless, if both were to be described by temperatures, we would say that these monomer are relatively cold. The 6^1 monomer is between 30-40 K and the 0^0 monomer is perhaps closer to 20 K. The complex from which the V.P. occurred was at 5 K when it was laser excited.

1. O, Parmenter and Su, Ber. Bunsenges, Phys. Chem. 92, 253-258 (1988).

Address of Elston and Parmenter: Department of Chemistry, Indiana University, Bloomington, IN 47405
Address of Butz: Department of Chemistry, Griffith University, Natha QLD 4111 Australia
Address of Su: Department of Chemistry, Butler University, 4600 Sunset Ave, Indianapolis, IN 46208

FC5 (9:33)

VIBRATIONAL PREDISSOCIATION OF THE p-DIFLUOROBENZENE-N_2 VAN DER WAALS COMPLEX

B.D. Gilbert, K.W. Butz, M.-C. Su, and C.S. Parmenter

The dissociation of the p-difluorobenzene-Ar (pDFB-Ar) van der Waals complex has been extensively characterized. To continue the study of vibrational predissociation (VP) of van der Waals complexes, pDFB-N_2 and pDFB-NO have been characterized using S_1-S_0 fluorescence spectroscopy. In the case of pDFB-NO there was no fluorescence evident that could be assigned to the complex. pDFB-N_2 however, has been characterized by its fluorescence excitation and single vibronic level fluorescence (SVLF) spectra, which can be compared to those of pDFB-Ar.

The $\overline{0}^0$, $\overline{6}^1$, $\overline{5}^1$ and $\overline{6}^2$ levels of pDFB-N_2 have been pumped and their SVLF spectra assigned. In both pDFB-N_2 and pDFB-Ar, there is no VP observed when the $\overline{0}^0$ level is pumped. When $\overline{6}^1$ is pumped both complexes have the same VP channels and similar rates. When the $\overline{5}^1$ level is pumped, the VP rates change significantly for certain channels in pDFB-N_2 when compared to pDFB-Ar. When the $\overline{6}^2$ level is pumped, the VP rate is less efficient for pDFB-N_2 than for the same channels in pDFB-Ar. In both $\overline{5}^1$ and $\overline{6}^2$ SVLF spectra, significant new features are present in pDFB-N_2.

Address of Gilbert and Parmenter: Department of Chemistry, Indiana University, Bloomington, IN 47405
Address of Butz: Department of Chemistry, Griffith University, Nathan, QLD 4111 Australia
Address of Su: Department of Chemistry, Butler University, 4600 Sunset Ave, Indianapolis, IN 46208

FC6 (9:50)

SELENOFORMALDEHYDE: A ROTATIONAL ANALYSIS OF THE $\tilde{A}^1A_2$ - $\tilde{X}^1A_1$ 735 nm BAND SYSTEM OF $H_2C^{73}Se$, $H_2C^{80}Se$ and $D_2C^{80}Se$ FROM HIGH RESOLUTION LASER FLUORESCENCE EXCITATION SPECTRA.

DENNIS J. CLOUTHIER, R.H. JUDGE, D.C. MOULE AND DUCK-LAE JOO

High resolution laser fluorescence excitation spectra of vibronic bands in the $\tilde{A}^1A_2$ - $\tilde{X}^1A_1$ system of selenoformaldehyde have been observed with Doppler-limited resolution. The results of the rotational analysis of the origin band of $D_2C^{80}Se$ and the 4^1_0 bands of $H_2C^{80}Se$ and $H_2C^{76}Se$ will be presented.

The electronic transition is shown to be singlet-singlet in nature and the band polarizations are consistent with previous vibronic assignments. Erratic perturbations are observed in all three bands. The derived excited state r_0 structure is similar to that of H_2CS, suggesting that selenoformaldehyde adopts a near-planar equilibrium structure in the excited state.

Some preliminary results of the ongoing analysis of the triplet-singlet system will also be presented.

Address of Clouthier and Joo: Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.
Address of Judge: Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141-2000.
Address of Moule: Department of Chemistry, Brock University, St. Catharines, ONT L2S 3A1.

Intermission

FC7 (10:20)

RESONANCE ENHANCED MULTIPHOTON IONIZATION SPECTRA OF CF_2Cl AND $CFCl_2$ RADICALS

Jeffrey W. Hudgens, Russell D. Johnson III, and Bilin P. Tsai

$CFCl_2$ and CF_2Cl radicals were observed between 365-410 nm using resonance enhanced multiphoton ionization spectroscopy. Both spectra were generated by two-photon resonances with planar 3p Rydberg states. A third laser photon ionized the radicals. The CF_2Cl spectrum displayed a vibrational progression assigned to the out-of-plane bending ν'_4 (b_1) (OPLA) mode ($\omega'_4 = 745$ cm^{-1}), with the origin at 406.2 nm ($\nu_{0-0}=49,230$ cm^{-1}). Assignments for the $CFCl_2$ radical included the ν'_4 (b_1) OPLA ($\omega'_4 = 590$ (20) cm^{-1}) and the ν'_3 (a_1) CCl_2 scissors ($\omega'_2 = 270$ (30) cm^{-1}) modes, with the origin at 401.1 nm ($\nu_{0-0}=49,850$ cm^{-1}).

Address of Hudgens and Johnson: Chemical Kinetics Division, Center for Chemical Technology
National Institute of Standards and Technology, Gaithersburg, MD 20899.

Address of Tsai: Department of Chemistry, University of Minnesota at Duluth, Duluth, MN, 55812.

FC8 (10:37)

THE METHYL TORSION MODES OF S_0 THIOACETONE FROM BULB AND SUPERSONIC JET LASER EXCITATION SPECTROSCOPY.

Y. G. Smeyers, M. Senent, D. C. Moule, R. H. Judge, D. J. Clouthier and J. Karolczak

Laser excitation spectra of thioacetone $(CH_3)_2CS/(CD_3)_2CS$ have been recorded over the region 17250 - 17750 cm^{-1} at 300 K and under supersonic jet conditions. The pattern of the vibronic bands in the jet spectrum was observed to be very simple and could be assigned to the sulphur wagging and the methyl torsion modes.

Ab initio M. O. calculations were performed with a 4 - 31G + d basis. A two dimensional potential surface $V(\theta_1, \theta_2)$ was obtained for the S_0 state, where θ_1 and θ_2 are the torsional angles of the two groups. This surface was found to have a an energy maximum at 440 cm^{-1} and a saddle point at 220 cm^{-1}. It was incorporated into the two dimensional Hamiltonian matrix and symmetrized by the G_{36} point group into sixteen blocks and solved by the variational method for the nine symmetry species. The supersonic jet spectrum showed clearly the origin bands at 17327.8/17349.8 cm^{-1} in $(CH_3)_2CS/(CD_3)_2CS$. Frequency intervals of 153.2/114.7 cm^{-1} between the origin band and a set of hot bands were assigned to fundamental frequencies of the S_0 ground state. A comparison of the calculated A_1 fundamentals, 146.78 /118.07, showed good agreement with the experimental data.

Address of Smeyers and Senent: Instituto de Material Science, c/Serrano, 119, 28006 Madrid, Spain
Address of Moule: Dept. of Chemistry, Brock University, St Catharines, Ont., L2S3A1, CANADA.
Address of Judge: Department of Chemistry, University of Wisconsin - Parkside, Kenosha, WI. 53141, USA
Address of Clouthier and Karolczak: Department of Chemistry, The University of Kentucky, Lexington, KY. 40506-0055, USA.

FC9 (10:54)

ROTATIONALLY RESOLVED LASER INDUCED FLUORESCENCE SPECTROSCOPY OF JET-COOLED SUBSTITUTED CYCLOPENTADIENYL RADICALS

DAVID W. CULLIN, LIAN YU, JAMES M. WILLIAMSON and TERRY A. MILLER

Substitution of the cyclopentadienyl radical introduces a splitting of the originally degenerate $X\,^2E_1''$ state due to lowering of the D_{5h} symmetry to C_{2v}. We have obtained rotationally resolved laser induced fluorescence spectra of the fluoro- and chloro- substituted cyclopentadienyl radicals in a supersonic free jet expansion. The radicals were generated by ArF photolysis of 2-fluoro and 2-chloroanisoles. A detailed rotational analysis and the resulting implications for electronic state assignments and molecular structure will be presented along with a discussion of the effect of various substitutions on the electronic structure of the C_5H_5 ring.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210

FC10 (11:11)

A REINVESTIGATION OF THE JET-COOLED PHENYL NITRENE SPECTRUM

DAVID W. CULLIN, LIAN YU, JAMES M. WILLIAMSON AND TERRY A. MILLER

The origin band of the electronic transition at 368 nm, long attributed to gaseous triplet phenyl nitrene, has been investigated using a very high-resolution pulsed laser to interrogate molecules, via LIF, cooled in a supersonic free jet expansion. The spectrum was observed from the photolysis of a variety of stable precursor molecules. The observed rotational and spin structure of this band is inconsistent with simple ideas of triplet phenyl nitrene's structure and spectra. The detailed rotational analysis of this spectrum will be presented along with a suggested alternative carrier for the spectrum.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210

FC11 (11:28)

THE ELECTRONIC SPECTRUM OF THE CCl_3 RADICAL

Jeffrey W. Hudgens, Russell D. Johnson III, Bilin P. Tsai[a], and S. Kafafi,

The electronic spectrum of $C^{35}Cl_3$ radicals was observed between 336-440 nm using mass resolved resonance enhanced multiphoton ionization (REMPI) spectroscopy. This spectrum arose from two-photon resonances with planar Rydberg states. A third laser photon ionized the radicals. One Rydberg series of quantum defect $\delta = 0.545$ is comprised of the $\tilde{E} \, ^2E'$ (3p) state ($\nu_{0-0}=47170$, $\omega_1(a_1'$ sym str$) = 544(6)$, $\omega_2'(a_2''$ OPLA$) = 509(21)$, spin-orbit splitting $= 33(5)$ cm^{-1}) and the $\tilde{K} \, ^2E'$ (4p) state ($\nu_{0-0}= 56236$, $\omega_2'= 526(16)$ cm^{-1}). A second Rydberg series of $\delta=0.50$ is comprised of the $\tilde{F} \, ^2A_2''$ (3p) state ($\nu_{0-0}=47868$ cm^{-1}, $\omega_2'=528(4)$ cm^{-1}) and the $\tilde{L} \, ^2A_2''$ (4p) state ($\nu_{0-0}=56409$, $\omega'_2=533(15)$ cm^{-1}). A third Rydberg series ($\delta=0.216$) was comprised of the $\tilde{G}$ (3d) ($\nu_{0-0}=51218$ cm^{-1}, $\omega_2'=520(17)$ cm^{-1}) and $\tilde{M}$ (4d) ($\nu_{0-0}=57733$ cm^{-1}, $\omega_2'=542(3)$ cm^{-1}) states. A fit of the Rydberg formula to these series found the adiabatic ionization potential of the CCl_3 radical to be $IP_a=8.109(5)$ eV. The $\tilde{J} \, ^2A_1'$ (4s) Rydberg state ($\nu_{0-0}= 53471$, $\omega_2'=530(20)$ cm^{-1}) was also observed. The REMPI spectrum exhibited the $\nu_2''=1-4$ vibrational hot bands of the $\tilde{X} \, ^2A_1$ (C_{3v}) radical. Modeling of these hot bands derived the inversion barrier, $B_{inv} = 460 \pm 40$ cm^{-1}.

Address of Hudgens and Johnson: Chemical Kinetics Division, Center for Chemical Technology
National Institute of Standards and Technology, Gaithersburg, MD 20899.

Address of Tsai: Department of Chemistry, University of Minnesota at Duluth, Dulth, MN, 55812.

Address of Kafafi: Department of Environmental Chemistry and Biology, Johns Hopkins University School of Hygiene and Public Health, 615 Norr Wolfe Street, Baltimore, MD 21205.

FC12 (11:45)

MICROWAVE-UV DOUBLE RESONANCE SPECTROSCOPY OF ND3

S.A. Henck, M.A. Mason, K.K. Lehmann

We have constructed a strip line double resonance cell that allows us to perform microwave detected, microwave-optical double resonance experiments for frequencies of 1.8 GHz and below. We have used this cell, combined with a excimer pumped double dye laser, to study the $v_2=0,1$, and 2 vibrational states of the A electronic state of ND3. We obtained rotatinally resolved spectra up to the 14_{12} level of $v_2=1$.

Combining this data with earlier data on NH3, NH2D, and NHD2, also obtained via double resonance, we have estimated r_0 and the diagonal force constants and compared these with ab initio estimates. We also established the vibrational and rotational state dependence of the homogeneous width which reflects the predissociation lifetime.

Address of Henck, Mason and Lehmann: Department of Chemistry, Princeton University, Princeton NJ 08544

FC13 (12:02)

Vibrational Structure and Dynamics of p-Cresol Dimer from the Excitation Spectrum

Shuxin Yan and Lee H. Spangler
Department of Chemistry, Montana State University, Bozeman, MT 59717

The fluorescence excitation spectrum of p-Cresol dimer displays over 20 vibrational transitions in the first 50 cm^{-1} of the spectrum. Most of these can be assigned as combinations and overtones of two nearly harmonic modes of 8.5 and 13 cm^{-1} which are attributed to the intermolecular bend and torsion. The spectrum also exhibits a 109 cm^{-1} mode and its overtone at 217 cm^{-1} which are due to the the intermolecular stretch, but shows no transitions above 450 cm^{-1}. This is in sharp contrast to the p-cresol·H$_2$O spectrum which displays prominant ring modes up to 800 cm^{-1}. Comparison of the dimer and water complex hydrogen bond strengths by use of their stretching frequencies and a crude diatomic model shows the H bonding to be appreciably stronger in the dimer. Thus the lack of intesity above 450 cm^{-1} in the dimer spectrum cannot be attributed to direct dissociation of the dimer, but is most likely due to IVR which may then be followed by dissociation.

FC14 (12:12)

Spectral Evidence for Through the Ring Coupling of the Nitrogen Inversion and Methyl Torsion in p-Methylaniline

Shuxin Yan, Steven G. Mayer and Lee H. Spangler
Department of Chemistry, Montana State University, Bozeman, MT 59717

Two peaks in the p-methylaniline fluorescence excitation spectrum show an unusual splitting that is not evident in the other vibrational bands, or in the aniline spectrum. These bands both display a large deuterium shift (~200 cm^{-1}) in the ND_2 molecule and are thus attributed to the inversion and torsion of the amine group. The presence of the splittings in the amine modes in p-methylaniline, coupled with its absence in the bare aniline suggests that the methyl torsion may be coupled to the mine motion at the opposite end of the ring. Supporting evidence for this interpretation will be presented.

WG 11 (5:00)**

TUNABLE FAR INFRARED LASER SPECTROSCOPY OF JET-COOLED CARBON CLUSTERS: THE ν_2 BENDING VIBRATION OF C_3

C.A. SCHMUTTENMAER, R.C. COHEN, N. PUGLIANO, J.R. HEATH, A.L. COOKSY, K.L. BUSAROW and R.J. SAYKALLY

Seven rovibrational transitions of the $(01^10) \leftarrow (00^00)$ fundamental bending band of C_3 have been measured with high precision using a tunable far-infrared laser spectrometer. The C_3 molecules were produced by laser vaporization of a graphite rod and cooled in a supersonic expansion. This is the first determination of the astronomically important ν_2 fundamental frequency near 63 cm^{-1}. These measurements provide the basis for studies of C_3 in the interstellar medium with far-infrared astronomy.

Address: Department of Chemistry, University of California, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

**THIS PAPER WAS ADDED TO THE PROGRAM MOMENTS BEFORE IT WENT TO THE PRINTERS. THAT EXPLAINS WHY IT IS REPRODUCED HERE

INDEX