

Forty-Fourth

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symposium on

MOLECULAR SPECTROSCOPY

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THE OHIO STATE UNIVERSITY -

June 12-16, 1989

UNDER THE SPONSORSHIP OF
THE DEPARTMENT OF PHYSICS
THE DEPARTMENT OF CHEMISTRY
THE GRADUATE SCHOOL
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SOME LAST MINUTE INFORMATION: 44TH MOLECULAR SPECTROSCOPY SYMPOSIUM
(JUNE 12-16TH 1989)

(I) ADDITIONAL PAPERS (NOT INCLUDED IN THE ABSTRACTS BOOK) THAT WILL BE PRESENTED ARE DETAILED BELOW. THE ABSTRACTS OF THESE PAPERS ARE DISPLAYED ON A WALL NEAR THE REGISTRATION DESK:

(A) The following three papers related to "IONS" will be presented in the session RA (Chair: CHIKASHI YAMADA)

- (1) Millimeter Wave Spectrum of the N_2F^+ Ion by M. Bogey, C. DEMUYNCK and J. L. Destombes, Universite de Lille-Flandres-Artois, France as RA12 for 10 min. commencing at 11:45.
- (2) Infrared Microwave Double Resonance of HN_2^+ using a color center laser by W. C. Ho, C. J. Pursell, D. P. WELLIKY and T. Oka, University of Chicago as RA13 for 10 min. commencing at 11:57.
- (3) Observation of the ν_2 Band of NH_3^+ by SZETSEN LEE and T. Oka, University of Chicago as RA14 for 10 min. commencing at 12:09.

(B) The following papers will be presented in session TG (Chair: BRENDA WINNEWISSER):

- (1) Quadrupole N_2 Lines S(10) and S(12) observed at $4.1 \mu m$ using a Diode Laser with a 5.016 km absorption path by PAUL BALOG, D. W. Ferguson, M. E. Mickelson, and K. Narahari Rao, Ohio State and Denison Universities for 10 min. as TG9 at 3:46.
- (2) Infrared Spectroscopy of Jet-Cooled Transient Molecules by R. F. Curl, K. K. Murray, M. Petrie, M. Richnow, and F. K. Tittel, Rice University, for 10 min. as TG10 at 3:58.

(C) The following five papers from the University of Colorado at Boulder will be presented in sessions ME (Chair: L. H. COUDERT), TF (Chair: R. L. KUCZKOWSKI) and FB (Chair: G. T. FRASER).

- (1) The Band Potential of the Quasi-linear Hydrogen Bond in CO_2-HF by David J. Nesbitt and C. M. LOVEJOY for 15 min. as ME13 commencing at 5:12.
- (2) Band-stretch Coupling and Predissociation in NeDF by C. M. LOVEJOY and David J. Nesbitt as TF13 for 10 min. commencing at 5:07.
- (3) HeHF, HeDF, and HeHCl - How Little Can a Spectrum Reveal? by C. M. LOVEJOY and David J. Nesbitt for 10 min. as TF14 commencing at 5:19.
- (4) Tunneling in the HCl and DCl Dimers by M. D. Schuder, D. D. Nelson, Jr., C. M. LOVEJOY, and D. J. Nesbitt for 10 min. as FB11 commencing at 11:30.
- (5) The near-IR Spectra of NeDCl and ArDCl by M. D. Schuder, D. D. Nelson, Jr. and D. J. Nesbitt for 10 min. as FB12 commencing at 11:42.

(D) The following two papers from the University of California at Berkeley will be presented in session RF (Chair: V. MALATHY DEVI):

- (1) Observation of Free Internal Rotation of H_2O and NH_3 Subunits in Hydrated Ammoniated Ammonium Ions by M. W. CROFTON, J. M. Price and Y. T. Lee for 10 min. as RF12 commencing at 4:17.
- (2) Observation of Rotational Structure in the Vibration Predissociation Spectrum of H_5^+ by M. W. CROFTON, G. Niedner-Schatteburg, J. M. Price and Y. T. Lee for 10 min. as RF13 commencing at 4:29.

(II) ACKNOWLEDGEMENT: We are indeed very grateful to the Dow Chemical Company for supporting the "Seminar on Spectroscopy of High Temperature Superconductors" and to Dr. Don T. Dix in particular for his efforts in obtaining this sponsorship.

MONDAY, JUNE 12, 1989 -- 8:45 A.M.

Auditorium, Independence Hall

Chair: KATHRYN S. KALASINSKY, Mississippi State Chemical Laboratory
Mississippi State University, Mississippi State, Mississippi

Plenary Session

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

MA1. INFRARED SPECTROSCOPY AND STATE-TO-STATE DYNAMICS OF
WEAKLY BONDED MOLECULAR COMPLEXES 35 min.

ROGER E. MILLER, The University of North Carolina at
Chapel Hill, Venable and Kenan Laboratories
Chapel Hill, North Carolina 27599

MA2. VARIATIONAL CALCULATIONS OF ROTATION-VIBRATION ENERGIES AND
INTENSITIES FOR TRIATOMIC MOLECULES' 35 min.

PER JENSEN, Physikalisches-Chemisches Institut
Justus-Liebig-Universität Gießen, D-6300 Gießen,
West Germany

MA3. LASER AND FOURIER TRANSFORM SPECTROSCOPY OF TRANSIENT SPECIES:
DIATOMICS TO ORGANOMETALLICS' 35 min.

PETER BERNATH, The University of Arizona,
Department of Chemistry, Tucson, Arizona 85721

Intermission

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

MA4. SECOND HARMONIC GENERATION AS A PROBE OF SURFACE STRUCTURE
AND INTERFACIAL DYNAMICS AT THE SOLID/LIQUID INTERFACE). 35 min.

GERALDINE L. RICHMOND, Department of Chemistry,
University of Oregon, Eugene, Oregon 97403

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MONDAY, JUNE 12, 1989 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chair Before Intermission: ROGER E. BUMGARNER, California Institute of Technology, Pasadena, California.

Chair After Intermission: L. H. COUDERT, National Institute of Standards and Technology, Gaithersburg, Maryland.

ME1. THE CONTINUUM ABSORPTION OF LARGE METHANOL CLUSTERS IN THE CO_2^1 LASER REGION.....15 min.(1:30)

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

ME2. VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF DEUTERATED ANALOGS OF METHANOL DIMER IN THE CO_2 LASER REGION.....15 min.(1:47)

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

ME3. VIBRATIONAL PREDISSOCIATION STUDIES OF SOLVATED ALKALI IONS.....15 min.(2:04)

JEFFREY A. DRAVES, JAMES M. LISY, School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois, 61801; and WEN-LONG LIU, Rohm & Haas Company, Philadelphia, Pennsylvania.

ME4. THE MICROWAVE SPECTRUM OF THE Ar-SO_2^1 VAN DER WAALS COMPLEX.....15 min.(2:21)

L. H. COUDERT, K. MATSUMURA, and F. J. LOVAS, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

ME5. TUNABLE FAR-INFRARED LASER SPECTROSCOPY OF VAN DER WAALS BONDS: NEW MEASUREMENTS OF VIBRATION-ROTATION TRANSITIONS IN $\text{Ar-H}_2\text{O}$15 min.(2:38)

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

ME6. CHARACTERIZATION OF THE Ar_2Cl_2^1 AND Ar_3Cl_2^1 VAN DER WAALS MOLECULES.....15 min.(2:55)

C. R. BIELER, K. C. JANDA, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; and D. D. EVARD, Institute für Physikalische Chemie, Universität Basel, CH-4096 Basel, Switzerland.

Intermission

ME7. INFRARED AND MICROWAVE STUDY OF ANGULAR-RADIAL COUPLING IN Ar-HCN15 min(3:30)

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

ME8. A MODEL POTENTIAL FOR Ar-HCN15 min.(3:47)

H. O. LEUNG, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, 02138; M. D. MARSHALL, Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002; and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

ME9. THE POTENTIAL ENERGY SURFACE OF Ar-HCN15 min.(4:04)

D. YARON and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

- ME10. A COUPLED LASER ABLATION PULSED FOURIER TRANSFORM MICROWAVE SPECTROMETER - INITIAL TESTS'.....15 min.(4:21)
- R. D. SUENRAM, F. J. LOVAS, and K. MATSUMURA, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.
- ME11. A BROADLY TUNABLE, AUTOMATED MICROWAVE SPECTROMETER FOR THE OBSERVATION OF WEAKLY-BOUND COMPLEXES.....15 min.(4:38)
- R. E. BUMGARNER and G. A. BLAKE, Division of Geology and Planetary Sciences, MS 170-25, CalTech, Pasadena, California, 91125.
- ME12. TUNABLE FAR IR LASER SPECTROSCOPY OF WEAKLY-BOUND CLUSTERS.....15 min.(4:55)
- G. A. BLAKE and R. E. BUMGARNER, Division of Geology and Planetary Sciences, MS 170-25, CalTech, Pasadena, California, 91125.

MONDAY, JUNE 12, 1989 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chair: CHRIS BENNER, College of William and Mary, Williamsburg, Virginia.

MF1. THE TORSIONAL SPECTRUM OF CH_3CD_3 AND C_2D_615 min.(1:30)

N. MOAZZEN-AHMADI, T. AMANO, J.W.C. JOHNS, A.R.W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6; and I. OZIER, Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada, V6T 2A6.

MF2. ANALYSIS OF THE LOWEST LYING DEGENERATE FUNDAMENTAL OF CH_3CD_315 min.(1:47)

N. MOAZZEN-AHMADI, J.W.C. JOHNS, A.R.W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6; I. MUCKHOPADHYAY, I. OZIER, and R. I. THOMPSON, Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada, V6T 2A6.

MF3. ROTATIONAL PARAMETERS OF THE ETHANE TORSIONAL STATE FROM COMBINATION DIFFERENCES IN $\nu_9 + \nu_4 - \nu_4$15 min.(2:04)

W. E. BLASS, G. W. HALSEY, Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee, 37996-1200; JOEL SUSSKIND, D. C. REUTER, and D. E. JENNINGS, Goddard Space Flight Center, Greenbelt, Maryland, 20771. HALSEY also at Goddard.

MF4. LINESHAPES OF TRANSFERRED SPIKES IN $^{15}\text{NH}_3$ OBSERVED BY INFRARED-INFRARED FOUR-LEVEL DOUBLE RESONANCE.....15 min.(2:21)

YUKARI MATSUO and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

MF5. OBSERVATION OF TRANSFERRED SPIKES IN $^{13}\text{CH}_3\text{F}$ BY INFRARED-INFRARED FOUR-LEVEL DOUBLE RESONANCE.....15 min.(2:38)

YUKARI MATSUO and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

MF6. INTENSITY ANOMALIES DUE TO A CORIOLIS RESONANCE IN THE SPECTRUM OF H^{13}CNO ...15 min.(2:55)

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

MF7. THE HIGH RESOLUTION INFRARED AND MICROWAVE SPECTRA OF ISOCYANOGEN, CNCN15 min.(3:12)

F. STROH, M. WINNEWISSER, Physikalisch-Chemisches Institut, Justus Liebig Universität, D-6300 Giessen, Federal Republic of Germany; and M.C.L. GERRY, Abteilung Chemische Physik am Institut für Physikalische Chemie, Universität Kiel, D-2300 Kiel, Federal Republic of Germany. On leave from: Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6.

Intermission

MF8. VIBRATIONAL LADDERS, STATE DENSITIES, AND DISSOCIATION PATHWAYS: APPLICATIONS OF SPECTROSCOPY TO LASER PHOTOCHEMISTRY.....10 min.(3:40)

ROBIN S. McDOWELL, BURTON J. KROHN, and JOHN L. LYMAN, University of California, Los Alamos National Laboratory, Los Alamos, New Mexico, 87545.

MF9. INFRARED SPECTRA OF THE ν_3 BAND IN CD_315 min.(3:52)

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

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
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FIELD	GROUP	SUB-GROUP	Molecular Spectroscopy, Spectroscopy, Spectrums, Symposium		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The forty-fourth symposium on Molecular Spectroscopy was held as scheduled. A report containing the abstracts of papers presented has been published by the Ohio State University. Key words included: Infrared Spectroscopy, Molecular Vibrational, Molecular Potential, Laser Spectroscopy, Four Level Spectroscopy, Surface Chemistry, Absorption, Clustering, Molecular Structure, Diatomic, Microwave Spectrometers, Chemical Dissociation, Van Der Waals Forces, Potential Energy, Photochemical Reactions, Vibrational Spectra, Electronic States, Gases, Organic Compounds, Metal Compounds, Ionization, Excitation.					
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Electron Transfer, Collisions (1)

- MF10. HIGH RESOLUTION INFRARED STUDY OF THE $\nu_3+\nu_6+\nu_6$ BAND OF $^{12}\text{CH}_3\text{F}$15 min.(4:09)
HAN G. CHO, YUKARI MATSUO, and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.
- MF11. HIGH RESOLUTION INFRARED AND INFRARED RADIO FREQUENCY DOUBLE RESONANCE STUDY OF THE ν_2 VIBRATIONAL BANDS OF $\text{CD}_3^{79}\text{Br}$ AND $\text{CD}_3^{81}\text{Br}$...15 min.(4:24)
HAN G. CHO and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.
- MF12. HIGH RESOLUTION INFRARED SPECTRA OF ISOTOPIC BENZENES, $^{13}\text{C}_6\text{H}_6$ AND $^{12}\text{C}_6\text{D}_6$15 min.(4:42)
J. PLIVA, Department of Physics, Pennsylvania State University, University Park, Pennsylvania, 16802; J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6; L. GOODMAN, Wright and Riemann Chemistry Laboratories, Rutgers University, New Brunswick, New Jersey, 08903; A. VALENTIN, and L. HENRY, Laboratoire de Physique Moléculaire et Atmosphérique, CNRS 060136, Université Pierre et Marie Curie, 75230 Paris, France.
- MF13. ABSOLUTE INTENSITIES OF THE ν_5 FUNDAMENTAL AND NEARBY TWO QUANTUM HOTBANDS OF ACETYLENE IN THE 14μ REGION USING A TUNABLE DIODE LASER.....15 min.(4:59)
M. WEBER, W. E. BLASS, KAREN R. CZOR, and J. F. BRANNON, Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee, 37966-1200.

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.

MONDAY, JUNE 12, 1989 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chair: D. L. SNAVELY, Bowling Green State University, Bowling Green, Ohio.

MG1. ESR OF TRANSITION-METAL DIATOMIC IONS: Cu_2^+ , Ag_2^+ , Au_2^+15 min.(1:30)R. J. VAN ZEE and W. WELTNER, JR., Department of Chemistry,
University of Florida, Gainesville, Florida, 32611.MG2. GROUND ELECTRONIC STATES OF THE VNi , VPd , VPt , NbNi , AND NbPd MOLECULES.....10 min.(1:47)M. CHEESEMAN, R. J. VAN ZEE, and W. WELTNER, JR., Department of
Chemistry, University of Florida, Gainesville, Florida, 32611.

MG3. TWO PHOTON STUDIES OF MATRIX ISOLATED IODINE.....15 min.(1:59)

M.A.P. MACLER and M. C. HEAVEN, Department of Chemistry, Emory
University, Atlanta, Georgia, 30322.MG4. ANALYSIS OF THE VIBRATIONAL BANDS OF ELECTRONICALLY EXCITED ArHO
AND ArDOM. C. HEAVEN, Department of Chemistry, Emory University, Atlanta,
Georgia, 30322.MG4 WILL BE GIVEN
AS WG6 (SEE PAGE
78)MG5. PRODUCTION OF TRIPLET TRIMETHYLSILYLNITRENE BY DECOMPOSITION OF THE
PARENT AZIDE.....10 min.(2:16)ROBERT F. FERRANTE, Department of Chemistry, U.S. Naval Academy,
Annapolis, Maryland, 21402.MG6. A THEORETICAL STUDY OF C_4O AND C_6O10 min.(2:28)D. W. EWING, Department of Chemistry, John Carroll University,
Cleveland, Ohio, 44118.

INTERMISSION WILL BE AFTER PAPER MG7 BETWEEN 2:57 AND 3:10 P. M.

MG7. INFRARED MATRIX ISOLATION STUDIES OF HYDROGEN BONDS INVOLVING C-H BONDS:
ALKYNES WITH BASES CONTAINING N,P,O, AND S DONORS.....15 min.(2:40)MEI-LEE H. JENG and BRUCE S. AULT, Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio, 45221.MG8. THE VIBRATIONAL SPECTRA OF MOLECULAR IONS ISOLATED IN SOLID NEON. I. CO_2^+
AND CO_2^-15 min.(3:10)MARILYN E. JACOX, Molecular Spectroscopy Division, National Institute
of Standards and Technology, Gaithersburg, Maryland, 20899; and
WARREN E. THOMPSON, National Science Foundation, Washington, D.C.,
20550; Guest worker at the National Institute of Standards and
Technology.MG9. THE VIBRATIONAL SPECTRA OF MOLECULAR IONS ISOLATED IN SOLID NEON. II. O_4^+
AND O_4^-15 min.(3:27)WARREN E. THOMPSON, National Science Foundation, Washington, D.C.,
20550; Guest worker at the National Institute of Standards and
Technology; and MARILYN E. JACOX, Molecular Spectroscopy Division,
National Institute of Standards and Technology, Gaithersburg,
Maryland, 20899.

MG10. DETERMINATION OF TWO-DIMENSIONAL CRYSTAL STRUCTURES BY IR SPECTROSCOPY.....15 min.(3:44)

OTTO BERG and GEORGE E. EWING, Department of Chemistry, Indiana
University, Bloomington, Indiana, 47405.

- MG11. VIBRATIONAL RELAXATION PROCESSES OF CO ON NaCl(100).....15 min. (4:01)
C. NODA, H.-C. CHANG, and G. E. EWING, Department of Chemistry,
 Indiana University, Bloomington, Indiana, 47405.
- MG12. IR PHOTOMETRY OF THIN FILMS ON SINGLE CRYSTAL DIELECTRIC SUBSTRATES.....15 min. (4:18)
HUAN-CHEN CHANG, CHIFURU NODA, GEORGE EWING, Department of
 Chemistry, Indiana University, Bloomington, Indiana, 47405;
 and HUGH RICHARDSON, Department of Chemistry, Ohio University,
 Athens, Ohio, 45701.
- MG13. BAND SHAPE OF ESTER CARBONYL IN SOLUTION.....Arrived Late.....10 min. (4:35)
C. CHAPADOS, Y. CAUMARTIN, and M. TRUDEL, Département de Chimie-
 Biologie, Université du Québec à Trois-Rivières, C.P. 500,
 Trois-Rivières, Québec, Canada, G9A 5H7.
- MG14. STRANGE BEHAVIOR OF THE PAIR ν_3 AND $\nu_2+\nu_6$ IN SOLID ARGON....Arrived Late....10 min. (4:47)
C. CHAPADOS, Département de Chimie-Biologie, Université du Québec
 à Trois-Rivières, C.P. 500, Trois-Rivières, Québec, Canada, G9A 5H7.
- MG15. EVIDENCE FROM ESR OF NONLINEAR CHARACTER IN C_4 FORMED BY VUV PHOTOLYSIS
 IN AN ARGON MATRIX.....Late Paper.....15 min. (4:59)
 H. M. Cheung and W.R.M. Graham, Department of Physics, Box 32915,
 Texas Christian University, Fort Worth, Texas, 76129.

MG15 appears for the first time in this
 Book of Abstracts

To all Ladies and Gentlemen who are
 chairing sessions:

Please follow the program as given in this Book
 of Abstracts. All changes as of May 1 have
 been incorporated into it.
 Some of our past chairpersons preferred to use
 the listing of papers that we send out in
 April due to ease of its handling. If you
 wish to do the same, please note that a few
 papers have been added to some of the sessions
 after the mailing was sent out in April. All
 these newly added papers have been identified
 in this Abstracts Book by a note like the one
 above for MG15.

Thanks for your help.

MONDAY, JUNE 12, 1989 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chair Before Intermission: BARBARA SWEETING, The Ohio State University,
Columbus, Ohio.

Chair After Intermission: MENG-CHIH SU, Butler University,
Indianapolis, Indiana.

MH1. EVOLUTION OF MOLECULAR DISSOCIATION THROUGH AN ELECTRONIC CURVE CROSSING:
POLARIZED EMISSION SPECTROSCOPY OF CH_3I AT 266 nm.....15 min.(1:30)

K. Q. LAO, M. D. PERSON, P. XAYARIBOUN, and L. J. BUTLER, The
James Franck Institute and Department of Chemistry, University of
Chicago, Chicago, Illinois, 60637.

MH2. VIBRATIONAL DEPENDENCE OF THE ROTATIONAL STRUCTURE AND DISSOCIATION RATES OF
THE \bar{A} STATE OF NH_3 , NH_2D , NHD_2 AND ND_315 min.(1:47)

STEVEN A. HENCK, WEN-BIN YAN, and KEVIN K. LEHMANN, Department of
Chemistry, Frick Chemical Laboratory, Princeton University,
Princeton, New Jersey, 08544-1009.

MH3. EFFECTS OF ISOTOPIC SUBSTITUTION ON THE CHEMILUMINESCENCE SPECTRA
OBTAINED DURING THE REACTION OF F_2 WITH CS_210 min.(2:04)

R. J. GLINSKI and C. D. TAYLOR, Department of Chemistry,
Tennessee Technological University, Cookeville, Tennessee, 38505.

MH4. EMISSION, ABSORPTION AND QUANTUM YIELDS IN THE C_2N_2 $\text{A}^1\Sigma^- + \text{X}^1\Sigma^+$ TRANSITION..10 min.(2:16)

J. B. HALPERN and S. A. BARTS, Department of Chemistry, Howard
University, Washington, D.C., 20059.

MH5. VIBRATIONAL LEVEL DENSITY AND CORIOLIS COUPLING OF S_0 H_2CO AT 28000 cm^{-1}15 min.(2:28)

ALAN RITTER, DONALD FRYE, WALTER MERRY, and HAI-LUNG DAI, Department
of Chemistry, University of Pennsylvania, Philadelphia, 19104.

Intermission

MH6. PYROLYSIS JET SPECTROSCOPY OF THE S_1 AND T_1 STATES OF THIOFORMALDEHYDE.....10 min.(3:00)

JAMES R. DUNLOP, 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, 60-780 Poznan, Poland.

MH7. HIGH RESOLUTION LASER SPECTROSCOPY OF CuOH15 min.(3:12)

C. N. JARMAN, W.T.M.L. FERNANDO, and P. F. BERNATH, Department of
Chemistry, University of Arizona, Tucson, Arizona, 85721.

MH8. FOURIER TRANSFORM OBSERVATION OF JET COOLED EMISSION FROM THE CH_3N
AND CCN RADICALS.....15 min.(3:29)

C. R. BRAZIER, P. G. CARRICK, Advanced Research in Energy Storage,
Air Force Astronautics Laboratory/LSX, Edwards Air Force Base,
California, 93523; N. H. OLIPHANT, and P. F. BERNATH, Department
of Chemistry, University of Arizona, Tucson, Arizona, 85721.

MH9. ROTATIONALLY-RESOLVED LASER EXCITED FLUORESCENCE SPECTRUM OF THE
 HCCO RADICAL..... Cancelled (MH11 Will be presented here)15 min.(3:46)

M. A. HANRATTY and H. H. NELSON, Chemistry Division, Code 6110,
Naval Research Laboratory, Washington, D.C., 20375-5000.

MH10. THE RESOLVED EMISSION AND HIGH RESOLUTION ABSORPTION SPECTRA OF THE
 $n \rightarrow \pi^*$ TRANSITION IN FORMYL CYANIDE, CHOCN10 min.(4:03)

R. H. JUDGE, Department of Chemistry, University of Wisconsin-
Parkside, Kenosha, Wisconsin, 53403-2000; D. J. CLOUTHIER,
Department of Chemistry, University of Kentucky, Lexington,
Kentucky, 40506; and D. C. MOULE, Department of Chemistry, Brock
University, St. Catharines, Ontario, Canada, L2S 3A1.

See page 10
for newly
added MH11,
MH12 & MH13

TUESDAY, JUNE 13, 1989 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chair: C. W. GILLIES, Rensselaer Polytechnic Institute, Troy, New York.

TA1. INFLUENCE OF THE AC STARK EFFECT ON MULTIPHOTON TRANSITIONS IN MOLECULES....15 min.(8:30)

W. LEO MEERTS, Fysisch Laboratorium, Katholieke Universiteit Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands; IRVING OZIER, Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada, V6T 2A6; and JON T. HOUGEN, Division of Molecular Spectroscopy, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

TA2. GROUP-THEORETICAL TREATMENT OF SELECTION RULES FOR VIBRATIONAL TRANSITIONS IN MOLECULES EXHIBITING LARGE AMPLITUDE TUNNELING MOTIONS.....15 min.(8:47)

LAURENT H. COUDERT and JON T. HOUGEN, Molecular Spectroscopy Division, National Institute for Standards and Technology, Gaithersburg, Maryland, 20899.

TA3. THE ASSIGNMENTS AND ANALYSIS OF NEAR INFRARED SPECTRA OF (H₂O)₂ BASED ON VIB-ROTATIONAL SELECTION RULES DERIVED FROM A PARTIAL PI GROUP.....15 min.(9:04)

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

TA4. MICROWAVE ELECTRIC-RESONANCE OPTOTHERMAL SPECTROSCOPY OF (H₂O)₂.....15 min.(9:21)

G. T. FRASER, R. D. SUENRAM, and L. H. COUDERT, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

TA5. MICROWAVE SPECTRUM OF THE D₂O DIMER.....15 min.(9:38)

R. D. SUENRAM, G. T. FRASER, and F. J. LOVAS, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

TA6. VIBRATIONAL EXCHANGE UPON INTERCONVERSION TUNNELING IN (HF)₂ AND (HCCH)₂....15 min.(9:55)

G. T. FRASER, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

Intermission

TA7. THEORETICAL TREATMENT OF TUNNELING SPLITTINGS IN THE AMMONIA DIMER.....15 min.(10:30)

JON T. HOUGEN and LAURENT H. COUDERT, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

TA8. TUNNELING - ROTATIONAL SPECTRUM AND STRUCTURE OF (H₂CO)₂.....15 min.(10:47)

F. J. LOVAS, R. D. SUENRAM, L. H. COUDERT, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899; T. A. BLAKE, K. G. GRANT, and STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457. Current address for BLAKE: Department of Chemistry, University of Washington, Seattle, Washington, 98195.

TA9. ROTATIONAL SPECTRUM AND STRUCTURE OF THE H₂O-SO₂ COMPLEX.....15 min.(11:04)

K. MATSUMURA, F. J. LOVAS, and R. D. SUENRAM, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

TA10. STRUCTURE AND TUNNELING OF THE HYDROGEN BONDED COMPLEX WATER-CO.....15 min.(11:21)

D. YARON, D. ZOLANDZ, W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138; K. I. PETERSON, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island, 02881; R. D. SUENRAM, and F. J. LOVAS, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

TA11. INTERNAL ROTATION IN WATER-N₂O AND WATER-CO₂.....15 min.(11:38)

D. YARON, W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138; and K. I. PETERSON, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island, 02881.

Continued from page 8

The following three late papers appear for the first time in this Abstracts book.

MH11. THE ELECTRONIC AND GEOMETRIC STRUCTURES OF SEVERAL MOLECULAR STATES OF SCANDIUM NITRIDE15 min.(3:46)

KATHRYN L. KUNZE and JAMES F. HARRISON, Department of Chemistry, Michigan State University, East Lansing, Michigan 48824-1322.

MH12. RESONANCE RAMAN SPECTROSCOPY OF THE ALLYL RADICAL15 min.(4:15)

J. D. GETTY, M. J. BURMEISTER, AND P. B. KELLY, Department of Chemistry, University of California, Davis, California 95616.

MH13. RESONANCE RAMAN SPECTROSCOPY OF THE METHYL RADICAL.....15 min.(4:32)

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

TUESDAY, JUNE 13, 1989 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chair Before Intermission: MICHAEL HOKE, Air Force Geophysics Laboratory,
Hanscom Air Force Base, Massachusetts.

Chair After Intermission: WOLFGANG URBAN, University of Bonn, Bonn,
West Germany.

TB1. DECOMP: A FOURIER TRANSFORM SPECTRUM DECOMPOSITION PROGRAM.....15 min.(8:30)

M. C. ABRAMS, Department of Physics, University of California at Berkeley, Berkeley, California, 94720; and J. W. BRAULT, National Solar Observatory, Tucson, Arizona, 85726.

TB2. NEURAL NETWORK COMPUTATIONAL PARADIGMS IN HIGH RESOLUTION SPECTROSCOPY.....15 min.(8:47)

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

TB3. A NEW METHOD FOR COLLECTING DIGITIZED DIODE LASER SPECTRA WHICH PROVIDES A VERY ACCURATE FREQUENCY SCALE.....15 min.(9:04)

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

TB4. C.W. OVERTONE CARBON MONOXIDE LASER EMISSION BETWEEN 2.6 AND 4.0 μm15 min.(9:21)

WOLFGANG URBAN, Institute for Applied Physics, University of Bonn, Bonn, West Germany.

TB5. "ANOMALOUS" RO-VIBRATIONAL INTENSITIES IN THE $\Delta v=1$ BANDS OF SH($X^2\Pi$).....10 min.(9:38)

A. BENIDAR, R. FARRENG, G. GUELACHVILI, Universite de Paris-Sud., Laboratoire d'Infrarouge, Campus d'Orsay, 91405 Orsay, France; and C. CHACKERIAN, JR., NASA-Ames Research Center, Moffett Field, California, 94035.

TB6. DIODE LASER SPECTROSCOPY OF VIBRATIONALLY EXCITED SH⁺.....15 min.(9:50)

S. CIVIS, C. E. BLOM, and P. JENSEN, Physikalisch-Chemisches Institut, Justus Liebig Universität, D-6300 Giessen, Federal Republic of Germany.

Intermission

TB7. PHOTOACOUSTIC MEASUREMENT OF DIFFERENTIAL BROADENING OF THE Λ DOUBLETS IN NO($X^2\Pi_{1/2}$, $v=2-0$) BY Ar.....15 min.(10:25)

A. S. PINE, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

TB8. AIR-, NITROGEN-, AND OXYGEN-BROADENED HALFWIDTH COEFFICIENTS AND PRESSURE-INDUCED LINE SHIFTS IN THE ν_3 FUNDAMENTAL OF $^{13}\text{CH}_4$10 min.(10:42)

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

TB9. TEMPERATURE DEPENDENCE OF COLLISION-INDUCED LINE SHIFTS IN THE ν_4 -FUNDAMENTAL OF $^{12}\text{CH}_4$ AT PLANETARY ATMOSPHERIC TEMPERATURES.....15 min.(10:54)

S. CHUDAMANI and P. VARANASI, Institute for Atmospheric Sciences, State University of New York, Stonybrook, New York, 11794-2300.

TB10. THE CH STRETCHING SPECTRUM OF GASEOUS CYCLOPENTANE-D9:
COUPLING OF STRETCHING AND PSEUDOROTATION.....15 min.(11:11)

E. J. VARIYAR and R. A. MACPHAIL, Department of Chemistry, Duke
University, Durham, North Carolina, 27706.

TB11. PSEUDOROTATIONAL DYNAMICS OF LIQUID CYCLOPENTANE FROM CH
STRETCHING SPECTRA.....15 min.(11:28)

E. J. VARIYAR and R. A. MACPHAIL, Department of Chemistry, Duke
University, Durham, North Carolina, 27706.

ACKNOWLEDGEMENTS

We are indeed very grateful to:

Prof. D. L. COX, Department of Physics, The
Ohio State University, and

Prof. R. M. PITZER, Chairman, Department of
Chemistry, The Ohio State
University

for arranging the Seminar on "Spectroscopy of High
Temperature Superconductors"

It is also a pleasure to acknowledge the time and
effort put in by Prof. R. D. KNIGHT, Vice Chairman,
Department of Physics, The Ohio State University in
organizing the Seminar on "Highly excited States of
Molecular Hydrogen".

Many thanks to Dr. V. MALATHY DEVI, College of
William and Mary, for patiently taking care of the
myriads of details in arranging the papers into the
various sessions.

Finally, we are especially grateful to Prof. C. WELDON
MATHEWS, Vice Chairman, Department of Chemistry, The
Ohio State University, for his incisive comments and
keen interest in all aspects related to this symposium.

TUESDAY, JUNE 13, 1989 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chair Before Intermission: V. F. KALASINSKY, Mississippi State University,
Mississippi State, Mississippi.

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

- TC1. ANALYSIS OF THE ROTATIONAL SPECTRUM OF METHANOL AND ITS ISOTOPIC
VARIANTS TO MICROWAVE ACCURACY.....15 min.(8:30)
T. ANDERSON, E. HERBST, 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.
- TC2. SUBMILLIMETER LASER STARK SPECTROSCOPY OF CD₃OH WITH HCN LASER.....15 min.(8:47)
J. C. SARKER, Department of Electrical Engineering, University of
Idaho, Moscow, Idaho, 83843; G. R. SUDHAKARAN, Department of Physics,
State University of New York at Oswego, Oswego, New York, 13126;
I. MUKHOPADHYAY, Department of Physics, University of British
Columbia, Vancouver, British Columbia, Canada, V6T 2A6; 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.
- TC3. DIRECT MEASUREMENT OF $\Delta J=n$ PROCESSES IN METHYL FLUORIDE.....15 min.(9:04)
H. O. EVERITT and F. C. DE LUCIA, Department of Physics, Duke
University, Durham, North Carolina, 27706.
- TC4. ANALYSIS OF THE ROTATIONAL SPECTRUM OF DIMETHYL ETHER.....15 min.(9:21)
S. L. SHOSTAK, T. M. GOYETTE, T. ANDERSON, E. HERBST, and
F. C. DE LUCIA, Department of Physics, Duke University, Durham,
North Carolina, 27706.
- TC5. ANOMALOUS BEHAVIOUR IN THE ROTATIONAL SPECTRUM OF THE $v_8=2$ AND 3
VIBRATION FOR THE ¹²CH₃¹³C¹⁵N MOLECULE IN THE FREQUENCY RANGE 17-95 GHz.....10 min.(9:38)
M. AL-SHARE, J. A. ROBERTS, University of North Texas, Denton,
Texas, 76204; and H. S. TAM, University of Kansas, Lawrence,
Kansas, 66045.
- TC6. AN IAM THEORY FOR INTERNAL ROTATION IN COMPLETELY ASYMMETRIC MOLECULES.
APPLICATION TO THE ANALYSIS OF THE MICROWAVE SPECTRA OF CH₂DOH AND CHD₂OH...15 min.(9:50)
MUJIAN LIU and C. RICHARD QUADE, Department of Physics, Texas
Tech University, Lubbock, Texas, 79409.
- Intermission
- TC7. MICROWAVE SPECTRUM OF meso-BISOXIRANE.....15 min.(10:25)
C. F. SU, R. L. COOK, Department of Physics and Astronomy,
Mississippi State University, Mississippi State, Mississippi,
39762; S. SUBRAMANIAM, and V. F. KALASINSKY, Department of
Chemistry, Mississippi State University, Mississippi State,
Mississippi, 39762.
- TC8. MICROWAVE SPECTRUM, DIPOLE MOMENT, BARRIER TO INTERNAL ROTATION, AND
MOLECULAR STRUCTURE OF GERMYLAZIDE.....10 min.(10:42)
P. GRONER, J. F. SULLIVAN, and J. R. DURIG, Department of Chemistry,
University of South Carolina, Columbia, South Carolina, 29208.
- TC9. MICROWAVE SPECTRUM, STRUCTURE AND CONFORMATIONAL ANALYSIS OF
CHLOROCYCLOPENTANE.....10 min.(10:54)
M. J. LEE, P. GRONER, and J. R. DURIG, Department of Chemistry,
University of South Carolina, Columbia, South Carolina, 29208.

TC10. RAMAN AND INFRARED SPECTRA, NORMAL COORDINATE CALCULATIONS AND VIBRATIONAL ASSIGNMENT FOR 1,1,1,3,3,3-HEXAFLUORO-2-PROPANIMINE.....10 min.(11:06)

J. R. DURIG, T. G. SHEEHAN, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208; and N. E. LINDSAY, Ford Motor Company, 20000 Rotunda Drive, Dearborn, Michigan, 48121.

TC11. CONFORMATIONAL STABILITY, BARRIERS TO INTERNAL ROTATION, VIBRATIONAL ASSIGNMENT AND AB INITIO CALCULATIONS OF 2-FLUOROPROPENOYL FLUORIDE.....15 min.(11:18)

J. R. DURIG, A. Y. WANG, T. S. LITTLE, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208; P. A. BRLETIC, and J. R. BUCENELL, Department of Chemistry, Washington and Jefferson College, Washington, Pennsylvania, 15301.

TC12. VIBRATIONAL SPECTRA OF SOME SUBSTITUTED VINYLIC COMPOUNDS.....15 min.(11:35)

D. T. DURIG, Department of Chemistry, University of the South, Sewanee, Tennessee, 37375; T. S. LITTLE, J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208; and G. A. GUIRGIS, Mobay Corporation, Dyes and Pigment Division, Analytical and Environmental Department, Charleston, South Carolina, 29411.

45TH MOLECULAR SPECTROSCOPY SYMPOSIUM
JUNE 11-15, 1990

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

A. D. BUCKINGHAM, CAMBRIDGE UNIVERSITY, U. K.

G. T. FRASER, NATIONAL INSTITUTE OF STANDARDS
AND TECHNOLOGY (FORMERLY NBS)

J. L. LISY, UNIVERSITY OF ILLINOIS AT URBANA-
CHAMPAIGN

TUESDAY, JUNE 13, 1989 -- 8:30 A.M.

Room 1008, Evans Chemical Laboratory

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

TD1. INTERATOMIC POTENTIALS FOR VAN DER WAALS COMPLEXES OF GROUP 13 METAL ATOMS WITH RARE GASES.....15 min.(8:30)

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

TD2. LASER VAPORIZATION OF ALLOYS: FLUORESCENCE AND ELECTRONIC STRUCTURE OF AlCu.....15 min.(8:47)

KOESUN PAK, MING-FANG CAI, SHANG-JIH TSAY, THOMAS P. DZUGAN, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and VLADIMIR E. BONDYBEY, Institut für Physikalische und Theoretical Chemie der Technischen Universität München, D-8046 Garching, München, West Germany.

TD3. A LASER INDUCED FLUORESCENCE STUDY OF ELECTRONIC TRANSITIONS OF THE ALUMINUM DIMER.....15 min.(9:04)

MING-FANG CAI, CHRISTOPHER C. CARTER, THOMAS P. DZUGAN, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and VLADIMIR E. BONDYBEY, Institut für Physikalische und Theoretical Chemie der Technischen Universität München, D-8046 Garching, München, West Germany.

TD4. A HIGH RESOLUTION LASER SPECTROSCOPIC STUDY OF ELECTRONIC TRANSITIONS IN METAL DIATOMICS.....15 min.(9:21)

CHRISTOPHER C. CARTER, MING-FANG CAI, THOMAS P. DZUGAN, SHANG-JIH TSAY, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and VLADIMIR E. BONDYBEY, Institut für Physikalische und Theoretical Chemie der Technischen Universität München, D-8046 Garching, München, West Germany.

TD5. PERMANENT ELECTRIC DIPOLE MOMENT MEASUREMENTS OF TRANSITION METAL OXIDES...15 min.(9:38)

J. E. SHIRLEY, D. F. NACHMAN, and T. C. STEIMLE, Department of Chemistry, Arizona State University, Tempe, Arizona, 85287.

TD6. EXAMINATION OF SOME NEW SINGLET TRANSITIONS IN Li_215 min.(9:55)

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

Intermission

TD7. SPECTROSCOPY OF RARE EARTH OXIDES: RECENT OBSERVATIONS.....15 min.(10:30)

GUO BUJIN, C. H. CHENG, and C. LINTON, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada, E3B 5A3.

TD8. HIGH RESOLUTION SPECTROSCOPY AND PHOTOPHYSICS OF TRANSITION METAL CONTAINING DIATOMIC MOLECULES: THE VISIBLE SPECTRUM OF VANADIUM NITRIDE.....15 min.(10:47)

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

- TD9. HIGH RESOLUTION SPECTROSCOPY AND PHOTOPHYSICS OF TRANSITION METAL CONTAINING DIATOMIC MOLECULES: THE $C^4\Sigma^- - X^4\Sigma^-$ SYSTEM OF NIOBIUM SULPHIDE.....15 min.(11:04)
- B. SIMARD and P. A. HACKETT, Laser Chemistry Group, Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.
- TD10. THE ELECTRONIC SPECTRUM OF GAS-PHASE Nb_2 5 min.(11:21)
- S. A. MITCHELL, C. L. CALLENDER, and P. A. HACKETT, Laser Chemistry Group, Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.
- TD11. VIBRONIC SPECTROSCOPY AND DYNAMICS IN THE JET-COOLED SILVER TRIMER.....15 min.(11:28)
- P. Y. CHENG and M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, Georgia, 30602.
- TD12. DETERMINING DIATOM DISSOCIATION LIMITS AND LONG-RANGE POTENTIAL COEFFICIENTS FROM DIRECT FITS TO VIBRATIONAL ENERGIES AND ROTATIONAL CONSTANTS.....Late Paper.....15 min.(11:45)
- Mark R. Davies and Robert J. Le Roy, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L3G1, Canada.

**TD12 appears for the first time in this
Book of Abstracts**

TUESDAY, JUNE 13, 1989 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chair Before Intermission: LINDA BROWN, Jet Propulsion Laboratory, California
Institute of Technology, Pasadena, California.

Chair After Intermission: R. L. HAWKINS, Air Force Geophysics Laboratory,
Hanscom Air Force Base, Massachusetts.

TE1. FTIR SPECTROSCOPY OF AEROSOLS.....15 min.(1:30)

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

TE2. INFRARED INTENSITY ANALYSIS: APPLICATION TO THE SPECTRA OF
MATRIX-ISOLATED THIOURACILS.....15 min.(1:47)

WILLIS B. PERSON, K. KUBULAT, K. SZCZEPANIAK, Department of
Chemistry, University of Florida, Gainesville, Florida, 32611;
and J. R. LESZCZYNSKI, Department of Chemistry, University of
Alabama, Birmingham, Alabama, 35294.

TE3. INTENSITIES OF ASYMMETRIC SPECIES BANDS AND HERMAN-WALLIS FACTORS FOR
CARBON DIOXIDE CALCULATED BY DIRECT NUMERICAL DIAGONALIZATION.....15 min.(2:04)

R. B. WATTSON, A. NEWBURGH, G. GALICA, 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, 01731.

TE4. REDUCING BACKGROUND EFFECTS IN NONLINEAR LEAST-SQUARES LINE INTENSITY
ESTIMATES.....10 min.(2:21)

R. L. HAWKINS, Infrared Physics Branch, Optical Physics Division,
Air Force Geophysics Laboratory, Hanscom Air Force Base,
Massachusetts, 01731.

TE5. TEMPERATURE DEPENDENT MEASUREMENTS AND MODELING OF ABSORPTION BY
CO₂-N₂ MIXTURES IN THE FAR WING OF THE 4.3 μm CO₂ BAND.....10 min.(2:33)

M. Y. PERRIN, J. M. HARTMANN, and L. ROSENMANN, Laboratoire E.M.2.C
du CNRS(UPR 73) et de l'Ecole Centrale des Arts et Manufactures,
Ecole Centrale, Grande voie des Vignes, 92295 Chatenay-Malabry, France.

TE6. LINE POSITIONS OF HIGH TEMPERATURE CO₂ IN THE 15 μm REGION.....10 min.(2:45)

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.

TE7. MOLECULAR CONSTANTS AND INTENSITIES OF CARBON DIOXIDE BANDS IN THE 2395 TO
2760 CM⁻¹ SPECTRAL REGION.....10 min.(2:57)

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

Intermission

TE8. MOLECULAR PARAMETERS FOR CARBON DIOXIDE BANDS IN THE 1820-2050 CM⁻¹
SPECTRAL REGION.....10 min.(3:25)

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

- TE9. THE $^{16}\text{O}_3$ ABSORPTION SPECTRUM NEAR $3.3 \mu\text{m}$10 min.(3:37)
J.-M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et 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; V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; and A. BARBE, Groupe de Spectrométrie Moléculaire et Atmosphérique, Faculté des Sciences, 51062 Reims, France.
- TE10. IMPROVED LINE PARAMETERS FOR OZONE BANDS IN THE 4.8 AND $10 \mu\text{m}$ SPECTRAL REGIONS.....15 min.(3:49)
C. P. RINSLAND, M.A.H. SMITH, Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225; V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; J.-M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris, France; and A. GOLDMAN, Department of Physics, University of Denver, Denver, Colorado, 80208.
- TE11. MEASUREMENTS OF SELF-BROADENING OF OZONE.....10 min.(4:06)
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.
- TE12. NEW MEASUREMENTS AND ANALYSIS OF H_2^{16}O , H_2^{17}O , AND H_2^{18}O IN THE $6.2 \mu\text{m}$ REGION.....15 min.(4:18)
R. A. TOTH, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.
- TE13. THE SPECTRUM OF H_2^{16}O BETWEEN 9500 AND 11500 cm^{-1}10 min.(4:35)
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.
- TE14. LOW-TEMPERATURE TUNABLE DIODE LASER MEASUREMENTS OF LINE POSITIONS, INTENSITIES, AND AIR-BROADENING COEFFICIENTS IN THE HNO_3 $7.5 \mu\text{m}$ BAND.....15 min.(4:47)
R. D. MAY and C. R. WEBSTER, Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-301, Pasadena, California, 91109.
- TE15. FAR INFRARED FT SPECTROSCOPY OF CHF_3Late Paper.....15 min.(5:02)
Jochen Fries, Dieter Hausmann, and Volker Tank, Institute of Optoelectronics, German Aerospace, Research Est., D-8031 Oberpfaffenhofen, FRG.

TE15 appears for the first time in this
 Book of Abstracts

TUESDAY, JUNE 13, 1989 -- 1:30 P.M.

Room 1009, Physics Department

Chair Before Intermission: HAI-LUNG DAI, University of Pennsylvania,
Philadelphia, Pennsylvania.

Chair After Intermission: R. L. KUCZKOWSKI, University of Michigan,
Ann Arbor, Michigan.

TF1. MICROWAVE AND INFRARED ELECTRIC-RESONANCE OPTOTHERMAL SPECTROSCOPY OF
HF-HCl AND HCl-HF.....15 min.(1:30)

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

TF2. ClO DIMER, ITS ROTATIONAL SPECTRUM, STRUCTURE, AND ATMOSPHERIC IMPORTANCE...15 min.(1:47)

M. BIRK, R. R. FRIEDL, E. A. COHEN, H. M. PICKETT, and S. P. SANDER,
Jet Propulsion Laboratory, California Institute of Technology,
Pasadena, California, 91109.

TF3. VAN DER WAALS COMPLEXES OF CHEMICALLY REACTIVE GASES: OZONE-ACETYLENE.....15 min.(2:04)

J. Z. GILLIES, C. W. GILLIES, Department of Chemistry, Rensselaer
Polytechnic Institute, Troy, New York, 12180; F. J. LOVAS,
K. MATSUMURA, and R. D. SUENRAM, Molecular Spectroscopy Division,
National Institute of Standards and Technology, Gaithersburg,
Maryland, 20899.

TF4. ROTATIONAL SPECTRA AND STRUCTURE OF ETHYLENE-OZONE COMPLEX.....15 min.(2:21)

J. Z. GILLIES, C. W. GILLIES, Department of Chemistry, Rensselaer
Polytechnic Institute, Troy, New York, 12180; R. D. SUENRAM,
F. J. LOVAS, Molecular Spectroscopy Division, National Institute of
Standards and Technology, Gaithersburg, Maryland, 20899; and
W. STAHL, Institut für Physikalische Chemie, Universität Kiel,
230 Kiel, Germany.

TF5. THE MICROWAVE SPECTRA OF THE ETHYLENE-SO₂ AND BENZENE-SO₂ DIMERS.....15 min.(2:38)

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

TF6. THE MICROWAVE SPECTRA OF THE TRIMETHYLAMINE-SO₂ AND PYRIDINE-SO₂ DIMERS.....15 min.(2:55)

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

Intermission

TF7. SPECTROSCOPIC DETERMINATION OF THREE STABLE ISOMERS OF THE MIXED BINARY
COMPLEX N₂O-HCN.....15 min.(3:30)

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

TF8. THE EFFECTS OF NON-RIGIDITY ON THE HYPERFINE STRUCTURE OF (C₂D₂)₂.....15 min.(3:47)

L. H. COUDERT, Molecular Spectroscopy Division, National Institute
of Standards and Technology, Gaithersburg, Maryland, 20899.

TF9. THE ISOMERIC STRUCTURES AND VAN DER WAALS VIBRATIONAL FREQUENCIES OF
(GLYOXAL)_n·(Ar)_m COMPLEXES.....15 min.(4:04)

LUC LAPIERRE, DONALD FRYE, and HAI-LUNG DAI, Department of Chemistry,
University of Pennsylvania, Philadelphia, Pennsylvania, 19104.

TF10. A PAIR-POTENTIAL MODEL FOR THE STRUCTURES AND VAN DER WAALS VIBRATIONAL
FREQUENCIES OF GLYOXAL•Ar_n COMPLEXES.....15 min.(4:21)

DONALD FRYE, LUC LAPIERRE, and HAI-LUNG DAI, Department of Chemistry,
University of Pennsylvania, Philadelphia, Pennsylvania, 19104.

TF11. ELECTRONIC STRUCTURE VIA SIMULATED ANNEALING TECHNIQUES: SOLVENT SHIFTS OF
GUEST ATOM TRANSITION FREQUENCIES IN RARE GAS CLUSTERS.....10 min.(4:38)

CHIACHIN TSOO and SHERWIN J. SINGER, Department of Chemistry,
The Ohio State University, Columbus, Ohio, 43210.

TF12. AI IONIZATION POTENTIALS FROM EFFECTIVE POTENTIAL QMC WITH CORE
POLARIZATION.....15 min.(4:50)

P. A. CHRISTIANSEN, Department of Chemistry, Clarkson University,
Potsdam, New York, 13676.

TUESDAY, JUNE 13, 1989 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chair: BRENDA WINNEWISSER, Justus-Liebig Universitat, Giessen, West Germany.

TG1. OBSERVATION OF FINE STRUCTURE IN THE $Q_{1+0}(1)$ TRANSITION OF ORTHOHYDROGEN IMPURITY IN SOLID PARAHYDROGEN.....15 min.(1:30)

MAN-CHOR CHAN, BRENT D. REHFUSS, TAKESHI OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637; and MITCHIO OKUMURA, Division of Chemistry, California Institute of Technology, Pasadena, California, 91125.

TG2. INFRARED STUDIES OF HD AND D₂ IMPURITIES IN SOLID PARAHYDROGEN.....15 min.(1:47)

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

TG3. OBSERVATION OF THE ν_3 AND ν_4 FUNDAMENTALS OF METHANE IMPURITY EMBEDDED IN SOLID PARAHYDROGEN.....15 min.(2:04)

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

TG4. INFRARED TRANSITIONS IN SOLID HYDROGEN INDUCED BY THE BOMBARDMENT OF 3 MeV ELECTRON BEAM.....15 min.(2:21)

MAN-CHOR CHAN, TAKESHI OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637; and MITCHIO OKUMURA, Division of Chemistry, California Institute of Technology, Pasadena, California, 91125.

TG5. PREDICTED INTENSITIES FOR NEW RAMAN TRANSITIONS IN SOLID HD.....15 min.(2:38)

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

TG6. INTENSITIES OF R_v(0) TRANSITIONS IN SOLID HD.....15 min.(2:55)

R. H. TIPPING, Department of Physics, University of Alabama, Tuscaloosa, Alabama, 35487-0324; J. D. POLL, Department of Physics, University of Guelph, Guelph, Ontario, Canada, N1G 2W1; S. Y. LEE, Applied Optics Laboratory, Korea Advanced Institute of Science and Technology, Cheongryang, Seoul, South Korea; S-i. LEE, Department of Physics, Pohang Science and Technology Institute, Pohang, South Korea; T. W. NOH, LASSP, Cornell University, Ithaca, New York, 14853; and J. R. GAINES, Department of Physics, University of Hawaii at Manoa, Honolulu, Hawaii, 96822.

TG7. INFRARED SPECTRA OF HYDROGEN DIMERS.....15 min.(3:12)

A.R.W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

TG8. IMPROVED POTENTIAL ENERGY SURFACES FOR THE INTERACTION OF H₂ WITH Ar.....Late Paper.....15 min.(3:29)

Claudio Chuagui and Robert J. Le Roy, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L3G1, Canada.

**TG8 appears for the first time in this
Book of Abstracts**

TUESDAY, JUNE 13, 1989 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chair Before Intermission: E. RIEDLE, Universität München,
West Germany.

Chair After Intermission: LEIGH B. CLARK, University of California at
San Diego, La Jolla, California.

TH1. STIMULATED EMISSION SPECTROSCOPY OF SINGLET CH₂: THE BENDING BARRIER
HEIGHT AND THE \tilde{a} - \tilde{b} SPLITTING.....15 min.(1:30)

WEI XIE, CARMEL HARKIN, and HAI-LUNG DAI, Department of Chemistry,
University of Pennsylvania, Philadelphia, Pennsylvania, 19104.

TH2. AN ISOTOPIC SUBSTITUTION TEST FOR ORBITING H ATOMS IN VIBRATIONALLY HIGHLY
EXCITED $\tilde{X} \ ^1\Sigma_g^+$ ACETYLENE.....15 min.(1:47)

YIT-TSONG CHEN J. K. LUNDBERG, R. W. FIELD, Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts,
02139; J. P. PIQUE, Laboratoire de Spectrometrie Physique,
Universite Scientifique et Medicale de Grenoble, Grenoble, France;
and Y. CHEN, Department of Chemistry, University of Southern
California, Los Angeles, California, 90089-0482.

TH3. U.V. OPTICAL DOUBLE RESONANCE STUDY OF THE PREDISSOCIATED $\tilde{C} \ ^1A_g$ STATE
OF ACETYLENE.....15 min.(2:04)

J. K. LUNDBERG, R. W. FIELD, Department of Chemistry, Massachusetts
Institute of Technology, Cambridge, Massachusetts, 02139; J. P. PIQUE,
Laboratoire de Spectrometrie Physique, Universite Scientifique et
Medicale de Grenoble, Grenoble, France; and Y. CHEN, Department of
Chemistry, University of Southern California, Los Angeles, California,
90089-0482.

TH4. THE FIRST SINGLET ELECTRONIC STATE IN ACETYLENE.....15 min.(2:21)

T. R. HUET and M. HERMAN, Laboratoire de Chimie Physique Moléculaire,
CP. 160, Université Libre de Bruxelles, 1050 Brussels, Belgium.

TH5. THE BENDING VIBRAITONAL LEVELS IN C₂D₂.....10 min.(2:38)

T. R. HUET, M. HERMAN, Laboratoire de Chimie Physique Moléculaire,
CP. 160, Université Libre de Bruxelles, 1050 Brussels, Belgium; and
J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research
Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

Intermission

TH6. ROTATIONAL ANALYSIS OF LASER INDUCED FLUORESCENCE SPECTRA OF ArOH AND ArOD..15 min.(3:05)

WAFAA M. FAWZY, Department of Chemistry, Brookhaven National
Laboratory, Upton, New York, 11973.

TH7. ELECTRONIC SPECTRA OF ArOH/ArOD AND CHARGE TRANSFER.....15 min.(3:22)

WAFAA M. FAWZY, Department of Chemistry, Brookhaven National
Laboratory, Upton, New York, 11973; and M. C. HEAVEN, Department
of Chemistry, Emory University, Atlanta, Georgia, 30324.

TH8. ZERO FIELD LEVEL CROSSING IN THE CLEMENTS E BAND OF SO₂.....15 min.(3:39)

J. S. MUENTER, Department of Chemistry, University of Rochester,
Rochester, New York, 14627; and JOHN DEUTSCH, Department of
Chemistry, State University of New York at Geneseo, Geneseo,
New York, 14454.

TH9. FLUORESCENCE EXCITATION SPECTRUM OF CCl_2 IN A SUPERSONIC FREE JET.....15 min.(3:56)

J.-I. CHOE, S. TANNER, and M. D. HARMONY, Department of
Chemistry, University of Kansas, Lawrence, Kansas, 66045.

TH10. THE HIGH RESOLUTION ABSORPTION SPECTRUM OF THE HCN_2 FREE RADICAL.....15 min.(4:13)

B. R. SWEETING and C. W. MATHEWS, Department of Chemistry, The
Ohio State University, Columbus, Ohio, 43210.

TH11. SF_2 OBSERVED FROM 280 TO 500 NM BY RESONANCE ENHANCED MULTIPHOTON
IONIZATION SPECTROSCOPY.....Late Paper.....15 min.(4:30)

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

**TH11 appears for the first time in this
Book of Abstracts**

WEDNESDAY, JUNE 14, 1989 -- 8:45 A.M.

Auditorium, Independence Hall

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

Plenary Session

WA1. HIGH RESOLUTION DOUBLE RESONANCE SPECTROSCOPY OF
MOLECULES AND SMALL CLUSTERS 35 min.

WOLFGANG E. ERNST, Freie Universität Berlin
Fachbereich Physik, Institut für Molekülphysik
Arnimallee 14, D-1000 Berlin 33, West Germany

WA2. INTRINSICALLY UNASSIGNABLE VIBRATIONAL SPECTRA: SEP,
STATISTICS, AND DYNAMICS 35 min.

ROBERT W. FIELD, Massachusetts Institute of Technology,
Department of Chemistry, Cambridge, Massachusetts 02139

Intermission

WA3. THE EXCITED ELECTRONIC STATE STRUCTURE OF THE LITHIUM DIMER . . . 35 min.

ROBERT A. BERNHEIM, The Pennsylvania State University,
Department of Chemistry, 152 Davey Laboratory
University Park, Pennsylvania 16802

WA4. MANIFESTATIONS OF CHANNEL INTERACTIONS IN SPECTRA
OF MOLECULAR HYDROGEN* 35 min.

CH. JUNGEN, Laboratoire de Photophysique
Moléculaire du CNRS, Université de Paris-Sud, 91405
Orsay Cedex, France

* This talk by Dr. CH. JUNGEN introduces the "Seminar on Highly Excited States of Molecular Hydrogen"

WEDNESDAY, JUNE 14, 1989 -- 1:00 P.M.

Room 1153, Physics Laboratory

SEMINAR ON SPECTROSCOPY OF HIGH TEMPERATURE SUPERCONDUCTORS

INVITED PAPERS

Chair Before Intermission: R. M. PITZER, The Ohio State University,
Columbus, Ohio.

Chair After Intermission: D. L. COX, The Ohio State University,
Columbus, Ohio.

WE1. ELECTRONIC STRUCTURE AND MECHANISM FOR HIGH T_c SUPERCONDUCTORS..25 min.(1:00)

WILLIAM A. GODDARD, Division of Chemistry and Chemical
Engineering, California Institute of Technology,
Pasadena, California, 91109.

WE2. ON THE PHOTOEMISSION SPECTRUM AND OPTICAL GAP IN La_2CuO_425 min.(1:30)

RICHARD L. MARTIN, Los Alamos National Laboratory,
P.O. Box 1663, Los Alamos, New Mexico, 87545.

WE3. BAND-LIKE ELECTRONIC STRUCTURE AND FERMI EDGE OF $YBa_2Cu_3O_{6.9}$
SINGLE CRYSTALS AS DETERMINED BY PHOTOEMISSION SPECTROSCOPY.....25 min.(2:00)

A. J. ARKO, Los Alamos National Laboratory, P-10 Group,
Los Alamos, New Mexico, 87545.

WE4. THE SPECTROSCOPY OF HIGH TEMPERATURE SUPERCONDUCTORS.....25 min.(2:30)

NICHOLAS W. WINTER, Lawrence Livermore National
Laboratory, P.O. Box 808, Livermore, California, 94550.

Intermission

WE5. MANY-BODY HAMILTONIAN PARAMETERS AND SPECTROSCOPY OF La_2CuO_4 25 min.(3:15)

R. M. MARTIN, Department of Physics, University of
Illinois, Urbana, Illinois, 61801.

WE6. PHOTOEMISSION AND CORE-LEVEL SPECTROSCOPY OF HIGH TEMPERATURE
SUPERCONDUCTORS.....25 min.(3:45)

JÜNGEN FINK, Kernforschungszentrum Karlsruhe, Institut
für Nukleare Festkörperphysik, D-7500 Karlsruhe,
Federal Republic of Germany.

WE7. ABSORPTION AND PHOTOINDUCED ABSORPTION STUDIES OF
SEMICONDUCTING $YBa_2Cu_3O_{7-\delta}$25 min.(4:15)

R. P. MCCALL, Department of Physics, The Ohio State
University, Columbus, Ohio, 43210.

Research collaborators of the seminar speakers will be
identified during the conference.

WEDNESDAY, JUNE 14, 1989 -- 1:30 P.M.

Room 1009, Physics Department

Chair Before Intermission: G. GRANER, Universite de Paris-Sud,
ORSAY, France

Chair After Intermission: D. S. PERRY, University of Akron,
Akron, Ohio.

WF1. MOLECULAR STRUCTURE, FORCE FIELD, AND CORIOLIS INTERACTION OF HBO.....15 min.(1:30)

Y. KAWASHIMA, Kanagawa Institute of Technology, 1030 Shimo-ogino,
Atsugi, Kanagawa 243-02, Japan; Y. ENDO, College of General
Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153,
Japan; K. KAWAGUCHI, T. SUZUKI, M. FUJITAKE, and E. HIROTA,
Institute for Molecular Science, Okazaki, 444, Japan.

WF2. DIODE LASER SPECTROSCOPY OF METAL OXIDES IN LOW PRESSURE FLAMES.....15 min.(1:47)

H. G. HEDDERICH and C. E. BLOM, Physikalisch-Chemisches Institut,
Justus Liebig Universität, D-6300 Giessen, Federal Republic of
Germany.

WF3. THE INFRARED SPECTRUM OF THE LiO RADICAL.....10 min.(2:04)

CHIKASHI YAMADA and EIZI HIROTA, Institute for Molecular Science,
Okazaki 444, Japan.

WF4. LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF NCS IN A FREE JET EXPANSION.....15 min.(2:16)

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

WF5. THE INFRARED SPECTRUM OF THE ETHYL RADICAL AROUND 18.9 μm10 min.(2:33)

TREVOR J. SEARS, Department of Chemistry, Brookhaven National
Laboratory, Upton, New York, 11973; and JOAN M. FRYE, Department
of Chemistry, Argonne National Laboratory, Argonne, Illinois, 60439.

WF6. INFRARED SPECTRUM OF $\text{SiH}_2 \nu_2$ BAND BY DIODE LASER KINETIC SPECTROSCOPY.....15 min.(2:45)

CHIKASHI YAMADA, EIZI HIROTA, Institute for Molecular Science,
Okazaki 444, Japan; HIDETO KANAMORI, The University of Tokyo,
Komaba, Japan; NOBUKI NISHIWAKI, NAOSHI ITABASHI, KOZO KATO,
and TOSHIO GOTO, Nagoya University, Nagoya 460, Japan.

WF7. DETERMINATION OF REACTION RATE AND DIFFUSION CONSTANTS OF THE SiH_3
RADICAL IN SILANE PLASMAS.....15 min.(3:02)

CHIKASHI YAMADA, EIZI HIROTA, Institute for Molecular Science,
Okazaki 444, Japan; NAOSHI ITABASHI, KOZO KATO, NOBUKI NISHIWAKI,
and TOSHIO GOTO, Nagoya University, Nagoya 460, Japan.

Intermission

WF8. INFRARED SPECTROSCOPY OF LARGE CO_2 CLUSTERS.....15 min.(3:30)

R. DISSELKAMP and G. E. EWING, Department of Chemistry, Indiana
University, Bloomington, Indiana, 47405.

WF9. VIBRATION-TUNNELING ENERGY LEVELS OF $(\text{HF})_2$ FROM CLOSE-COUPLING CALCULATIONS
ON AN AB INITIO POTENTIAL SURFACE.....15 min.(3:47)

M. D. MARSHALL, Department of Chemistry, Amherst College, Amherst,
Massachusetts, 01002; P. R. BUNKER, P. C. GOMEZ, Herzberg Institute
of Astrophysics, National Research Council of Canada, Ottawa, Ontario,
Canada, K1A 0R6; M. KOFRANEK, H. LISCHKA, and A. KARPEN, Institut
für Theoretische Chemie und Strahlenchemie der Universität Wien,
Währingerstrasse 17, A-1090 Wien, Austria.

WF10. AN AB INITIO SEMIRIGID BENDER CALCULATION OF THE ROTATION AND TRANS-TUNNELLING SPECTRA OF (HF)₂ AND (DF)₂.....15 min.(4:04)

P. R. BUNER, P. C. GOMEZ, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6; M. D. MARSHALL, Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002; M. KOFRANEK, H. LISCHKA, and A. KARPFEN, Institut für Theoretische Chemie and Strahlenchemie der Universität Wien, Währingerstrasse 17, A-1090 Wien, Austria.

WF11. A CALCULATION OF THE ROTATION-TORSION ENERGY LEVELS OF (HF)₂ AND (DF)₂.....15 min.(4:21)

P. R. BUNKER, P. C. GOMEZ, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6; M. D. MARSHALL, Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002; M. KOFRANEK, H. LISCHKA, and A. KARPFEN, Institut für Theoretische Chemie and Strahlenchemie der Universität Wien, Währingerstrasse 17, A-1090 Wien, Austria.

WF12. INVERSION-ROTATION SPECTRUM OF HF DIMER.....15 min.(4:38)

S. P. BELOV, E. N. KARYAKIN, I. N. KOZIN, A. F. KRUPNOV, O. L. POLYANSKY, M. YU. TRETYAKOV, N. F. ZOBOV, Institute of Applied Physics, Academy of Sciences of the USSR, Gorky, USSR; R. D. SUENRAM, and W. J. LAFFERTY, Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

WF13. STATE-TO-STATE VIBRATIONAL PREDISSOCIATION.....15 min.(4:55)

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

WEDNESDAY, JUNE 14, 1989 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chair: JAMES COE, The Ohio State University, Columbus, Ohio.

WG1. THE QUADRATIC VIBRATIONAL FORCE FIELD OF n-BUTANE.....15 min.(1:30)

W. F. MURPHY, Division of Chemistry, National Research Council of
Canada, Ottawa, Ontario, Canada, K1A 0R6.

WG2. AB INITIO MOLECULAR ORBITAL CALCULATIONS OF THE INFRARED SPECTRUM OF THE
HYDROXYLAMINE DIMER.....15 min.(1:47)

G. A. YEO and T. A. FORD, Department of Chemistry, University of the
Witwatersrand, Johannesburg, Wits 2050, South Africa.

WG3. VIBRATIONAL SPECTRA OF 1-FLUOROCYCLOBUTENE.....10 min.(2:04)

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

WG4. REVISED VIBRATIONAL ASSIGNMENT FOR CYCLOBUTENE.....10 min.(2:16)

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

WG5. FERMI RESONANCE ANALYSIS OF VIBRATIONAL OVERTONE SPECTRUM OF PYRROLE.....15 min.(2:28)

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

WG6. ANALYSIS OF THE VIBRATIONAL BANDS OF ELECTRONICALLY EXCITED ArHO
AND ArDO.....15 min.(2:45)

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

(THIS PAPER WAS ORIGINALLY SCHEDULED AS MG4 AND SO THE ABSTRACT
APPEARS AS MG4 ON PAGE 59).

A 10 min. break is
planned between
sessions WG and WG'

WEDNESDAY, JUNE 14, 1989 -- 3:00 P.M.

Room 1005, Physics Laboratory

Chair: JAMES COE, The Ohio State University, Columbus, Ohio.

WG'1. ELECTRONIC TRANSITION MOMENT DIRECTIONS IN BIPHENYLENE.....10 min. (3:10)

ROBERT HERCZEGH and LEIGH B. CLARK, Department of Chemistry,
University of California at San Diego, La Jolla, California,
92093-0342.

WG'2. POLARIZED VACUUM UV SPECTRA OF CRYSTALLINE UREA.....10 min. (3:22)

BLAIR F. CAMPBELL, Rocketdyne Division, Rockwell International
Corporation, 6633 Canoga Avenue, Canoga Park, California, 91303;
and LEIGH B. CLARK, Department of Chemistry, University of
California at San Diego, La Jolla, California, 92093-0342.

WG'3. PRERESONANCE RAMAN EXCITATION PROFILES: COMPARISON WITH MORE DIRECT
PROBES OF DIPOLE-FORBIDDEN EXCITED ELECTRONIC STATES.....15 min. (3:34)

I. SZTAINBUCH and G. E. LEROI, Department of Chemistry and the
Laser Laboratory, Michigan State University, East Lansing,
Michigan, 48824-1322.

WG'4. TWO-PHOTON EXCITATION SPECTRUM OF PERYLENE IN SOLUTION.....15 min. (3:51)

JEONG-A YU, DANIEL G. NOCERA, and GEORGE E. LEROI, Department of
Chemistry and the Laser Laboratory, Michigan State University,
East Lansing, Michigan, 48824-1322.

WG'5. SPECTROSCOPY OF [2,2]PARACYCLOPHANE COMPLEXES WITH BENZENE.....15 min. (4:08)

JEONG-A YU, GEORGE E. LEROI, and DANIEL G. NOCERA, Department of
Chemistry and the Laser Laboratory, Michigan State University,
East Lansing, Michigan, 48824-1322.

WG'6. PRESSURE EFFECT ON THE ZERO-FIELD SPLITTINGS OF AROMATIC TRIPLETS.....15 min. (4:25)

I. Y. CHAN and XIUQI QIAN, Department of Chemistry, Brandeis
University, Waltham, Massachusetts, 02254-9110.

WG'7. PRESSURE EFFECT ON ZERO-FIELD SPLITTINGS IN TRIPLET CARBONYLS:
 $\pi\pi^*-\pi\pi^*$ COUPLING.....15 min. (4:42)

I. Y. CHAN and XIUQI QIAN, Department of Chemistry, Brandeis
University, Waltham, Massachusetts, 02254-9110.

WG'8. SOLVENT RELAXATION EFFECTS ON THE LUMINESCENCE PROPERTIES OF
7-HYDROXYFLAVONE:-STEADY STATE AND TIME RESOLVED STUDIES.....15 min. (4:59)

MUNNA SARKAR and P. K. SENGUPTA, Nuclear Chemistry Division, Saha
Institute of Nuclear Physics, 1/AF Bidhannagar, Calcutta 700 064,
India.

THURSDAY, JUNE 15, 1989 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chair: CHIKASHI YAMADA, Institute for Molecular Science, Okazaki, Japan.

- RA1. INFRARED LASER ABSORPTION SPECTROSCOPY OF FAST ION BEAMS: DETERMINATION OF ABSOLUTE ABSORPTION CROSS SECTIONS OF MOLECULAR IONS.....15 min.(8:30)
- J. V. COE, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; E. R. KEIM, J. C. OWRUTSKY, N. V. AGMAN, and R. J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720.
- RA2. ASSIGNMENT OF THE $2\nu_2$ BAND OF THE H_3^+ ION IN EMISSION.....20 min.(8:47)
- W. A. MAJEWSKI, P. A. FELDMAN, J.K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6; S. MILLER, and J. TENNYSON, Department of Physics and Astronomy, University College London, London WC1E 6BT, England.
- RA3. INFRARED STUDIES ON VIBRATIONALLY EXCITED H_3^+15 min.(9:09)
- LI WEI XU, BRENT D. REHFUSS, CHARLES GABRYS, T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637; and MOUNGI BAWENDI, AT&T Bell Laboratories, Murray Hill, New Jersey, 07974.
- RA4. MICROWAVE SPECTRA OF THE HD^+ AND D_2^+ IONS AT THEIR DISSOCIATION LIMITS.....15 min.(9:26)
- ALAN CARRINGTON, IAIN R. MCNAB, CHRISTINE A. MONTGOMERIE, Department of Chemistry, Southampton University, Southampton SO9 5NH, United Kingdom; and JOHN M. BROWN, Physical Chemistry Laboratories, Oxford OX1 3QZ, United Kingdom.
- RA5. OBSERVATION OF HIGHLY EXCITED VIBRATIONAL STATES OF $X^3\Sigma^-OH^+$15 min.(9:43)
- B. D. REHFUSS, M.-F. JAGOD, L.-W. XU, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637.
- RA6. OBSERVATION OF HIGHLY EXCITED STATES OF PROTONATED NITROGEN, N_2H^+15 min.(10:00)
- B. D. REHFUSS, L.-W. XU, and T. OKA, Department of Chemistry and Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637.
- Intermission
- RA7. THE INTERNAL ROTATION SPLITTINGS IN $C_2H_3^+$15 min.(10:30)
- P. R. BUNKER and P. C. GOMEZ, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.
- RA8. THE LABORATORY DETECTION OF H_2COH^+15 min.(10:47)
- T. AMANO and H. E. WARNER, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.
- RA9. INFRARED SPECTROSCOPY OF AN H_2/O_2 DISCHARGE: I - THE H_3O^+ ION.....15 min.(11:04)
- W. C. HO, C. J. PURSELL, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637.
- RA10. INFRARED SPECTROSCOPY OF AN H_2/O_2 DISCHARGE: II - THE H_2O^+ ION.....15 min.(11:21)
- C. J. PURSELL, W. C. HO, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois, 60637.

RA11. THE INFRARED DETECTION OF HOSi^+ AND DOSi^+15 min.(11:38)

H. E. WARNER, T. AMANO, N. MOAZZEN-AHMADI, A.R.W. MCKELLAR,
Herzberg Institute of Astrophysics, National Research Council of
Canada, Ottawa, Ontario, Canada, K1A 0R6; A. FOX, and D. BOHME,
Department of Chemistry, York University, North York, Ontario,
Canada, M3J 1P3.

THURSDAY, JUNE 15, 1989 -- 8:30 A.M.

Room 1009, Physics Laboratory

SEMINAR ON HIGHLY EXCITED STATES OF MOLECULAR HYDROGEN
(Invited Papers)

Chair: R. D. KNIGHT, The Ohio State University, Columbus, Ohio.

- RB1. NEW MEASUREMENTS OF THE IONIZATION POTENTIAL AND
DISSOCIATION ENERGY OF H₂.....30 min.(8:30)

E. E. EYLER, E. McCORMACK, and J. M. GILLIGAN, Department
of Physics, Yale University, New Haven, Connecticut,
06511-8167.

- RB2. DISSOCIATION AND IONIZATION OF EXCITED STATES OF H₂.....30 min.(9:05)

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

- RB3. UNDERSTANDING HIGH-L STATES OF H₂: EXPERIMENT AND THE
POLARIZATION MODEL.....30 min.(9:40)

S. R. LUNDEEN, Department of Physics, University of Notre
Dame, Notre Dame, Indiana, 46556.

INTERMISSION

- RB4. LASER STUDIES OF AUTOIONIZATION PROCESSES IN MOLECULAR
HYDROGEN.....30 min.(10:35)

S. T. PRATT, P. M. DEHMER, J. L. DEHMER, F. S. TOMKINS,
Argonne National Laboratory, Argonne, Illinois, 60439;
and M. A. O'HALLORAN, Department of Physics and Astronomy,
University of Oklahoma, Norman, Oklahoma, 73019.

- RB5. ROTATIONAL AND VIBRATIONAL DISTRIBUTIONS IN RESONANCE ENHANCED
MULTIPHOTON IONIZATION OF MOLECULES..... 30 min.(11:10)

V. McKOY, M. BRAUNSTEIN, H. RUDOLPH, J. A. STEPHENS,
Noyes Laboratory of Chemical Physics, California Institute
of Technology, Pasadena, California, 91125; S. N. DIXIT,
Lawrence Livermore National Laboratory, L-446, Livermore,
California, 94550; and D. L. LYNCH, Department of
Chemistry, University of Nevada, Reno, Nevada, 89557.

THURSDAY, JUNE 15, 1989 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chair: ERNEST DORKO, Air Force Weapons Laboratory, Albuquerque, New Mexico.

RC1. PREDISSOCIATION LINE WIDTHS OF THE SCHUMANN-RUNGE BANDS OF O₂.....10 min.(8:30)

A.S.-C. CHEUNG, S. S.-I. CHIU, 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, 60 Garden Street, Cambridge, Massachusetts, 02138.

RC2. PHOTOABSORPTION COEFFICIENTS FOR CARBON MONOXIDE ABSORPTION BANDS BETWEEN 94.0 nm AND 100.4 nm.....10 min.(8:42)

G. STARK, Department of Physics, Wellesley College, Wellesley, Massachusetts, 02181; K. YOSHINO, P. L. SMITH, D. ZUCKER, W. H. PARKINSON, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts, 02138; and K. ITO, Photon Factory, National Laboratory for High Energy Physics, Tsukuba 305, Japan.

RC3. FOURIER TRANSFORM SPECTROSCOPY IN THE VACUUM ULTRAVIOLET REGION, THE FOURTH POSITIVE BANDS OF CO.....10 min.(8:54)

A. P. THORNE, Imperial College of Science and Technology, London SW72BZ, England; K. YOSHINO, and W. H. PARKINSON, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts, 02138.

RC4. ULTRAVIOLET SPECTROSCOPY OF CARBON MONOXIDE.....15 min.(9:06)

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

RC5. FOURIER TRANSFORM SPECTROSCOPY OF BC, BD, CuD AND ZnD.....15 min.(9:23)

W.T.M.L. FERNANDO, L. C. O'BRIEN, and P. F. BERNATH, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

RC6. DETERMINATION OF MOLECULAR CONSTANTS OF THE $X^4\Sigma^- (v=4-7)$ LEVELS OF C₂⁺ USING STIMULATED EMISSION PUMPING SPECTROSCOPY.....15 min.(9:40)

F. G. CELII, Naval Research Laboratory, Code 6174, Washington, D.C., 20375-5000; and J. P. MAIER, Institut für Physikalische Chemie, Universität Basel, CH-4056 Basel, Switzerland.

Intermission

RC7. SPECTRA, RADIATIVE LIFETIMES, AND BAND OSCILLATOR STRENGTHS OF THE A¹Π-X¹Σ⁺ TRANSITION OF BH.....15 min.(10:15)

C. H. DOUGLASS, Applied Research Corporation, 8201 Corporate Drive, Landover, Maryland, 20785; H. H. NELSON, and JANE K. RICE, Chemistry Division, Naval Research Laboratory, Washington, D.C., 20375-5000.

RC8. PERMANENT ELECTRIC DIPOLE MOMENT OF CH.....10 min.(10:32)

DAVID F. NACHMAN, TIMOTHY C. STEIMLE, Department of Chemistry, Arizona State University, Tempe, Arizona, 85287-1604; DAVID A. FLETCHER, and JOHN M. BROWN, Physical Chemistry Laboratory, Oxford University, Oxford OX1 3QZ, England.

RC9. MICROWAVE OPTICAL DOUBLE RESONANCE STUDIES OF NiH.....10 min.(10:44)

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

- RC10. THE APPLICATION OF MRS AND SOODRZ TO THE ELECTRONIC SPECTRA OF TRANSITION METAL HYDRIDES.....15 min.(10:56)
- M. C. MCCARTHY, M. LI, and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
- RC11. HIGH RESOLUTION SPECTROSCOPY OF CoH AND CoD.....15 min.(11:13)
- THOMAS D. VARBERG, ERNEST J. HILL, and ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
- RC12. RYDBERG STATES OF CaF OBSERVED BY OPTICAL-OPTICAL DOUBLE RESONANCE.....15 min.(11:30)
- J. MURPHY, J. M. BERG, and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
- RC13. SPIN-ORBIT CI POTENTIAL CURVES FOR CuF.....15 min.(11:47)
- NORA M. WALLACE and RUSSELL M. PITZER, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

THURSDAY, JUNE 15, 1989 -- 8:30 A.M.

Room 1008, Evans Chemical Laboratory

Chair: JONATHAN KENNY, Tufts University, Medford,
Massachusetts.

- RD1. ROTATIONALLY RESOLVED ONE- AND TWO-PHOTON SPECTROSCOPY OF BENZENE:
INVESTIGATION OF INTRAMOLECULAR COUPLINGS.....15 min.(8:30)

E. RIEDLE, TH. WEBER, and H. J. NEUSSER, Institut für Physikalische
und Theoretische Chemie, TU München, Lichtenbergstrasse 4, D-8046
Garching, West Germany.

- RD2. ROTATIONAL BANDSHAPES OF JET COOLED BENZYL RADICAL.....10 min.(8:47)

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

- RD3. LIF STUDY OF o,m,p METHYL BENZYL RADICALS.....15 min.(8:59)

TAI-YUAN DAVID LIN, CHRISTOPHER C. CARTER, SANG K. LEE, and
TERRY A. MILLER, Laser Spectroscopy Facility, Department of
Chemistry, The Ohio State University, Columbus, Ohio, 43210.

- RD4. HIGH RESOLUTION LIF SPECTROSCOPY OF JET-COOLED PHENYL NITRENE.....15 min.(9:16)

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.

- RD5. ROTATIONAL STRUCTURE IN THE SINGLET-TRIPLET EXCITATION SPECTRA OF
POLYATOMIC MOLECULES.....15 min.(9:33)

L. H. SPANGLER, Department of Chemistry, Montana State University,
Bozeman, Montana, 59717; K. W. HOLTZCLAW, Physical Sciences, Inc.,
Research Park, Andover, Massachusetts, 01810; and D. W. PRATT,
Department of Chemistry, University of Pittsburgh, Pittsburgh,
Pennsylvania, 15260.

- RD6. HIGH RESOLUTION FLUORESCENCE EXCITATION SPECTRA OF THE 1- AND
2-HYDROXYNAPHTHALENES. DISTINGUISHING THE CIS AND TRANS ROTAMERS.....15 min.(9:50)

J. R. JOHNSON, D. F. PLUSQUELLIC, J. L. TOMER, and D. W. PRATT,
Department of Chemistry, University of Pittsburgh, Pittsburgh,
Pennsylvania, 15260.

Intermission

- RD7. HIGH RESOLUTION FLUORESCENCE EXCITATION SPECTRA OF THE 1- AND
2-AMINONAPHTHALENES.....15 min.(10:25)

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

- RD8. TORSIONAL BARRIERS IN LARGE MOLECULES. A HIGH RESOLUTION STUDY OF THE 1-
AND 2-METHYLNAPHTHALENES.....15 min.(10:42)

X.-Q. TAN, D. F. PLUSQUELLIC, D. W. PRATT, Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; and
W. A. MAJEWSKI, Division of Physics, National Research Council of
Canada, Ottawa, Ontario, Canada, K1A 0R6.

- RD9. ALL-TRANS-1,4-DIPHENYL-1,3-BUTADIENE. A ROTATIONALLY RESOLVED FLUORESCENCE
EXCITATION SPECTRUM OF THE ONE-PHOTON $S_1 \rightarrow S_0$ OPTICAL TRANSITION.....15 min.(10:59)

J. F. PFANSTIEL, B. B. CHAMPAGNE, D. F. PLUSQUELLIC, D. W. PRATT,
Department of Chemistry, University of Pittsburgh, Pittsburgh,
Pennsylvania, 15260; and W. A. MAJEWSKI, Division of Physics,
National Research Council of Canada, Ottawa, Ontario, Canada,
K1A 0R6.

- RD10. ROTATIONALLY RESOLVED LIF SPECTRUM OF $\tilde{A}^2A_1 \rightarrow \tilde{X}^2E$ TRANSITION OF CH_3S AND THE \tilde{A}^2A_1 STATE SPIN-ROTATION CONSTANT OF CH_3O15 min.(11:16)

XIANMING LIU, LIAN YU, JAMES M. WILLIAMSON, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; YEN-CHU HSU, Institute of Atomic & Molecular Science, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan, Republic of China; and STEPHEN C. FOSTER, Department of Chemistry, Florida State University, Tallahassee, Florida, 32306-3006.

- RD11. HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF THE ETHOXY FREE RADICAL.....15 min.(11:33)

CRISTINO P. DAMO, XIANMING LIU, LIAN YU, JAMES M. WILLIAMSON, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and STEPHEN C. FOSTER, Department of Chemistry, Florida State University, Tallahassee, Florida, 32306-3006.

- RD12. THE DISTRIBUTION OF EXCESS CHARGE IN WATER CLUSTERS BY NEGATIVE ION PHOTOELECTRON SPECTROSCOPY....Last Minute Addition..Abstract on page 175...10 min.(11:50)

S. T. Arnold, J. G. Eaton, G. H. Lee, K. H. Bowen: Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218.
J. V. Coe: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210.
C. Ludewigt, H. Haberland: Fakultat fur Physik, Universitat Freiburg, Freiburg West Germany.

RD12 appears for the first time in this Book of Abstracts.

THURSDAY, JUNE 15, 1989 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chair: PAUL BALOG, Battelle Columbus Division, Columbus, Ohio.

RE1. PRESSURE BROADENING IN THE ROTATIONAL SPECTRUM OF O_215 min.(1:30)

J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6; and D. J. KENDALL, Space Division, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6.

RE2. THE FAR INFRARED SPECTRUM OF C_3O_215 min.(1:47)

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

RE3. THE VIBRATION-ROTATION SPECTRUM OF THE BISMUTH HYDRIDE AND BISMUTH DEUTERIDE MOLECULES.....10 min.(2:04)

A.M.R.P. BOPEGEDERA, P. F. BERNATH, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721; and C. R. BRAZIER, Advanced Research in Energy Storage, Air Force Astronautics Laboratory/LSX, Edwards Air Force Base, California, 93523.

RE4. INTERNUCLEAR POTENTIAL AND EQUILIBRIUM STRUCTURE OF N_2O10 min.(2:16)

J.-L. TEFFO, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris, France; and A. CHÉDIN, Laboratoire de Météorologie Dynamique, CNRS, Ecole Polytechnique, Route Départementale 36, 91128 Palaiseau, France.

RE5. THE ν_6 BAND OF H_2O_2 - $(n,\tau)=(0,1)(0,3)$, $(1,1)(1,3)$ AND $(2,1)$ TORSIONAL STATES.....15 min.(2:28)

A. PERRIN, J.-M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris, France; and A. GOLDMAN, Department of Physics, University of Denver, Denver, Colorado, 80208.

RE6. THE FAR INFRARED SPECTRUM OF H_2O_2 . FIRST OBSERVATION OF THE STAGGERING OF THE LEVELS.....15 min.(2:45)

J.-M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris, France; J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A OR6; and B. CARLI, IROE-CNR, Via Panciatichi 64, 50127 Firenze, Italy.

Intermission

RE7. ASSIGNMENT OF THE ν_1 AND $2\nu_2$ BANDS OF COF_2 AT $5.2 \mu m$15 min.(3:20)

L. R. BROWN and E. A. COHEN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

RE8. HOT BANDS IN SYMMETRIC TOP SPECTRA: PROPYNE AS A TEST CASE.....15 min.(3:37)

G. GRANER, Laboratoire d'Infrarouge, Université de Paris-Sud, 91405 Orsay, France.

RE9. CYANO-ACETYLENE: SPECTROSCOPY FOR PLANETOLOGICAL PURPOSES.....15 min.(3:54)

E. ARIE, PH. ARCAS, DANG NHU M., G. GRANER, Laboratoire d'Infrarouge, Université de Paris-Sud, 91405 Orsay, France; H. BÜRGER, and G. PAWELKE, Anorganische Chemie, FB 9, Universität, 5600 Wuppertal 1, West Germany.

- RE10. INFRARED SPECTRA OF JET-COOLED 1-BUTYNE AND ETHANOL IN THE METHYL STRETCH REGION.....10 min.(4:11)
G. A. BETHARDY, J. GO, S. HAMMAD, and D. S. PERRY, Department of Chemistry, University of Akron, Akron, Ohio, 44325.
- RE11. SLICED-JET SPECTROSCOPY - A NEW TECHNIQUE FOR SUB-DOPPLER INFRARED SPECTROSCOPY OF SUPER-COOLED MOLECULES.....10 min.(4:23)
SAMEER A. HAMMAD, LOUIS R. MERCORELLI, and DAVID S. PERRY, Department of Chemistry, University of Akron, Akron, Ohio, 44325.
- RE12. HIGH RESOLUTION SPECTROSCOPY OF THE ν_3 BAND OF NEPTUNIUM HEXAFLUORIDE.....Late Paper.....15 min.(4:35)
R. N. Mulford, K. C. Kim, Burton J. Krohn, and J. P. Baiardo, Los Alamos National Laboratory, Los Alamos, New Mexico.
- RE13. TIME-RESOLVED INFRARED SPECTROSCOPY: WHAT IS THE BEST METHOD?..Late Paper..15 min.(4:52)
HUGH H. RICHARDSON, VERNON W. PABST, AND JARED A. BUTCHER Jr., Department of Chemistry, Ohio University, Athens, Ohio 45701.
- RE14. HIGH RESOLUTION INFRARED SPECTRA OF THE ν_5 , ν_6 AND ν_7 BANDS OF CYANOACETYLENE.....Last Minute Addition...Abstract on page 175.....10 min.(5:09)
A. V. Peters, S. J. Daunt, Department of Chemistry, Concordia University, H-1139, 1455 de Maisonneuve Blvd. W., Montreal, Quebec H3G 1M8, Canada.
S. J. Daunt, W. E. Blass, Department of Physics & Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200.

RE12, RE13 & RE14 appear for the first time in
this Book of Abstracts

THURSDAY, JUNE 15, 1989 -- 1:30 P.M.

Room 1009, Physics Laboratory

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

- RF1. MICROWAVE SPECTRA OF UNSTABLE SPECIES IN A DISCHARGE OF A MIXTURE OF CS₂ AND N₂.....15 min.(1:30)
TAKAYOSHI AMANO and TAKAKO AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.
- RF2. COLLISIONALLY COOLED SPECTROSCOPY: PRESSURE BROADENING BELOW 5 K.....15 min.(1:47)
D. R. WILLEY, D. N. BITTNER, and F. C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.
- RF3. COLLISIONAL COOLING AT 77 K.....15 min.(2:04)
T. M. GOYETTE, W. L. EBENSTEIN, and F. C. DE LUCIA, Department of Physics, Duke University, Durham, North Carolina, 27706.
- RF4. THE MICROWAVE SPECTRUM OF THE LiO RADICAL.....10 min.(2:21)
CHIKASHI YAMADA, MASAHARU FUJITAKE, and EIZI HIROTA, Institute for Molecular Science, Okazaki 444, Japan.
- RF5. THE MICROWAVE SPECTRUM OF AlO.....10 min.(2:33)
CHIKASHI YAMADA, MASAHARU FUJITAKE, EIZI HIROTA, Institute for Molecular Science, Okazaki 444, Japan; and EDWARD A. COHEN, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

Intermission

- RF6. DETECTION OF THE NaO RADICAL BY MICROWAVE SPECTROSCOPY.....10 min.(3:00)
CHIKASHI YAMADA, MASAHARU FUJITAKE, and EIZI HIROTA, Institute for Molecular Science, Okazaki 444, Japan.
- RF7. THE ROTATIONAL SPECTRA OF THE KO RADICAL IN THE X²Π₁ AND A²Σ⁺ STATES.....10 min.(3:12)
CHIKASHI YAMADA, MASAHARU FUJITAKE, EIZI HIROTA, Institute for Molecular Science, Okazaki 444 Japan; SHUJI SAITO, and SATOSHI YAMAMOTO, Nagoya University, Nagoya 460, Japan.
- RF8. DETECTION OF THE RbO RADICAL BY MICROWAVE SPECTROSCOPY.....10 min.(3:24)
CHIKASHI YAMADA, MASAHARU FUJITAKE, and EIZI HIROTA, Institute for Molecular Science, Okazaki 444, Japan.
- RF9. SUBSTITUTION STRUCTURE OF THE CCH RADICAL FROM THE ANALYSIS OF THE ROTATIONAL SPECTRA OF VARIOUS ISOTOPIC FORMS.....10 min.(3:36)
M. BOGEY, C. DEMUYNCK, and J. L. DESTOMBES, Université de Lille-Flandres-Artois, Laboratoire de Spectroscopie Hertzienne, CNRS, 59655 Villeneuve d'Ascq, France.
- RF10. MILLIMETER WAVE SPECTRUM OF MgCl X ²Σ⁺ AND ISOTOPOMERS IN DIFFERENT VIBRATIONAL STATES. DETERMINATION OF MASS INVARIANT PARAMETERS.....10 min.(3:48)
M. BOGEY, C. DEMUYNCK, and J. L. DESTOMBES, Université de Lille-Flandres-Artois, Laboratoire de Spectroscopie Hertzienne, CNRS, 59655 Villeneuve d'Ascq, France.
- RF11. MICROWAVE SPECTRA AND STRUCTURES OF THE N₂O-HF and N₂O-DF COMPLEXES.....Late Paper.....15 min.(4:00)
S. G. Kukolich, D. J. Fauley, Department of Chemistry, University of Arizona, Tucson, Arizona 85721.
R. E. Bunzger, Division of Geology and Planetary Sciences, MS 170-25, California Institute of Technology, Pasadena, California, 91125.

RF11 appears for the first time in this
 Book of Abstracts

THURSDAY, JUNE 15, 1989 -- 1:30 P.M.

Room 1005, Physics Laboratory

SEMINAR ON HIGHLY EXCITED STATES OF MOLECULAR HYDROGEN(CONTINUED)

Chair: JOHN E. SOHL, The Ohio State University, Columbus, Ohio.

- RG1. THE DISSOCIATIVE RECOMBINATION OF MOLECULAR HYDROGEN IONS
Invited Paper.....30 min. (1:30)

J.B.A. MITCHELL, F. B. YOUSIF, P. VANDERDONK, and H. HUS,
 Department of Physics, The University of Western Ontario,
 London, Ontario, Canada, N6A 3K7.

- RG2. STATIC AND DYNAMIC STARK EFFECTS IN THE HIGH, RYDBERG LEVELS
 OF H_2Contributed Paper.....15 min. (2:05)

JAN P. HESSLER, Chemistry Division, Argonne National
 Laboratory, Argonne, Illinois, 60439; and WALLACE L. GLAB,
 Department of Chemical Sciences, Pacific Northwest Laboratory,
 Richland, Washington, 99352.

- RG3. AUTOIONIZATION RATES AND ENERGY LEVELS OF TRIPLET $v=1$ RYDBERG
 STATES OF PARA-AND ORTHO- H_2 MEASURED BY HIGH-RESOLUTION LASER
 SPECTROSCOPY.....Contributed Paper.....15 min. (2:22)

MARK D. LINDSAY, A. W. KAM, J.R. LAWALL, F. M. PIPKIN, and
 PING ZHAO, Lyman Laboratory of Physics, Harvard University,
 Cambridge, Massachusetts, 02138.

Intermission

- RG4. DETERMINATION OF THE (0,1)-(0,3) ROTATIONAL SPLITTING OF H_2^+
 FROM MICROWAVE SPECTROSCOPY OF H_2 RYDBERG STATES
Contributed Paper.....15 min. (3:00)

P. W. ARCUNI, ZHUO-WU FU, and S. R. LUNDEEN, Department of
 Physics, University of Notre Dame, Notre Dame, Indiana,
 46556.

- RG5. OPTOGALVANIC SPECTRA AND PREDISSOCIATION OF $c^3\Pi_u$ STATE OF
 H_2 AND D_2Contributed Paper.....15 min. (3:17)

Y. KAWASHIMA, Kanagawa Institute of Technology, 1030 Shimo-
 ogino, Atsugi, Kanagawa 243-02, Japan.

- RG6. DOUBLY EXCITED STATES OF H_2Contributed Paper.....15 min. (3:34)

M. GLASS-MAUJEAN, Laboratoire de Spectroscopie Hertzienne
 de l'ENS, Université Pierre et Marie Curie, 75252 Paris,
 France.

- RG7. QUANTUM DEFECT CALCULATIONS OF H_2^+Contributed Paper.....15 min. (3:51)

HONG GAO and CHRIS H. GREENE, JILA and Department of Physics,
 University of Colorado, Boulder, Colorado, 80309.

THURSDAY, JUNE 15, 1989 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chair: M. C. HEAVEN, Emory University, Atlanta, Georgia.

- RH1. FLUORESCENCE SPECTROSCOPY AND DYNAMICS OF INELASTIC COLLISIONS BETWEEN RARE GASES AND VIBRATIONALLY EXCITED I_215 min.(1:30)
 K. BUTZ, HONG DU, C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405; and D. KRAJNOVICH, IBM Almaden Research Center, K07/803, 650 Harry Road, San Jose, California, 95120.
- RH2. THE DISSOCIATION OF p-DIFLUOROBENZENE-Ar VAN DER WAALS COMPLEXES. THEORY AND SPECTROSCOPY.....15 min.(1:47)
HYE-KEUN O, CHARLES S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405; and MENG-CHIH SU, Department of Chemistry, Butler University, Indianapolis, Indiana, 46208.
- RH3. REACTION PATHWAYS IN THE PHOTOLYSIS OF ACETIC ACID.....15 min.(2:04)
S. S. HUNNICUTT, L. D. WAITS, and J. A. GUEST, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221.
- RH4. COLLISION-INDUCED ELECTRONIC QUENCHING OF $BH(A^1\Pi)$15 min.(2:21)
 C. H. DOUGLASS, Applied Research Corporation, 8201 Corporate Drive, Landover, Maryland, 20785; and J. K. RICE, Chemistry Division, Code 6111, Naval Research Laboratory, Washington, D.C., 20375-5000.
- RH5. ELECTRONIC QUENCHING OF THE $SO A(3\Pi_1, v'=1)$ STATE.....10 min.(2:38)
 M. J. MCAULIFFE, M. BOHN, and E. A. DORKO, AFWL/ARDI, Air Force Weapons Laboratory, Kirtland Air Force Base, New Mexico, 87117-6008.
- RH6. SINGLE ROTATIONAL LEVEL PHOTOPHYSICS OF S_1 THIOFORMALDEHYDE.....15 min.(2:50)
JAMES R. DUNLOP, DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, Kentucky, 40506-0055; and RICHARD H. JUDGE, Department of Chemistry, University of Wisconsin-Parkside, Kenosha, Wisconsin, 53141-2000.
- RH7. BINDING ENERGIES OF THREE IODINE COMPLEXES.....15 min.(3:07)
 T. D. MCLEAN, B. B. RATCLIFF, J. Z. PASTALAN, and K. K. INNES, Department of Chemistry, State University of New York at Binghamton, Binghamton, New York, 13901.
- RH8. ROTATIONAL ENERGY TRANSFER IN THE $B^3\Pi(0_+)$ STATES OF IF AND ICl : A SYSTEMATIC STUDY OF STATE-TO-STATE RATE COEFFICIENTS.....Late Paper.....15 min.(3:24)
 S. J. DAVIS and K. W. HOLTZCLAW, Physical Sciences Incorporated, Research Park, P.O. Box 3100, Andover, Massachusetts, 01810.
- RH9. SECOND HARMONIC GENERATION STUDIES OF COPPER ELECTRODEPOSITION ON GOLD.....Late Paper.....15 min.(3:41)
 M. Bennahmias, H. S. Lakkaraju, Dept. of Physics, San Jose State University, San Jose, CA 95192.
 K. Ashley, and B. Stone, Dept. of Chemistry, San Jose State University, San Jose, California, 95192.

RH9 appears for the first time in this
 Book of Abstracts

FRIDAY, JUNE 16, 1989 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chair: WAFAA M. FAWZY, Brookhaven National Laboratory, Upton, New York.

FA1. COLLISIONALLY-EXCITED NAPHTHALENE IN THE GAS PHASE.....15 min.(8:30)

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

FA2. IDENTIFICATION OF SVL'S OF TWO ISOMERS OF GUAIAZULENE BY POPULATION LABELING SPECTROSCOPY.....15 min.(8:47)

ANTHONY C. BEVILACQUA and JONATHAN E. KENNY, Department of Chemistry,
Tufts University, Medford, Massachusetts, 02155.

FA3. THE $n \rightarrow 3s$ RYDBERG TRANSITION OF JET-COOLED TETRAHYDROPYRAN, 1,4-DIOXANE, AND 1,4-DIOXANE- d_8 STUDIED BY 2+1 RESONANCE ENHANCED MULTIPHOTON IONIZATION.....10 min.(9:04)

TIMOTHY CORNISH, TOMAS BAER, and LEE G. PEDERSEN, Department of
Chemistry, University of North Carolina, Chapel Hill, North Carolina,
27599-3290.

FA4. HIGH RESOLUTION LIF SPECTROSCOPY OF JET-COOLED CYCLOPENTADIENYL RADICALS, C_5H_5 AND C_5D_5 : STRUCTURE AND JAHN-TELLER EFFECT.....15 min.(9:16)

LIAN YU, DAVID W. CULLIN, JAMES M. WILLIAMSON, TERRY A. MILLER,
Laser Spectroscopy Facility, Department of Chemistry, The Ohio
State University, Columbus, Ohio, 43210; and STEPHEN C. FOSTER,
Department of Chemistry, Florida State University, Tallahassee,
Florida, 32306-3006.

FA5. ROTATIONALLY RESOLVED SPECTRA OF JAHN-TELLER ACTIVE VIBRATIONS IN AN ELECTRONICALLY ALLOWED $A \leftarrow E$ TRANSITION.....15 min.(9:33)

LIAN YU, JAMES M. WILLIAMSON, TERRY A. MILLER, Laser Spectroscopy
Facility, The Ohio State University, Columbus, Ohio, 43210; and
STEPHEN C. FOSTER, Department of Chemistry, Florida State University,
Tallahassee, Florida, 32306-3006.

Intermission

FA6. HIGH RESOLUTION LIF SPECTROSCOPY OF JET-COOLED METHYLCYCLOPENTADIENYL RADICAL, $C_5H_4CH_3$15 min.(10:05)

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.

FA7. LIF SPECTROSCOPY OF FREE RADICAL - RARE GAS VAN DER WAALS COMPLEXES.....15 min.(10:22)

JAMES M. WILLIAMSON, DAVID W. CULLIN, LIAN YU, and TERRY A. MILLER,
Laser Spectroscopy Facility, Department of Chemistry, The Ohio
State University, Columbus, Ohio, 43210.

FA8. VIBRATIONAL SHIFTS IN p-DICHLOROBENZENE - RARE GAS VAN DER WAALS COMPLEXES..15 min.(10:39)

W. D. SANDS, Department of Chemistry, University of Pittsburgh,
Pittsburgh, Pennsylvania, 15260; R. MOORE, and L. F. JONES,
Department of Chemistry, Virginia Commonwealth University, Richmond,
Virginia, 23284.

FA9. AB INITIO STUDY OF THE GEOMETRY AND ELECTRONIC STRUCTURE OF SEMICONDUCTOR CLUSTERS.....15 min.(10:56)

M. SAWAMURA, Department of Physics and Engineering Physics, Stevens
Institute of Technology, Hoboken, New Jersey, 07030; M. M. MARINO,
W. C. ERMLER, Department of Chemistry and Chemical Engineering,
Stevens Institute of Technology, Hoboken, New Jersey, 07030; and
C. J. SANDROFF, Bell Communications Research, Red Bank, New Jersey,
07701.

FA10. A LIF-TOF STUDY OF IONIC CLUSTERS $C_6F_6^+-R_n$15 min.(11:03)

CHUNG-YI KUNG, ERIC S. ROBLES, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

FA11. THE EFFECT OF VIBRONIC COUPLING ON METHYL CONFORMATION IN p-CRESOL.....Late Paper.....15 min.(11:20)

Steve Mayer and Lee H. Spangler, Dept. of Chemistry, Montana State University, Bozeman, Montana, 59717.

FA12. SPECTROSCOPIC INVESTIGATION OF POLYMERIZATION IN p-METHYL STYRENE.....Late Paper.....10 min.(11:37)

Steve Mayer, Shuxin Yan, and Lee H. Spangler, Dept. of Chemistry, Montana State University, Bozeman, Montana, 59717.

FA11 and FA12 appear for the first time in
this Book of Abstracts

FRIDAY, JUNE 16, 1989 -- 8:30 A.M.

Room 1009, Physics Laboratory

- Chair: G. T. FRASER, National Institute of Standards and Technology, Gaithersburg, Maryland.
- FB1. DIODE LASER ABSORPTION SPECTROSCOPY OF SUPERSONIC CARBON CLUSTER BEAMS:
THE ν_3 VIBRATION OF C_515 min.(8:30)
J. R. HEATH, A. L. COOKSY, M.H.W. GRUEBELE, C. A. SCHMUTTENMAER, and
R. J. SAYKALLY, Department of Chemistry, University of California,
Berkeley, California, 94720.
- FB2. LABORATORY DETECTION OF C_5 BY DIODE LASER SPECTROSCOPY.....15 min.(8:47)
N. MOAZZEN-AHMADI, A.R.W. MCKELLAR, and T. AMANO, Herzberg Institute
of Astrophysics, National Research Council of Canada, Ottawa, Ontario,
Canada, K1A 0R6.
- FB3. VIBRATIONAL FREQUENCIES OF LINEAR CARBON MOLECULES.....10 min.(9:04)
D. W. EWING, Department of Chemistry, John Carroll University,
Cleveland, Ohio, 44118.
- FB4. MICROWAVE SPECTROSCOPY OF TRANSIENT PYROLYSIS PRODUCTS:
1,1-DIMETHYLSILAETHYLENE.....15 min.(9:16)
T. EMILSSON, JANE CHEN, P. J. HAJDUK, and H. S. GUTOWSKY, Noyes
Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.
- FB5. ROTATIONAL SPECTRA AND STRUCTURES OF THE $HCN-(CO_2)_2$ AND $HCN-(CO_2)_3$
CLUSTERS.....15 min.(9:33)
H. S. GUTOWSKY, P. J. HAJDUK, JANE CHEN, and R. S. RUOFF, Noyes
Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.
- Intermission
- FB6. RELAXATION OF CONFORMERS AND ISOMERS IN SEEDED SUPERSONIC JETS OF RARE
GASES.....15 min.(10:05)
R. S. RUOFF, T. D. KLOTS, T. EMILSSON, and H. S. GUTOWSKY, Noyes
Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.
- FB7. ROTATIONAL SPECTRA OF EXCITED Σ VIBRATIONAL STATES OF Ar-HCl AND Ar-DCl.....15 min.(10:22)
CARL CHUANG and H. S. GUTOWSKY, Noyes Chemical Laboratory, University
of Illinois, Urbana, Illinois, 61801.
- FB8. A STRUCTURAL STUDY OF THE $H_2S \cdot CO_2$ VAN DER WAALS COMPLEX.....15 min.(10:39)
J. K. RICE, Naval Research Laboratory, Washington, D. C., 20375-5000;
F. J. LOVAS, R. D. SUENRAM, L. H. COUDERT, K. MATSUMURA, Molecular
Spectroscopy Division, National Institute of Standards and Technology,
Gaithersburg, Maryland, 20899; W. STAHL, Institute for Physical
Chemistry, Universitat Kiel, 2300 Kiel 1, Federal Republic of Germany;
D. J. PAULEY, and S. KUKOLICH, University of Arizona, Tucson,
Arizona, 85721.
- FB9. THE STRUCTURE OF Kr-PF₃ DETERMINED FROM THE NUCLEAR QUADRUPOLE COUPLING
CONSTANTS OF ^{83}Kr -PF₃.....15 min.(10:56)
A. TALEB-BENDIAB, M. S. LABARGE, K.W. HILLIG II, and R. L. KUCZKOWSKI,
Department of Chemistry, University of Michigan, Ann Arbor, Michigan,
48109.
- FB10. THE MICROWAVE SPECTRUM OF THE WATER-PF₃ AND NEON-PF₃ DIMERS.....15 min.(11:13)
K. W. HILLIG II, M. S. LABARGE, and R. L. KUCZKOWSKI, Department of
Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

FRIDAY, JUNE 16, 1989 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chair: J. A. GUEST, University of Cincinnati, Cincinnati, Ohio.

FC1. ROVIBRONIC SPECTROSCOPY OF H_315 min.(8:30)

L. J. LEMBO, H. HELM, P. C. COSBY, D. L. HUESTIS, Molecular Physics Laboratory, SRI International, Menlo Park, California, 94025; and A. PETIT, Commissariat a L'Energie Atomique, Centre Etude Nucleaires, Saclay, France.

FC2. ELECTRONIC SPECTROSCOPY OF THE HYDROGEN MOLECULAR ION. D_2^+15 min.(8:47)

ALAN CARRINGTON, IAIN R. MCNAB, and CHRISTINE A. MONTGOMERIE, Department of Chemistry, Southampton University, Southampton SO9 5NH, United Kingdom.

FC3. TWO-PHOTON SPECTROSCOPY OF THE $F^1\Pi_g$ AND $f^3\Pi_g$ STATES OF F_215 min.(9:04)

G. W. FARIS, M. J. DYER, W. K. BISCHEL, and D. L. HUESTIS, Molecular Physics Laboratory, SRI International, Menlo Park, California, 94025.

FC4. A PARTIAL DIFFERENTIAL EQUATION FOR THE RKR INTEGRAL.....15 min.(9:21)

D. L. HUESTIS, Molecular Physics Laboratory, SRI International, Menlo Park, California, 94025.

FC5. INTERACTIVE ROTATIONAL ANALYSES OF DIATOMIC MOLECULAR SPECTRA.....15 min.(9:38)

M. C. ABRAMS, S. P. DAVIS, and R. PECYNER, Department of Physics, University of California at Berkeley, Berkeley, California, 94720.

FC6. NUCLEAR HYPERFINE STRUCTURE IN THE ELECTRONIC SPECTRUM OF $CuCl$10 min.(9:55)

IRENE BURGHARDT, LYNDON R. ZINK, DAVID A. FLETCHER, JOHN M. BROWN, Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, England; and IAN R. BEATTIE, Department of Chemistry, The University, Southampton, SO9 5NH, England.

FC7. SPECTROSCOPY OF HIGHLY ROTATIONALLY EXCITED $BaI C^2\Pi-X^2\Sigma^+$10 min.(10:07)

D. ZHAO, P. H. VACCARO, A. A. TSEKOURAS, and R. N. ZARE, Department of Chemistry, Stanford University, Stanford, California, 94305.

Intermission

FC8. A REINVESTIGATION OF THE GOODMAN BANDS OF IODINE.....10 min.(10:35)

T. D. MCLEAN, Department of Chemistry, State University of New York-Binghamton, Binghamton, New York, 13901; and G. W. KING, Department of Chemistry, McMaster University, Hamilton, Ontario, Canada, L8S-4M1.

FC9. MICROWAVE-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF $A^3\Pi(1) IC1$ NEAR THE DISSOCIATION LIMIT.....15 min.(10:47)

J. R. JOHNSON, T. J. SLOTTERBACK, K. C. JANDA, and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

FC10. HIGH RESOLUTION MOLECULAR-BEAM LASER SPECTROSCOPY OF STRONTIUM MONOFLUORIDE (SrF).....15 min.(11:04)

YOSHIRO AZUMA and WILLIAM J. CHILDS, Physics Division, Argonne National Laboratory, Argonne, Illinois, 60439.

FC11. VIBRATIONAL ANALYSIS OF THREE NEW STATES OF CrF.....15 min.(11:21)

T. C. DEVORE, Department of Chemistry, James Madison University,
Harrisonburg, Virginia, 22807; M. MCQUAID, and J. L. GOLE, School
of Physics, Georgia Institute of Technology, Atlanta, Georgia, 30332.

FC12. SINGLE-LASER OODR SPECTROSCOPY OF THE $2^1\Sigma_g^+$ STATE OF Li_210 min.(11:38)

R. A. BERNHEIM, L. P. GOLD, and CHUN HE, Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania, 16802.

FC13. THE EXCITED ELECTRONIC STATE STRUCTURE OF THE LITHIUM DIMER..Late Paper...15 min.(11:50)

R. A. Bernheim, 152 Davey Laboratory, The Pennsylvania State University,
University Park, Pennsylvania, 16802.

FC13 appears for the first time in this
Book of Abstracts

MA4 (11:10)

SECOND HARMONIC GENERATION AS A PROBE OF SURFACE STRUCTURE AND INTERFACIAL DYNAMICS AT THE SOLID/LIQUID INTERFACE

Geraldine L. Richmond

Over the past decade there has been a rapid growth in the studies using optical second harmonic generation (SHG) to probe surface properties of metals and semiconductors.¹ One of the major advantages of the technique is the ability to characterize surfaces in contact with other dense media. Our focus has been on metals and semiconductors in contact with liquids in an attempt to probe structural aspects of the surface and adjacent double layer.

The studies to be described in this talk are ones which examine the rotational anisotropy in the SH response from single crystal electrode surfaces as the surface is rotated azimuthally. For the spectroscopist, studying the anisotropy in the SH response from these crystalline surfaces can provide important insight into the tensor elements which play a role in the overall SH response. Wavelength dependent studies have the potential of providing information about the electronic structure of the surface and possible surface states at the liquid/solid interface. From a more applications oriented viewpoint, the technique has the potential to provide insight into the morphological aspects of the crystalline surface and deposited overlayers. When performed in a time-resolved mode, the kinetics of deposition, surface atom reorganization and related electron transfer effects can be examined. The presentation will be an overview of these topics into which our most recent results with various single crystal surfaces in solution will be incorporated.

1. For a recent review, see G.L. Richmond, J.M. Robinson and V.L. Shannon, Prog. in Surf. Sci. 28, 1 (1988).

ME1 (1:30)**THE CONTINUUM ABSORPTION OF LARGE METHANOL CLUSTERS IN THE CO₂ LASER REGION**

Jeffrey A. Draves, Jeffrey P. LaCrosse and James M. Lisy

We report the infrared absorption spectra of large methanol clusters ($(\text{CH}_3\text{OH})_N$, $N \approx 30$) generated in a supersonic expansion via vibrational predissociation. Spectra were recorded in the 9.6μ and 10.6μ region using a cw CO₂ laser. In addition to the absorption feature centered about 1040 cm^{-1} arising from the excitation of the C-O stretch (ν_4 mode) in the methanol monomers, a continuum absorption in the 10.6μ region from the excitation of the intermolecular modes has also been observed.

The internal temperature, energy redistribution and binding energies will be discussed with respect to the observed vibrational predissociation.

Address of Draves, LaCrosse and Lisy: School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Mathews Ave., Urbana, IL 61801.

ME2 (1:47)**VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF DEUTERATED ANALOGS OF METHANOL DIMER IN THE CO₂ LASER REGION**

Jeffrey P. LaCrosse and James M. Lisy

Vibrational predissociation spectra of isotopomers of methanol dimer have been recorded in the CO₂ laser region. Using the beam depletion method, we have observed vibrational transitions at 1028.6 and 1053.6 cm^{-1} for $(\text{CH}_3\text{OD})_2$ with Lorentzian linewidths of 4.8 and 2.1 cm^{-1} , respectively. These transitions are blue shifted from the fully protonated dimer by 2.3 and 1.3 cm^{-1} respectively. Spectra were also measured for the mixed dimer $(\text{CH}_3\text{OH})(\text{CH}_3\text{OD})$. Preliminary analysis shows that this spectrum can be described by equal contributions of the bonded and nonbonded C-O stretch for both the deuterated and protonated methanol subunits. This suggests that there is no preference of the deuterated subunit to occupy the donor or acceptor position in the mixed dimer.

Address of LaCrosse and Lisy: School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Mathews Ave., Urbana, IL 61801.

ME3 (2:04)**VIBRATIONAL PREDISSOCIATION STUDIES OF SOLVATED ALKALI IONS**

Jeffrey A. Draves, Wen-Long Liu and James M. Lisy

Vibrational predissociation spectra of mass selected $M^+(\text{MeOH})_N$ and $M^+(\text{EtOH})_N$ (where $M = \text{Na}^+, \text{K}^+, \text{Rb}^+$) have been observed by exciting the C-O stretching mode of the MeOH or the CH₃ wag of the EtOH in the 9.6μ region. The solvated ions are produced by combining a thermionic ion source with a supersonic nozzle. Spectra from cluster ions with as many as 25 solvent molecules have been observed.

From the spectral dependence on the solvent number surrounding the ion, we have observed the formation of solvation shells. Comparisons will be made to $\text{Cs}^+(\text{MeOH})_N^1$ and $\text{Cs}^+(\text{EtOH})_N$.

¹W.L. Liu and J.M. Lisy, *J. Chem. Phys.* **89**, 605 (1988)

Address of Draves and Lisy: School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Mathews Ave., Urbana, IL 61801.

Address of Liu: Rohm & Haas Company, Philadelphia PA.

ME4 (2:21)THE MICROWAVE SPECTRUM OF THE Ar-SO₂ VAN DER WAALS COMPLEX

L. H. COUDERT, K. MATSUMURA and F. J. LOVAS

The microwave and radiofrequency spectra of the Ar-SO₂ van der Waals molecule were first recorded by DeLeon, Yokozeki and Muentner¹. These authors showed that this molecule has two nonsuperimposable equilibrium configurations with C_s symmetry, and that it can tunnel between these two frameworks, resulting in a splitting of about 980 MHz of the rigid rotator energy levels. However, from these measurements, it was neither possible to determine the exact structure of the two equilibrium configurations, nor to elucidate the nature of the tunneling motion.

The microwave spectrum of Ar-SO₂ was therefore reinvestigated at NIST. Sixty-five new transitions were measured with a pulsed beam Fourier transform microwave spectrometer. These new data along with those from DeLeon *et al.*¹, were analysed using an IAM-like treatment² developed for multidimensional tunneling. Such a formalism can be used to investigate the complicated motions that the complex may undergo because of the looseness of the van der Waals bond. For instance it is not clear *a priori* whether the large amplitude motion is a pure C₂ rotation of the SO₂ subunit about its *b*-axis, an inversion-like wagging of this subunit about its *a*-axis, or something in between. These various possibilities as well as their consequences on the J and K dependence of the tunneling splitting will be discussed. The structural implications of the results obtained in the final analysis of the data will also be presented.

¹R. L. DeLeon, A. Yokozeki, and J. S. Muentner, *J. Chem. Phys.* **73**, 2044-2048 (1980).²J. T. Hougen, *J. Mol. Spectrosc.* **114**, 395-426 (1985).

Address: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.

ME5 (2:38)TUNABLE FAR-INFRARED LASER SPECTROSCOPY OF VAN DER WAALS BONDS: NEW MEASUREMENTS OF VIBRATION-ROTATION TRANSITIONS IN Ar-H₂O

R.C. COHEN, KERRY L. BUSAROW, Y.T. LEE, and R.J. SAYKALLY

Recent work by Hutson¹ has demonstrated that measurement of a few low frequency vibration-rotation bands in simple van der Waals clusters is sufficient for the determination of highly accurate global intermolecular potential surfaces. The difficulty in measuring such vibrations has prevented this technique from being applied in a wide array of systems. Extensive measurements of the vibration-rotation spectrum of Ar-H₂O using a tunable far-infrared laser to probe a cw planar supersonic expansion will be presented. These measurements, in addition to our previous measurements², provide the opportunity for the extension of theoretical techniques applied to atom-diatom systems to molecular systems of significantly greater complexity and demonstrate the possibility for rapid extension of our knowledge of atom-molecule intermolecular potentials by spectroscopic means. Preliminary descriptions of the Ar-H₂O potential will be discussed.

1. J.M. Hutson, *J. Chem. Phys.* **89**, 4550 (1988).2. R.C. Cohen, Kerry L. Busarow, K.B. Laughlin, Geoffrey A. Blake, Y.T. Lee, and R.J. Saykally, *J. Chem. Phys.* **89**, 4494 (1988).

Address of Cohen, Busarow, Lee, and Saykally: Department of Chemistry and Materials and Chemical Sciences Division, University of California and Lawrence Berkeley Laboratory, Berkeley, CA 94720.

ME6 (2:55)CHARACTERIZATION OF THE Ar₂Cl₂ and Ar₃Cl₂ VAN DER WAALS MOLECULES.

C. R. Bieler, D. D. Evard, and K. C. Janda.

The structure and bond energy of the Ar₂Cl₂ and Ar₃Cl₂ van der Waals molecules are studied by a laser pump-probe technique. Qualitative fitting of B-X excitation spectra produce structures for the complexes which are consistent with the observed bandshifts and in agreement with model intramolecular potential calculations using atom-atom potentials. Ar₂Cl₂ is nearly tetrahedral while in Ar₃Cl₂ the third argon forms a triangular Ar₃ complex positioned above the Cl-Cl bond. Chlorine fragment rotational distributions are used to determine total van der Waals bond energies which confirm the bond-bond additivity of van der Waals complexes.

Address of Bieler and Janda: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

Address of Evard: Institut für Physikalische Chemie, Universität Basel, CH-4096 Basel, Switzerland.

Intermission

ME7 (3:30)

INFRARED AND MICROWAVE STUDY OF ANGULAR-RADIAL COUPLING IN Ar-HCN

G. T. FRASER AND A. S. PINE

Microwave and infrared spectra of Ar-HCN have been obtained using an electric-resonance optothermal spectrometer. The microwave measurements extend to higher J the previous results of Leopold *et al.*¹ and Klots *et al.*², allowing the determination of higher-order centrifugal distortion constants for this quasilinear, highly non-rigid complex. A Padé approximate fit to the microwave data indicates a centrifugal alignment of the HCN subunit with the Ar-HCN axis due to angular-radial coupling. Infrared spectra are reported for the C-H stretching fundamental, ν_1 , and the combination band $\nu_1+\nu_5$ ¹, where ν_5 is the van der Waals bending vibration. The band-origin difference between these two bands gives $\nu_5 = -7.8 \text{ cm}^{-1}$, in rough agreement with the 10 cm^{-1} harmonic value predicted from the microwave-determined nuclear quadrupole coupling constant. The complexation-induced shift of the C-H stretching vibration is 2.69 cm^{-1} and the vibrational predissociation linewidths, Γ , are $< 10 \text{ MHz}$. The vibrationally excited complex predissociates before striking the bolometer detector, implying that the predissociation lifetime, $\tau < \sim 1 \text{ ms}$.

¹K.R. Leopold, G.T. Fraser, F.J. Lin, D.D. Nelson, Jr., and W. Klemperer, *J. Chem. Phys.* **81**, 4922 (1984).

²T.D. Klots, C.E. Dykstra, and H.S. Gutowsky, *J. Chem. Phys.* **90**, 30 (1989).

Address of Fraser and Pine: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

ME8 (3:47)

A MODEL POTENTIAL FOR Ar-HCN

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

In the original investigation of the ground vibrational state of the van der Waals molecule, Ar-HCN, much of the unusual behavior of this complex, including the large centrifugal distortion constant, sensitive to isotopic substitution, along with unexpected behavior of the average bending angle and the van der Waals bond length upon deuteration, was postulated to arise from very strong angular-radial coupling which might result from a double well potential.¹ This form of the potential was suggested by analogies to the very similar Ar-HCl complex and to the isoelectronic Ar-HCCH molecule. In a test of this hypothesis, we have used close-coupling calculations to adjust the parameters of such a model potential to reproduce the observed spectroscopic properties.

Our ability to successfully model the seemingly mysterious behavior of this molecule with a simple potential energy surface based on chemical intuition lends support to the suggestions of the original experimental study, but does not exclude the possibility of a potential of a different form. Additional experimental evidence is required to place further restrictions on the precise form of the surface, and predictions concerning the location and properties of excited vibrational states are presented to facilitate such comparison.

¹ K.R. Leopold, G.T. Fraser, F.J. Lin, D.D. Nelson, Jr., and W. Klemperer, *J. Chem. Phys.* **81**, 4922 (1984).

Address of Leung: Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138.

Address of Marshall: Department of Chemistry, Amherst College, Amherst, MA 01002.

Address of Klemperer: Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, MA 02138.

ME9 (4:04)

THE POTENTIAL ENERGY SURFACE OF AR-HCN

D. Yaron and W. Klemperer

The microwave spectrum of AR-HCN is superficially characteristic of a linear molecule with both unusually large centrifugal distortion and unexpectedly large bending amplitude.¹ Both the centrifugal distortion constants and the vibrationally averaged structure are unusually sensitive to isotopic substitution. Also, the average bending angle derived from the hyperfine interaction constants varies with rotational state.² One explanation for this unusual behavior is the presence of two minima, a global minimum at the hydrogen bonded, Ar-HF like structure with a secondary minimum at the T-shaped, Ar-HCCH like structure. Unusual isotopic dependences arise from tunneling into the secondary minimum, which is not a classically allowed region but is sufficiently low in energy that significant penetration does occur. The first excited bending states are classically allowed in the secondary minimum and are thus predicted to lie at unusually low energies. These low lying vibrational states contribute to the large centrifugal distortion. The secondary, T-shaped, minimum has a shorter center of mass separation than the hydrogen bonded minimum. This means the relative energetics of the two minima change with the overall rotational energy, leading to the observed dependance of the vibrationally averaged angle on rotational state.

In solving for the vibrational wavefunctions, a "reversed Born-Oppenheimer angular radial separation" technique is used to generate an approximate wavefunction. Numerical relaxation techniques are then used to bring the approximate wavefunctions into agreement with the full Hamiltonian of the ground vibrational state. Coriolis interactions with excited vibrational states are included perturbatively.

¹K.R. Leopold, G.T. Fraser, F.J. Lin, D.D. Nelson, and W. Klemperer, J. Chem. Phys. **81** (11), 4922 (1984).

²T.D. Klots, C.E. Dykstra, and H.S. Gutowsky, J. Chem. Phys. **90** (1), 30 (1989).

Address of Yaron and Klemperer: Dept. of Chem., Harvard University, Cambridge, MA 02138.

ME10 (4:21)

A COUPLED LASER ABLATION PULSED FOURIER TRANSFORM MICROWAVE SPECTROMETER - INITIAL TESTS

R. D. SUENRAM, F. J. LOVAS, AND K. MATSUMURA

A pulsed Nd-YAG ablation source has been coupled to a Fabry-Perot cavity, Fourier transform microwave spectrometer. The pulsed laser is used to vaporize "non-volatile" substances in the throat of a pulsed nozzle source. The vaporized substances are entrained in an inert carrier gas and pulsed into the Fabry-Perot cavity of the Fourier transform spectrometer. Initial experiments have involved the first microwave measurement of the interstellar species SiC₂. The 1₀₁₋₀₀₀ transition of ²⁸SiC₂ was observed at 23600.242(4) MHz and the corresponding transitions of ²⁹Si and ³⁰Si were also observed. SiC₂ was vaporized from a silicon carbide target rod. The electric dipole moment has also been measured and found to be 2.393(6) D. In another experiment the J = 3-2 and 2-1 transitions of KCl have been observed and measured. In this case, liquid KCl was used to coat the SiC rod. Descriptions of these and subsequent experiments will be given.

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

ME11 (4:38)

A BROADLY TUNABLE, AUTOMATED MICROWAVE SPECTROMETER FOR THE OBSERVATION OF WEAKLY-BOUND COMPLEXES.

R.E. BUMGARNER AND G.A. BLAKE

A microwave spectrometer operating from 20.0-60.0 GHz has been constructed for the observation of rotational spectra of weakly bound complexes. The complexes are created in an expansion through a 0.001" by 0.06-1.75" slit nozzle. The microwaves are frequency modulated at 50 kHz and free space propagated across the molecular beam after which they fall on a standard diode detector. Subsequent lock-in detection at twice the modulation frequency is performed to increase the signal-to-noise.

A phase-locked, GPIB controllable frequency synthesizer capable of operating at 10.0 MHz-20.0 GHz is used in combination with a doubler or tripler to generate the radiation. The lock-in amplifier is also GPIB controlled so that the entire experiment is computer interfaced. The broadbandness of the quasi-optical propagation scheme allows for sweeps of up to 20 GHz to be performed without operator intervention. Sweep rates of 200 MHz/hour are achievable with good signal-to-noise for weakly bound complexes. The higher frequency range of this spectrometer relative to currently operating Flygare-Balle type instruments should allow for a number of b-type transitions of near prolate complexes to be observed. Applications of this instrument to new measurements on Ar-HCl, Ar-HCN, (HCN)₂ and other molecules will be presented.

ADDRESS OF THE AUTHORS: Division of Geology and Planetary Sciences, MS 170-25, CalTech, Pasadena, Ca. 91125.

ME12 (4:55)

TUNABLE FAR IR LASER SPECTROSCOPY OF WEAKLY-BOUND CLUSTERS

G.A. BLAKE and R.E. BUMGARNER

A spectrometer consisting of a tunable far IR (FIR) laser system and a planar supersonic jet has been constructed for the observation of low energy vibrations and tunneling motions of weakly bound clusters. The tunable FIR radiation is produced by non-linear mixing of a line tunable FIR laser and tunable (2 GHz - 80 GHz) microwave radiation in a GaAs barrier diode. The planar supersonic jet is produced by gas expansion through a 0.001" by 1.75" slit nozzle. A mass flow control/gas mixing system allows systematic and reproducible variation of the gas mixture ratios and pressures to optimize production of the species of interest.

If the microwave spectrum of the species is known, this optimization may be performed while looking at a microwave signal with our microwave spectrometer (see R.E. Bumgarner and G.A. Blake paper presented at this symposium) prior to attempting the more tedious FIR experiment. FIR measurements on (HCN)₂, Ar-HCN and other species will be presented.

ADDRESS OF THE AUTHORS: Division of Geological and Planetary Sciences, MS 170-25, CalTech, Pasadena, Ca. 91125.

MF1 (1:30)

THE TORSIONAL SPECTRUM OF CH₃CD₃ AND C₂D₆

N. MOAZZEN-AHMADI, T. AMANO, J.W.C. JOHNS, A.R.W. MCKELLAR, AND I. OZIER

We have recorded the far-infrared spectrum of CH₃CD₃ and C₂D₆ in the regions of the forbidden torsional fundamentals under relatively large pressure-pathlength conditions. The observations were made using a modified Bomem spectrometer, with an absorption path of 20 m, a temperature of 230 K, pressures of 50-80 torr, and a resolution of 0.01 cm⁻¹. The most prominent features of the spectra are the unresolved Q-branches of the various torsional components of the $\nu_4=1-0$ band of C₂D₆ with an origin at about 208.5 cm⁻¹, and of the $\nu_6=1-0$ band of CH₃-CD₃ with an origin at about 252.70 cm⁻¹. To lower frequencies there are the partially-resolved Q-branches of the $\nu=2-1$ hot bands at about 193.0 cm⁻¹ for C₂D₆ and 227.9 cm⁻¹ for CH₃CD₃. The P- and R-branches of the fundamental consist of peaks about 0.2 cm⁻¹ wide due to unresolved clusters. These peaks can be followed up to J=30 in both branches.

We have also recorded both low (230 K) and room temperature spectra of the lowest lying allowed fundamental bands around 594 cm⁻¹ (C₂D₆) and 679 cm⁻¹ (CH₃CD₃) with a resolution of 0.0013 cm⁻¹. Over 1000 transitions have been identified in the ^PP-, ^RR-, ^PR-, and ^RP-branches for each molecule.

In addition, the millimeter wave spectrum of CH₃CD₃ has been recorded at around 240-360 GHz in the $\nu_6=0$ and 1 torsional states for several R-branch transitions. K-splitting has been observed for both states, but not σ -splitting.

We will present results for the ground vibrational state of both isotopes based on the analysis of the torsional fundamental together with combination differences obtained from the lowest lying allowed fundamentals and their corresponding hot bands.

Address of Moazzen-Ahmadi, Amano, Johns, and McKellar: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

Address of Ozier: Department of Physics, University of British Columbia, Vancouver, B.C. V6T 2A6, Canada.

MF2 (1:47)

ANALYSIS OF THE LOWEST LYING DEGENERATE FUNDAMENTAL OF CH₃CD₃

N. MOAZZEN-AHMADI, J.W.C. JOHNS, A.R.W. MCKELLAR, I. MUCKHOPADHYAY, I. OZIER, AND R.I. THOMPSON

The lowest lying vibrational fundamental ($\nu_{12}=1-0$) in CH₃CD₃ has been studied between 640 and 720 cm⁻¹ using a modified Bomem spectrometer with an unapodized resolution of 0.0013 cm⁻¹. The experimental conditions were: path=2 m, T=-145 C, P=0.4 Torr; and path=2 m, T=22 C, P=1.2 Torr. Over 1000 transitions have been identified obeying the selection rules $\Delta\nu_6=1$, $\Delta(k-l)=0$, and $\Delta J=0, \pm 1$, with $\Delta\nu_6=\Delta\sigma=0$, where ν_6 is the principal torsional quantum number and σ labels the torsional sublevels. The data clearly reveal that many of the ($\nu_{12}=1, \nu_6=0$) levels are resonantly perturbed by ($\nu_{12}=0, \nu_6=3$) levels of the ground vibrational state for several different (k, σ). The perturbation can be accounted for using a Hamiltonian model¹ explicitly including the effect of the Coriolis interaction and a higher order Coriolis-like term that arises from the off-diagonal part of the operator responsible for the l-type doubling. The overall data set consists of 4 microwave transitions and molecular beam data² in the ground vibrational state, in addition to the lines from the ν_{12} band up to K=11 and J=15. The model fits the observed frequencies to within experimental error except for transitions connected to the levels ($\nu_{12}=1, K=2, \sigma=1, l=1$) for J>6. These levels are severely perturbed and undergo a crossover.

¹N. Moazzen-Ahmadi, I. Ozier, and W.L. Meerts, J. Mol. Spectrosc., to be published.

²I. Ozier and W.L. Meerts, Can. J. Phys. 62, 1844-1854 (1984).

Address of Moazzen-Ahmadi, Johns, and McKellar: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

Address of Moazzen-Ahmadi, Muckhopadhyay, Ozier, and Thompson: Department of Physics, University of British Columbia, Vancouver, B.C. V6T 2A6, Canada.

MF3 (2:04)

ROTATIONAL PARAMETERS OF THE ETHANE TORSIONAL STATE FROM COMBINATION DIFFERENCES IN $\nu_9 + \nu_4 - \nu_4$

W. E. BLASS, G. W. HALSEY, JOEL SUSSKIND, D. C. REUTER and D. E. JENNINGS

Using interferometric spectra obtained on the McMath Solar Telescope FTS spectrometer in double pass configuration (0.0025cm^{-1} resolution), the $\nu_9 + \nu_4 - \nu_4$ hotband has been assigned. The torsional splittings, on the order of 0.1cm^{-1} , are clearly resolved. Lower state combination differences yield the following $B_{4\sigma}$ values: $0.6605099(77)$, $0.6605005(44)$, $0.6604930(54)$, $0.6604846(77)\text{cm}^{-1}$ for $\sigma = 0, 1, 2, 3$ respectively. $D_{4\sigma}^J$ is determined to be $1.0261(68)$, $1.0214(36)$, $1.0158(49)$, and $1.0147(74) \times 10^{-6}\text{cm}^{-1}$, respectively. $D_{4\sigma}^{JK}$ yields $2.74(16)$, $2.72(18)$, $2.73(12)$, and $2.68(18) \times 10^{-1}\text{cm}^{-1}$.

Making use of the Fourier expansion formalism introduced by Lin and Swalen¹ and further developed by Meerts and Ozier,² Wong *et al.*³ and used by Moazzen-Ahmadi *et al.*,⁴ the results above have been analyzed further.

We define effective constants by the following equations:

$$\begin{aligned} B_{\text{eff}}(\nu_4, \sigma) &= B_{r, \sigma} = B + \eta b(1/2) \langle \cos(6\gamma) \rangle + \xi b \langle P\gamma^2 \rangle \\ D_{\text{eff}}^J(\nu_4, \sigma) &= D_{r, \sigma}^J = D^J + \eta dj(1/2) \langle \cos(6\gamma) \rangle + \xi dj \langle P\gamma^2 \rangle \\ D_{\text{eff}}^{JK}(\nu_4, \sigma) &= D_{r, \sigma}^{JK} = D^{JK} + \eta dj k(1/2) \langle \cos(6\gamma) \rangle + \xi dj k \langle P\gamma^2 \rangle. \end{aligned}$$

In these equations, $\langle \dots \rangle$ are the diagonal values of the $\cos(6\gamma)$ and P^2 matrices in the representation which diagonalizes the torsional Hamiltonian. The terms ηx and ξx , $x = b, dj, dj k$, are constant coefficients determined herein by fitting the appropriate equation to the results quoted above. Predictions of higher excited torsional state rotational parameters are presented.

¹C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.* 31, 841-892 (1959).

²W. L. Meerts and I. Ozier, *J. Mol. Spectrosc.* 94, 38-54 (1982).

³M. Wong, I. Ozier, and W. L. Meerts, *J. Mol. Spectrosc.* 102, 89-111 (1983).

⁴N. Moazzen-Ahmadi, H. P. Gush, M. Halpren, H. Jagannath, A. Leung, and I. Ozier, private communication.

Address of Blass and Halsey: Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200

Address of Halsey, Susskind, Reuter, and Jennings: Goddard Space Flight Center, Greenbelt, Maryland 20771

MF4 (2:21)

LINESHAPES OF TRANSFERRED SPIKES IN $^{15}\text{NH}_3$ OBSERVED BY INFRARED-INFRARED FOUR-LEVEL DOUBLE RESONANCE¹

Yukari Matsuo and R. H. Schwendeman

The lineshapes of transferred spikes in the velocity distribution observed by infrared-infrared four-level double resonance have been analyzed by using a Keilson-Storer type collision kernel.² The transitions have been observed by pumping a fundamental transition that is in near coincidence with a CO_2 laser and probing a hot-band transition by means of an infrared microwave sideband laser spectrometer. Detailed analyses have been performed for the lineshapes of the double resonance effects in the saR(1,0) and saQ(3,3) transitions in the $2\nu_2 + \nu_2$ hot band under the influence of pumping of the asR(2,0) transition in the ν_2 band. Each lineshape consists of a Gaussian part centered on the resonance frequency of the probed transition and a transferred spike offset from the resonance frequency by the difference between the frequency of the pump laser and the resonance frequency of the pumped transition. The Gaussian part is subtracted from the experimental lineshape and the difference is fit to a sum of two Keilson-Storer lineshapes. We tentatively interpret the two contributions to the transferred spike to be the result of $\Delta J = \pm 1$ and $\Delta J = \pm 2$ collisionally-induced transitions. The transferred spike observed for the saR(1,0) transition ($\Delta K = 0$ collisions) is much sharper than that observed for the saQ(3,3) transition ($\Delta K = 3$ collisions). The pressure dependence of the observed double resonances will also be discussed.

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

²J. Keilson and J. E. Storer, *Q. Appl. Math.* 10, 243-253 (1952).

Address of Matsuo and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824.

MF5 (2:38)

OBSERVATION OF TRANSFERRED SPIKES IN $^{13}\text{CH}_3\text{F}$ BY INFRARED-INFRARED FOUR-LEVEL DOUBLE RESONANCE¹

Yukari Matsuo and R. H. Schwendeman

Infrared-infrared four-level double resonance has been observed by pumping the R(4,3) transition in the ν_3 fundamental band of $^{13}\text{CH}_3\text{F}$ by means of a CO_2 laser and by probing vibration-rotation transitions in the $2\nu_3 \leftarrow \nu_3$ hot band with an infrared microwave sideband laser spectrometer. Sharp transferred spikes in the velocity distribution were observed in transitions originating from (J,3) levels ($\Delta K = 0$), but not from other levels. The transferred spikes were observed for J values up to 22, corresponding to $\Delta J = 17$. The spikes are sharp up to about $\Delta J = 5$ and are rather broad for $\Delta J > 10$. If the principal selection rule for collisionally-induced transitions is $\Delta J = 0$ or ± 1 , the observation of spikes for J = 22 indicates that there is still some conservation of velocity after as many as 17 collisions. A value for the mean change in velocity upon collision will be reported and its variation with J will be discussed.

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

Address of Matsuo and Schwendeman, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

MF6 (2:55)

INTENSITY ANOMALIES DUE TO A CORIOLIS RESONANCE IN THE SPECTRUM OF H^{13}CNO

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

A collection of Coriolis-allowed bands have been observed in the far infrared spectrum of H^{13}CNO , recorded with the Bruker IFS 120 HR and a resolution of 0.003 cm^{-1} . These bands are not detectable at all in the parent species. Each of these bands acquires intensity from the Coriolis resonance between the $(\nu_4, \nu_5)^l = (02)^{0e}$ and $(10)^{1e}$ vibrational states. Further Coriolis-induced transitions have been found in the microwave region. The present work is concerned with deriving information from the intensity of the perturbation-allowed transitions.

Address of B. P. Winnewisser, G. Wagner and M. Winnewisser: Physikalisch-Chemisches Institut, Justus Liebig Universität, D-6300 Giessen, Federal Republic of Germany.

MF7 (3:12)**THE HIGH RESOLUTION INFRARED AND MICROWAVE SPECTRA OF ISOCYANOGEN, CNCN**

F. STROH, M. WINNEWISSER and M. C. L. GERRY

The rotational and rovibrational spectra of isocyanogen, CNCN, have been observed for the first time. In the region from 10 to 40 GHz the rotational transitions of the ground and four excited vibrational states as well as the ground state transitions of four isotopic species in natural abundance have been measured by FT-MW spectroscopy. The measurements were also extended to the MMW and SMMW regions. The rotational analysis and the analysis of the observed complex nuclear quadrupole hyperfine structure of the individual rotational transitions are in progress. From the obtained preliminary rotational constants we have determined the structure of the non-centrosymmetric molecule CNCN: $r(\text{C}\equiv\text{N})=117.5$ pm, $r(\text{N}-\text{C})=131.4$ pm and $r(-\text{C}\equiv\text{N})=116.0$ pm.

The vibrational fundamentals were observed by high resolution FT-IR spectroscopy using the Bruker IFS 120 HR. The band centers determined so far are located at $\tilde{\nu}_1=2302.00$ cm^{-1} , $\tilde{\nu}_2=2059.73$ cm^{-1} , $\tilde{\nu}_3\approx 975$ cm^{-1} , $\tilde{\nu}_4\approx 470$ cm^{-1} and $\tilde{\nu}_5=194.753$ cm^{-1} . Further measurements of these bands and their respective analysis will be reported at the meeting.

Address of F. Stroh and M. Winnewisser: Physikalisch-Chemisches Institut, Justus Liebig Universität, D-6300 Giessen, Federal Republic of Germany.

Address of M. C. L. Gerry: Abteilung Chemische Physik am Institut für Physikalische Chemie, Universität Kiel, D-2300 Kiel, Federal Republic of Germany. On leave from: Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, B. C. Canada V6T 1Y6.

Intermission**MF8 (3:40)****VIBRATIONAL LADDERS, STATE DENSITIES, AND DISSOCIATION PATHWAYS: APPLICATIONS OF SPECTROSCOPY TO LASER PHOTOCHEMISTRY**

ROBIN S. McDOWELL, BURTON J. KROHN, AND JOHN L. LYMAN

Vibrational ladders of the spherical-top molecules SiF_4 , SF_6 , and UF_6 will be discussed. Special attention will be paid to the ν_3 ladders, which can be easily pumped up to the vibrational "quasicontinuum" and on to dissociation. The differing vibrational state densities of these molecules result in differing behavior in multiphoton absorption and laser-induced photodissociation. Vibrational states have been calculated, with anharmonicity included, for these molecules for vibrational energies of up to 15,000 cm^{-1} and for state densities of up to 10^8 levels/ cm^{-1} ; comparison will be made with the results of the approximation method of Whitten and Rabinovitch.¹ The effect of anharmonicity in increasing the state densities, and implications for photochemistry and thermodynamics, will be discussed.

¹ G. Z. Whitten and B. S. Rabinovitch, J. Chem. Phys. 38, 2466 (1963).

Address: University of California, Los Alamos National Laboratory, Los Alamos, N.M. 87545

MF9 (3:52)**INFRARED SPECTRA OF THE ν_3 BAND IN CD_3**

Wafas M. Fawzy and Trevor J. Sears

Ro-vibrational spectra of the ν_3 fundamental infrared transition in the CD_3 radical have been recorded using a diode laser around 2380 cm^{-1} . The CD_3 radical was produced by photolyzing CD_3I using excimer laser (KrF) radiation at 248 nm.

Rotational analysis of the observed spectra is in progress. Ro-vibrational spectra and molecular parameters will be presented.

Address-Fawzy and Sears: Brookhaven National Laboratory, Chemistry Department, Upton, NY 11973

MF10 (4:09)

HIGH RESOLUTION INFRARED STUDY OF THE $\nu_3 + \nu_6 \leftarrow \nu_6$ BAND OF $^{12}\text{CH}_3\text{F}^1$

Han G. Cho, Yukari Matsuo, and R. H. Schwendeman

The $\nu_3 + \nu_6 \leftarrow \nu_6$ hot band of $^{12}\text{CH}_3\text{F}$ (1039 cm^{-1} , E ← E symmetry) has been recorded at Doppler-limited resolution by an infrared-microwave sideband laser spectrometer. More than 200 hotband transitions have been assigned in spectra taken with a sample at 0.5 Torr pressure in a White-type cell with 8-meter path. The transitions were identified by eliminating from the spectrum transitions in the ν_3 bands of $^{12}\text{CH}_3\text{F}$ and $^{13}\text{CH}_3\text{F}$ and in the $2\nu_3 \leftarrow \nu_3$ band of $^{12}\text{CH}_3\text{F}$. The frequencies of these transitions were predicted by the use of previously-reported constants. The assignment was assisted by the results of previous infrared and microwave studies of transitions involving the ν_6 and $\nu_3 + \nu_6$ vibrational states.

The spectra, which include a number of well-resolved l -doublets, were analyzed by using $\Delta k = 0$ and $\Delta l = 0$ selection rules. The molecular parameters determined for the ν_6 and $\nu_3 + \nu_6$ states, including the l -type doubling constants, will be discussed and compared to the values obtained in earlier work.

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

Address of Cho, Matsuo, and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824.

MF11 (4:24)

HIGH RESOLUTION INFRARED AND INFRARED RADIO FREQUENCY DOUBLE RESONANCE STUDY OF THE ν_2 VIBRATIONAL BANDS OF $\text{CD}_3\text{}^7\text{Br}$ and $\text{CD}_3\text{}^81\text{Br}^1$

Han-G. Cho and R. H. Schwendeman

The ν_2 vibrational bands of $\text{CD}_3\text{}^7\text{Br}$ (991.397 cm^{-1}) and $\text{CD}_3\text{}^81\text{Br}$ (991.388 cm^{-1}) have been recorded by an infrared-microwave sideband laser spectrometer. More than 100 rovibrational transitions have been assigned and analyzed for each species. In each case, it was necessary to include the effects of Coriolis coupling to the corresponding ν_6 band. In addition, the frequencies of approximately 200 pure quadrupole transitions have been measured for each species to an accuracy of few kHz by the method of infrared radio frequency double resonance. The infrared-microwave sideband laser operating in the cavity mode was used as the pumping source for the double resonance experiments.

Newly-determined rovibrational parameters for the ground and $\nu_2 = 1$ states will be reported for the two isotopic species. Quadrupole coupling constants, including centrifugal distortion terms, and spin-rotation interaction constants will also be presented.

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

Address of Cho and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824.

MF12 (4:42)

HIGH RESOLUTION INFRARED SPECTRA OF ISOTOPIC BENZENES, $^{13}\text{C}_6\text{H}_6$ AND $^{12}\text{C}_6\text{D}_6$
J. PLÍVA, J.W.C. JOHNS, L. GOODMAN, A. VALENTIN, AND L. HENRY

Three perpendicular bands of $^{13}\text{C}_6\text{H}_6$ and two bands of $^{12}\text{C}_6\text{D}_6$ have been measured with high resolution Fourier transform instruments to provide reliable data necessary for calculations of the force field for the benzene molecule. Analysis of the $^{13}\text{C}_6\text{H}_6$ bands ν_{14} , ν_{13} , and ν_{12} near 1018, 1454, and 3065 cm^{-1} respectively, and of the $^{12}\text{C}_6\text{D}_6$ bands ν_{14} and ν_{13} near 814 and 1335 cm^{-1} , yielded accurate values for the band origins, Coriolis coupling parameters, for the vibrational dependences of the rotational constants B and C, as well as for the ground state constants B_0 , D_J^0 , and D_{JK}^0 of these molecules. It is found that the observed isotopic shifts in the values of the Coriolis constants ζ_t on substitutions $^{12}\text{C}_6 \rightarrow ^{13}\text{C}_6$ and $\text{H}_6 \rightarrow \text{D}_6$ cannot be accurately accounted for by a general harmonic force field for the E_{1u} normal modes of benzene, probably due to anharmonic effects.

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

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

Address of Goodman: Wright and Riemann Chemistry Laboratories, Rutgers University, New Brunswick, N. J. 08903.

Address of Valentin and Henry: Laboratoire de Physique Moléculaire et Atmosphérique CNRS 060136, Université Pierre et Marie Curie, 75230 Paris, France.

MF13 (4:59)

ABSOLUTE INTENSITIES OF THE ν_5 FUNDAMENTAL AND NEARBY TWO QUANTUM HOTBANDS OF ACETYLENE IN THE 14μ REGION USING A TUNABLE DIODE LASER

M. WEBER, W.E. BLASS, KAREN R. CZOR, AND J.F. BRANNON

Using a TDL-system at 0.0005cm^{-1} resolution, absolute intensity measurements were conducted at the ν_5^1 fundamental and $\nu_4+\nu_5^0+\nu_4^1$ hotband of $^{12}\text{C}_2\text{H}_2$, and the ν_5 fundamental of the isotope $^{13}\text{C}^{12}\text{CH}_2$. The following vibrational intensities per unit partial pressure at 296°K were retrieved from our data: $578\pm 27\text{cm}^{-2}\text{atm}^{-1}$ for ν_5^1 , $13.4\pm 0.9\text{cm}^{-2}\text{atm}^{-1}$ for $\nu_4+\nu_5^0+\nu_4^1$, and $888\pm 57\text{cm}^{-2}\text{atm}^{-1}$ for $\nu_5^1(^{13}\text{C}^{12}\text{CH}_2)$. The retrieved intensity ratio of the ν_5^1 fundamental for the isotope and major species, here equal to 3/2, disagrees with the results of Varanasi *et al.*¹, from which a ratio of about one is inferred. Implications of our results on the question of the isotopic ratio $^{13}\text{C}/^{12}\text{C}$ in the Jovian atmosphere will be discussed.^{2,3} Extension of our measurements to other two quantum hotbands are under way. These results will be presented along with a discussion of the regional intensity distribution of acetylene in the 14μ region.

1. P. Varanasi, L.P. Giver, and F.P.J. Valero, JQSRT 30, 497(1983)
2. A. Chedin and N.A. Scott, JQSRT 32, 453(1984)
3. R. Courtin, D. Gautier, A. Marten, and V. Kunde, Icarus 53, 121(1983)

Address of Weber, Blass, Czor, and Brannon: Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37966-1200

MG1 (1:30)ESR OF TRANSITION-METAL DIATOMIC IONS: Cu_2^+ , Ag_2^+ , Au_2^+

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

The molecular cations Cu_2^+ , Ag_2^+ , and Au_2^+ were generated in neon matrices at 4 K by simultaneous laser vaporization of the appropriate metal and open-tube neon discharge (16.8 eV) photoionization.¹ The ESR spectra are all of $S = 1/2$ species exhibiting hyperfine splittings due to the $^{63}\text{Cu}(I = 3/2)$, $^{107,109}\text{Ag}(I = 1/2)$, and $^{197}\text{Au}(I = 3/2)$ nuclei. Variations in the hyperfine and g tensor components in the series are interesting and will be discussed. Comparison will be made with other, less gas-like, environments.²

¹ L. B. Knight, Jr., *Acc. Chem. Res.* **19**, 313 (1986).² C. E. Forbes and M. C. R. Symons, *Mol. Phys.* **27**, 467 (1974); Yu. N. Alenko, R. A. Zhitnikov, V. K. Krasikov, and D. P. Peregud, *Fiz, Tverd. Tela* **18**, 1552 (1976); J. R. Morton and K. F. Preston, *J. Magn. Reson.* **68**, 121 (1986).

Address of authors: Department of Chemistry, University of Florida, Gainesville, FL 32611.

MG2 (1:47)GROUND ELECTRONIC STATES OF THE VNi , VPd , VPt , NbNi , AND NbPd MOLECULES

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

These isovalent transition-metal diatomics were established to have 4Σ ground states from ESR spectra measured in neon and argon matrices at 4 K. Hyperfine splittings due to interaction with the ^{51}V , ^{195}Pt , and ^{93}Nb nuclei were observed. Zero-field splitting constants were not measured but deduced to be greater than 1 cm^{-1} .

The bonding in these 15 valence ($s + d$) electron molecules will be compared to that in the 13 valence-electron (2Σ) series ScNi , ScPd , YNi , YPd .¹

¹ R. J. Van Zee and W. Weltner, Jr., *High Temp. Science* **17**, 181 (1984); *Chem. Phys. Lett.* **150**, 329 (1988).

Address of authors: Department of Chemistry, University of Florida, Gainesville, FL 32611.

MG3 (1:59)

TWO PHOTON STUDIES OF MATRIX ISOLATED IODINE

M. A. P. Macler and M. C. Heaven

Visible laser excitation of matrix isolated iodine produced I.R. emissions that have been resolved into three components: the $\text{A}(^3\Pi_1) \rightarrow \text{X}(^1\Sigma_0^+)$ and $\text{A}'(^3\Pi_2) \rightarrow \text{X}$ systems of I_2 and the $\text{I } 2^2\Pi_{1/2} \rightarrow 2^2\Pi_{3/2}$ transition.¹ Single photon 193nm excitation of Ar isolated iodine produced a U.V. emission at 380 nm ($\text{D}'(^3\Pi_{2g}) \rightarrow \text{A}'(^3\Pi_{2u})$) and the I.R. emission systems.²

Further studies of visible excitation of concentrated rare-gas iodine matrices revealed A' fluorescence decay curves which were bi-exponential. The fast component ($\tau = 13 \pm 2 \text{ ms}$ in Ar) corresponded to radiative decay, while a weak, slow component ($\tau \approx 48 \pm 4 \text{ ms}$) was thought to be a consequence of energy transfer from shallow-bound metastable electronic states. Sequential 2-photon excitation was used to confirm this hypothesis. In one series of experiments 532nm pulses were used to excite the metastable states. Population in these states was monitored by using 308nm pulses to excite to the D' state. The metastable state decay lifetime was determined by following the D' \rightarrow A' emission intensity as a function of the delay between the 532 and 308nm pulses. A $51 \pm 7 \text{ ms}$ lifetime was observed, in excellent agreement with the rate at which population was transferred to the A' state.

Similar results were obtained with a 193nm pump 308nm probe sequence. In this case initial excitation of D' was followed by radiative relaxation into several valence states. The decay of these states was reflected in the delay dependence of the probe laser fluorescence.

Spectral and temporal analyses of these experiments will be discussed.

1. W. Fawzy, M. Macler, J. P. Nicolai and M. C. Heaven, submitted to *J. Chem. Phys.*

2. M. A. P. Macler and M. C. Heaven, RG 14, 43rd Symp. on Molec. Spectrosc. 1988, O.S.U.

Work supported by AFOSR under grant 88-0249

Address of Macler and Heaven: Department of Chemistry, Emory University, Atlanta, GA, 30322.

MG4 This paper is being presented as WG6

ANALYSIS OF THE VIBRATIONAL BANDS OF ELECTRONICALLY EXCITED ArHO AND ArDO

M. C. Heaven

Electronic spectra for ArHO^{1,2} and ArDO¹ have been reported recently. The complex has been detected via the vibronic bands associated with the OH(D) $A^2\Sigma^+ \leftarrow X^2\Pi_{3/2}$ transition. All bands recorded to date have originated from the ground state zero point level.

In the vicinity of the OH(D) A-X 1-0 and 0-0 transitions, several progressions involving excitation of the van der Waals modes were observed.^{1,2} These progressions could not be simultaneously fitted to simple polynomial expansions of the vibrational quantum numbers. Consequently, the vibrational eigenvalues have been calculated directly from trial three-dimensional potential energy surfaces. This was accomplished by diagonalizing the matrix of the Hamiltonian given by Le Roy and Carley,³ set up in an optimized numerical basis set. Preliminary calculations indicate a linear Ar-HO equilibrium structure, large amplitude bending, and extensive bend-stretch coupling. Details of the calculations and an approximate potential energy surface will be presented.

(Joel M. Bowman and Bela Gazdy are gratefully acknowledged for the program used in this work, and for several helpful discussions.)

1. W. M. Fawzy and M. C. Heaven, J. Chem. Phys. **89**, 7030 (1988); J. Chem. Phys. to be submitted.
2. M. T. Berry, M. R. Brustin, J. R. Adamo, and M. I. Lester, J. Phys. Chem. **92**, 5551 (1988); M. T. Berry, M. R. Brustin and M. I. Lester, Chem. Phys. Lett. **153**, 17 (1988).
3. R. J. Le Roy and J. S. Carley, Adv. Chem. Phys. **42**, 353 (1979).

Address of Heaven: Department of Chemistry, Emory University, Atlanta, GA 30322.

MG5 (2:16)

PRODUCTION OF TRIPLET TRIMETHYLSILYLNITRENE BY DECOMPOSITION OF THE PARENT AZIDE

Robert F. Ferrante

Earlier studies of the direct photolytic decomposition of t-butyl azide, $(\text{CH}_3)_3\text{CN}_3$, or trimethylsilyl azide, $(\text{CH}_3)_3\text{SiN}_3$, or their substituted congeners showed little evidence for the production of triplet nitrene intermediates. Furthermore, the absence of the expected imine photoproduct with the silicon analog suggested substantially different chemistry. The independent existence of the t-butyl nitrene radical $(\text{CH}_3)_3\text{CN}$ has been previously confirmed by sensitized photolysis experiments. Here, signals attributable to triplet trimethylsilylnitrene, $(\text{CH}_3)_3\text{SiN}$, are reported.

Fragmentation products formed when trimethylsilyl azide vapor interacts with metastable N_2 or Ar generated in a microwave discharge were trapped in N_2 or Ar matrices at 10 K. The ESR spectrum showed a strong xy line near 8000 G, indicating an axially symmetric triplet ground state molecule with $D = 1.56 \text{ cm}^{-1}$. The line appears as a poorly resolved triplet split by 13.5 G, comparable to the N hyperfine observed in other nitrenes. This signal could not be produced by photolysis, and decayed on UV irradiation or annealing to $T > 35 \text{ K}$. IR studies indicated a set of new bands that followed the behavior of the ESR line; these were substantially different from IR spectra produced by photolysis. Examination of the data suggests the formation of triplet trimethylsilylnitrene.

Address of Ferrante: Department of Chemistry, U.S. Naval Academy, Annapolis, MD 21402

MG6 (2:28)A THEORETICAL STUDY OF C₄O and C₆OD.W. Ewing

Ab initio calculations were performed which corroborate the interpretation of recent ESR data of Van Zee, Smith, and Weltner for C₄O and C₆O¹. Bond lengths, gross orbital spin populations, $1\Sigma^+ - X^3\Sigma^-$ energy differences, stabilities, dipole moments, and vibrational frequencies were obtained from Hartree-Fock calculations. Electron correlation was included via second, third, and fourth order Moller-Plesset perturbation theory.

¹R.J. Van Zee, G.R. Smith, and W. Weltner, Jr., J. Am. Chem. Soc. 110, 609 (1988).

Address of Ewing: Department of Chemistry, John Carroll University, Cleveland, OH 44118.

MG7 (2:40)

INFRARED MATRIX ISOLATION STUDIES OF HYDROGEN BONDS INVOLVING C-H BONDS: ALKYNES WITH BASES CONTAINING N, P, O and S DONORS. Mei-Lee H. Jeng and Bruce S. Ault.

The matrix isolation technique combined with infrared spectroscopy has been employed to isolate and characterize hydrogen bonded complexes between alkynes and a number of bases containing N, P, O and S donors. Distinct evidence for hydrogen bond formation was observed for each case, with a characteristic red shift of C-H stretching motion ν_s . These shifts, in the range of 30-300 cm⁻¹, were distinct and variable with the different alkynes and bases employed. The perturbed C≡C stretching vibration was also observed for most complexes, as was the alkyne hydrogen bending mode. In general, for any base, linear correlations were noted between the magnitude of shift of ν_s (hence the strength of interaction), the gas phase acidity of the alkynes and the Hammett substituent constants of the alkynes. For a given acid, the $\Delta\nu_s$ varied in the order Me₃N > Me₃P > Me₂O > Me₂S; NH₃ > PH₃ > H₂S. The degree of hydrogen bonding shown by a C-H bond was linearly dependent on the reaction partner (or bases) as well as the substituent groups on the alkyne. Lack of correlation of $\Delta\nu_s$ with either σ_I or σ_R alone suggests that both inductive and resonance contributions to the strength of the hydrogen bonding interaction are important.

Address of Jeng and Ault: Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221.

Intermission

THE VIBRATIONAL SPECTRA OF MOLECULAR IONS ISOLATED IN SOLID NEON. I. CO_2^+ AND CO_2^- *

MARILYN E. JACOX AND WARREN E. THOMPSON

When a Ne:CO₂ sample is codeposited with a beam of neon atoms excited in a microwave discharge, both CO_2^+ and CO_2^- are stabilized in sufficient concentration for the detection of their antisymmetric stretching absorption, ν_3 . The position of the absorption for CO_2^+ is in excellent agreement with that recently reported for the gas-phase ion. The positions of the corresponding absorptions of the carbon-13 and oxygen-18 substituted species, reported for the first time, support the assignment. The ν_3 absorption of CO_2^- is significantly shifted from the position previously reported for this fundamental of the M^+CO_2^- species (M = Li, Na, K, Cs) isolated in an argon matrix. Photodetachment of CO_2^- occurs when the sample is exposed to radiation in the visible spectral region. Evidence will be presented for the stabilization of the $\text{CO}_2 \cdots \text{CO}_2^-$ cluster ion in the present experiments.

* Work supported in part by the U. S. Army Research Office under Proposal No. 25664-CH.

Address of Jacox: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899.

Address of Thompson: National Science Foundation, Washington, DC 20550; Guest Worker at the National Institute of Standards and Technology.

MG9 (3:27)

THE VIBRATIONAL SPECTRA OF MOLECULAR IONS ISOLATED IN SOLID NEON. II. O_4^+ AND O_4^- *

WARREN E. THOMPSON AND MARILYN E. JACOX

The O_4^+ and O_4^- cluster ions have been stabilized in solid neon in sufficient concentration for detection of their infrared absorptions in the 700-3000 cm^{-1} spectral region. The absorption of O_4^- had previously been observed in systems in which an alkali metal atom was codeposited with an Ar:O₂ mixture. Its appearance in the present discharge sampling experiments definitively excludes the coordination of a metal atom in an MO_4 structure. Detailed isotopic substitution experiments support the assignment of four infrared absorptions to a vibrational fundamental and combination bands of O_4^+ , for which no spectroscopic data have previously been reported. Analysis of the spectrum provides information regarding the molecular structure of O_4^+ .

* Work supported in part by the U. S. Army Research Office under Proposal No. 25664-CH.

Address of Thompson: National Science Foundation, Washington, DC 20550; Guest Worker at the National Institute of Standards and Technology.

Address of Jacox: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899.

MG10 (3:44)

DETERMINATION OF TWO-DIMENSIONAL CRYSTAL STRUCTURES BY IR SPECTROSCOPY

Otto Berg and George E. Ewing

We have studied the infrared spectra of molecular monolayers on single crystals of sodium chloride. The unprecedented resolution of our experiments has revealed spectroscopic features which are due to dynamic coupling within the adsorbate array. Thanks to the relative passivity of the substrate, it is appropriate to describe the structure and vibrational motion of the monolayer as if it were a two-dimensional molecular crystal. The corresponding branch of symmetry theory involves 80 "plane groups". Plane group analysis has been instrumental to our determination of nontrivial monolayer structures. Examples from recent work will be discussed.

Address of Berg and Ewing: Department of Chemistry, Indiana University, Bloomington, IN 47405

MG11 (4:01)

VIBRATIONAL RELAXATION PROCESSES OF CO ON NaCl (100)

C. NODA, H.-C. CHANG, AND G. E. EWING

Vibrational relaxation processes have been investigated for CO physisorbed on NaCl (100) single crystal surfaces. Two approaches were employed for the study; the temperature dependence of the IR absorption line profile, and laser-induced photodesorption.

At 4K, the full width at half-maximum (FWHM) is 0.11 cm^{-1} partly due to inhomogeneous broadening, placing the lower limit for the lifetime of 50 ps for CO ($\nu=1$). The linewidth increases monitored between 4K and 55K. This behavior can be accounted for by a vibrational phase relaxation process, where the thermal coupling between the CO stretching motion and a low-frequency surface-CO bond motion causes dephasing of the vibrational motion. The frequency and the lifetime of the low-frequency mode was determined to be 50 cm^{-1} and 3 ps, respectively.

At 22K, indirect measurement of the photodesorption rate showed a quantum yield of this process to be less than 10^{-6} . It is believed that the low desorption efficiency is a consequence of energy mismatch between the vibrational quantum and the surface bond.

Address of Noda, Chang, and Ewing: Department of Chemistry, Indiana University, Bloomington, IN 47405

MG12 (4:18)

IR PHOTOMETRY OF THIN FILMS ON SINGLE CRYSTAL DIELECTRIC SUBSTRATES

Huan-Chen Chang, Chifuru Noda, Hugh Richardson and George Ewing

We have developed techniques for measuring high resolution infrared spectra of monolayers of small molecules such as CO or CO₂ on the (100) faces of single crystals of NaCl^{1,2}. The high quality of our data allows the photometry of these systems to be discussed quantitatively. Accordingly, we have developed Maxwell's equations to account for the adsorption of light by these thin films. The measured integrated absorbance for each of these monolayers is compared with the results of simple models which calculate this quantity from isolated gas phase properties. The discrepancy between calculated and measured values differs by 25% or less. Adsorption of molecules onto NaCl(100) therefore alters their optical properties only slightly.

1. H.-C. Chang, H.H. Richardson and E. Ewing, J. Chem. Phys. **89** (1988) 7561.

2. O. Berg and G. Ewing, Surf. Sci. (submitted).

Address of Chang, Noda and Ewing: Department of Chemistry, Indiana University, Bloomington, IN 47405

Address of Richardson: Department of Chemistry, Ohio University, Athens, OH 45701

MG13 (4:35)**BAND SHAPE OF ESTER CARBONYL IN SOLUTION.**
C. CHAPADOS, Y. CAUMARTIN and M. TRUDEL

In solid solutions of large molecules of biological interest such as chlorophylls¹ and proteins, the infrared spectra show large structureless bands. These characteristics are due to overlapping bands. To separate the components in the massive absorptions it is necessary to know the band shapes and bandwidths of the functional group involved in the absorption.

We have used methyl acetate in a CCl₄ solution as a model system for the ester band of solid chlorophyll. The spectra at several concentrations were obtained and merged to obtain a spectrum free of noise. Essentially a single band with an isotope satellite band were obtained. The bandwidth and band shape ratio (Lorentz index over the sum of Lorentz and Gauss indices) of the principal band are 12.6 cm⁻¹ and 0.77, respectively.

The band could not be entirely fit with a gaussian, lorentzian, or product function and signified the presence of weak side components. To retrieve these components we used the Fourier self-deconvolution technique to determine the number of components and locate their positions after which a simulation of the spectrum was performed. By this way we have identified several carbonyl components that we have assigned to different conformers of the molecule. The integrated intensity of the components was used to determine the relative concentration of the conformers.

¹ C. Chapados, Photochem. Photobiol. 47, 115-132 (1988)

Address of Chapados, Caumartin, and Trudel:

Département de chimie-biologie
Université du Québec à Trois-Rivières
C.P. 500, Trois-Rivières
Québec, Canada
G9A 5H7

MG14 (4:47)**STRANGE BEHAVIOR OF THE PAIR ν_3 AND $\nu_2+\nu_6$ IN SOLID ARGON.** **C. CHAPADOS.**

The infrared absorption of SF₆ from 32 to 3000 cm⁻¹ in the gaseous and liquid states has been reported recently¹. It was noted that a weak band containing $\nu_2+\nu_6$ was always found at higher frequencies than the much stronger bands containing ν_3 . In the liquid phase, the positions of these bands are lowered some 24 cm⁻¹ and the intensities tend toward equalization. The pair ν_3 and $\nu_2+\nu_6$ was the exception: while the ν_3 band was displaced 33 cm⁻¹ with a 37 % decreased in intensity, the position and intensity of the $\nu_2+\nu_6$ band were practically unchanged.

In liquid argon, the ν_3 mode shows a single strong band for the ³²S species accompanied with weaker isotopic species. Compared to the gas phase, the position of the band is lowered 8.2 cm⁻¹ while the $\nu_2+\nu_6$ band is undisplaced. In solution, the position of the bands containing ν_3 and $\nu_2+\nu_6$ is lowered by 12 cm⁻¹ on the average. In solid argon, at a temperature only a few degrees below solidification, the pair ν_3 and $\nu_2+\nu_6$ is completely perturbed. The spectrum shows 6 separated bands with weaker satellites in the region from 1000 to 880 cm⁻¹. We will report these results and compared them with those obtained in the gas, liquid, and solid phases. A possible assignment to the bands obtained for SF₆ in solid argon in this spectral region will be given.

¹ C. Chapados and G. Birnbaum, J. Mol. Spec. 132, 323-351 (1988)

Address of Chapados:

Département de chimie-biologie
Université du Québec à Trois-Rivières
C.P. 500, Trois-Rivières
Québec, Canada
G9A 5H7

MG15 (4:59)**EVIDENCE FROM ESR OF NONLINEAR CHARACTER IN C_4 FORMED BY VUV PHOTOLYSIS IN AN ARGON MATRIX**

H.M. CHEUNG AND W.R.M. GRAHAM

The C_4 molecule has been produced by trapping the products of the vacuum uv photolysis of diacetylene and butadiene in Ar at 12 K. Signals at the magnetic field positions of the xy_1 and xy_2 lines previously identified^{1,2} for triplet C_4 formed from graphite vapor, exhibit splitting into separate x and y components in the well resolved ESR spectra obtained by the photolytic decomposition of the C_4H_2 and C_4H_6 precursors in dilute mixtures of ~1:20,000 in argon. Derived zero-field splitting constants are $|D| = 0.2237(2)$ and $E = 2.52(1) \times 10^{-4} \text{ cm}^{-1}$.

The results of extensive annealing experiments at a wide range of mole ratios, argue against multiple trapping sites being responsible for the observed splitting. The spectrum is unaffected by using either parent molecule fully substituted with the deuterium isotope ($I = 1$), indicating that hyperfine splitting due to the presence of hydrogen atoms ($I = 1/2$) cannot account for the observed splittings. Further evidence suggesting nonlinear character for C_4 trapped in solid argon by the photolytic decomposition of C_4H_2 and C_4H_6 , is provided by the hyperfine splittings observed when butadiene, isotopically substituted with carbon-13, is used as the parent molecule.

¹W.R.M. Graham, K.I. Dismuke, and W. Weltner, Jr., *Ap. J.* **204**, 301 (1976).

²R.J. Van Zee, R.F. Ferrante, K.J. Zeringue, and W. Weltner, Jr., *J. Chem. Phys.* **88**, 3465 (1988).

Address of Cheung and Graham: Department of Physics, Box 32915, Texas Christian University, Fort Worth, TX 76129.

Evolution of Molecular Dissociation Through an Electronic Curve Crossing: Polarized Emission Spectroscopy of CH₃I at 266 nm

K. Q. Lao, M. D. Person, P. Xayariboun, and L. J. Butler

We present a study of the dissociation of CH₃I on coupled repulsive electronic potential energy surfaces by the technique of polarized emission spectroscopy. We excite CH₃I at 266 nm and disperse the photons emitted from the dissociating molecule by both frequency and angular distribution with respect to the polarization direction of the excitation laser. We thus measure the polarization of the first twelve C-I stretching emission features, corresponding to the spectral region between 266 and 316 nm. We also obtain the rotational envelope of selected emission features in higher resolution scans in order to detect the change in lineshape with emission into increasingly higher overtones; modelling of these lineshapes supports the polarization results. The polarization measurements show the emission into the first few low-lying C-I stretching vibrational levels is via a transition moment parallel to the absorbing one, consistent with excitation to and emission from the ³Q₀ (2A₁) repulsive surface. Emission to higher C-I stretching overtones shows an increasing contribution from emission via a transition moment perpendicular to the absorbing one, consistent with emission from a repulsive surface of E symmetry following excitation to the ³Q₀ state. We extract from the data the fraction of photons emitted via a perpendicular transition for each of the C-I stretch emission features. The analysis includes the derivation of simple analytical formulas for correcting for a finite detector acceptance angle. We discuss the results in relation to a simple model where photoabsorption excites the molecule to an A₁ repulsive surface (parallel transition moment) and amplitude develops on an E repulsive surface as the molecule dissociates through a curve crossing. The changes in amplitude of the molecular wavefunction on the A₁ versus the E repulsive surfaces during dissociation is thus probed. The simple quasidiatomic Landau-Zener crossing model utilized by other workers cannot fully explain the collection of experimental results over the last decade on the iodoalkane curve crossing. We do, however, suggest an approximation under this inadequate model to extract from our data the electronic energy at which the "curve crossing" occurs. This derived energy is compared to that given in model and ab initio calculations of the excited electronic potential energy surfaces.

Address: The James Franck Institute and Department of Chemistry University of Chicago, Chicago, Illinois 60637

MH 2 (1:47)

VIBRATIONAL DEPENDENCE OF THE ROTATIONAL STRUCTURE AND DISSOCIATION RATES OF THE \bar{A} STATE OF NH₃, NH₂D, NHD₂ AND ND₃,

STEVEN A. HENCK, WEN-BIN YAN, AND KEVIN K. LEHMANN

Microwave-ultraviolet double resonance experiments on the pre-dissociative first excited electronic state of ammonia are presented. Using microwave-ultraviolet double resonance, we are sensitive to only a few rotational transitions at a time. Thus, we have been able to determine the rotational constants and the rotational dependence of the dissociation rate for $\nu_2=0-4$. We have found that Fermi resonance is needed to explain the vibrational state dependence of the dissociation rate.

Address for all authors: Princeton University, Department of Chemistry, Frick Chemical Laboratory, Princeton, New Jersey 08544-1009, USA

MH3 (2:04)

EFFECTS OF ISOTOPIC SUBSTITUTION ON THE CHEMILUMINESCENCE SPECTRA OBTAINED DURING THE REACTION OF F₂ WITH CS₂

R. J. GLINSKI AND C. D. TAYLOR

Emission spectra have been obtained during the gas phase reaction of F₂ with CS₂ on substitution with carbon 13 and sulfur 34 in effort to identify the emission which lies between 550 and 880 nm. Absence of any measurable shift in the vibronic bands on substitution with carbon 13 suggests that carbon is not present in the emitting molecule and that the previous assignment to FCS should be discarded. The measured vibrational frequencies and their shifts on isotopic substitution with sulfur 34 are nearly identical to those that have been reported previously by other workers for the ground electronic state of SF₂.

Another distinct band system has been identified in this reaction system under different reaction conditions. The new bands extend from 700 nm to beyond 880 nm and spacing of approximately 310 cm⁻¹. Spectra obtained in the reactions of F₂ with OCS, CS₂, ³²O₂, and CS₂ ³⁶O₂ will also be presented.

Address: Department of Chemistry, Tennessee Technological University, Cookeville, TN 38505

MH4 (2:16)EMISSION, ABSORPTION AND QUANTUM YIELDS IN THE C_2N_2 $A^1\Sigma^- \leftarrow X^1\Sigma^+$ TRANSITIONJ.B. HALPERN AND S.A. BARTS

We have measured the absorption, emission and photodissociation spectra of cyanogen in the 220 and 210 nm regions near the 4_0^1 and $1_0^1 4_0^1$ bands of the $A^1\Sigma^- \leftarrow X^1\Sigma^+$ system. The spectra were excited with a frequency doubled Nd-YAG pumped dye laser. The doubled light was Raman shifted in high pressures of hydrogen gas. Emission spectra were measured by an unfiltered VUV photomultiplier. The emission spectra did not show all lines that appeared in the absorption spectra and almost all of the intensity was in the $1_0^1 4_0^1$ progression. The radiative lifetime of the emission was 660 ns. We used laser induced fluorescence to measure the relative yield of CN radicals as a function of photolysis wavelength. Above the dissociation threshold the yield generally followed the absorption spectrum. A few nascent quantum state distributions of CN were measured. Energy in the CN fragments appeared to be statistically distributed. These results can be understood if some of the excited C_2N_2 is crossing over into a non-dissociating triplet manifold.

We are attempting to establish quantum yields for dissociation and emission. If possible fluorescence spectra will also be measured. Dispersed fluorescence spectra will identify the emitting state.

Address of Halpern and Barts: Department of Chemistry, Howard University Washington, DC 20059, USA

MH5 (2:28)VIBRATIONAL LEVEL DENSITY AND CORIOLIS COUPLING OF S_0 H_2CO AT $28,000\text{ cm}^{-1}$ Alan Ritter, Donald Frye, Walter Merry, and Hai-Lung Dai

Stark Level-crossing Spectroscopy was used to study S_0 H_2CO vibrational levels at energies near the dissociation threshold to $H_2 + CO$. Laser induced fluorescence was detected from $3 S_1$, 4^1 , $J=1$ ($1_{01}, 1_{10}, 1_{11}$) levels via the $\bar{A} \leftarrow \bar{X}$ excitation. A Stark field was applied to induce a resonant interaction between the S_1 $J=1$ and a S_0 single vibration-rotation level. The resonance was identified as a loss in intensity and a shortening of the lifetime in the fluorescence from the S_1 level.

From the different numbers of S_1 - S_0 resonances encountered by the $K_a=1$ and $K_a=0$ S_1 levels, it was deduced that the K quantum numbers are mixed by Coriolis coupling. However, the mixing is weak enough to allow the S_0 levels to retain their individual tuning characteristics. Counting the number of resonances over the Stark tuning range of the S_1 level and after corrections due to electric field and the Coriolis effects, an S_0 vibrational level density of 75 ± 25 per cm^{-1} was obtained at $28,300\text{ cm}^{-1}$. This number exceeds the best calculated value of 20 per cm^{-1} from an anharmonic direct count.

Address: Chemistry Department, University of Pennsylvania, Phila., PA 19104

Intermission**MH6 (3:00)**PYROLYSIS JET SPECTROSCOPY OF THE S_1 AND T_1 STATES OF THIOFORMALDEHYDEJames R. Dunlop, Jerzy Karolczak, and Dennis J. Clouthier

Emission excitation spectra of the $\bar{a}-\bar{X}$ and $\bar{A}-\bar{X}$ band systems of H_2CS have been recorded at high resolution with jet cooling. Monomeric thioformaldehyde was generated by pyrolysis in the throat of a continuous free jet¹, yielding intense fluorescence and phosphorescence excitation spectra with rotational temperatures of 5-10 K. The spectra have been rotationally analyzed to obtain accurate band origins and rotational constants for a substantial number of upper state levels. In the triplet state, the major spin constants were determinable because transitions to the F_1 , F_2 , and F_3 components are observed. Extensive perturbations are observed in the spectra due to the near-degeneracy of ν_8' and ν_3' .

1) J. R. Dunlop, J. Karolczak and D. J. Clouthier, *Chem. Phys. Lett.* **151**, 362 (1988).

Address of Dunlop and Clouthier: Department of Chemistry, University of Kentucky, Lexington, KY, 40506-0055.

Permanent Address of Karolczak: Quantum Electronics Laboratory, Institute of Physics, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland.

HIGH RESOLUTION LASER SPECTROSCOPY OF CuOH

C. N. JARMAN, W. T. M. L. FERNANDO AND P. F. BERNATH

The emission spectrum of CuOH consist of a strong green band and some weaker bands in the red. Trkula and Harris¹ recorded the high resolution spectrum of the green system. We have detected the weaker red bands by dye laser spectroscopy.

CuOH was produced in a Broida oven by the reaction of Cu metal vapor with H₂O₂. A low resolution laser excitation spectrum showed that there are two distinct electronic transitions. Both of these transitions were then investigated at higher resolution using a single frequency dye laser.

One system centered at 6285Å revealed a very dense spectrum with no band heads. This system appears to obey parallel selection rules and we assign it to the lowest-lying singlet-singlet transition $\tilde{A}^1A' - \tilde{X}^1A'$.

High resolution spectra of the other system near 6600Å showed that the individual rotational lines were split into four components by the nuclear spin I=3/2 of Cu. The magnitude of this effect indicates that the upper electronic state has triplet character. Our preliminary analysis of both electronic systems will be discussed.

¹ M.Trkula and D. O. Harris, J. Chem. Phys., **79**(3), 1138 (1983).

Address of Jarman , Fernando and Bernath: Department of Chemistry, University of Arizona, Tucson AZ 85721.

MH8 (3:29)

Fourier Transform Observation of Jet Cooled Emission
from the CH₃N and CCN radicals

C. R. Brazier, P. G. Carrick, N. H. Oliphant and P. F. Bernath

An improved spectrum of the methyl nitrene radical has been obtained in emission from a corona excited supersonic expansion. Use of a slot nozzle reduces the Doppler broadened linewidth from 0.2 cm⁻¹ to 0.07 cm⁻¹. All of the sub-bands in the O₀⁰ band of the $\tilde{A}^3E - \tilde{X}^3A_2$ system can now be assigned. A rotational analysis using a full ³E-³A Hamiltonian will be presented.

Jet cooled emission from the $\tilde{A}^2\Delta - \tilde{X}^2\Pi$ system of CCN has also been recorded, using the Kitt Peak Fourier transform spectrometer. Emission to the 001, 002, and 100 levels of the $\tilde{X}^2\Pi$ state provides direct gas phase values for the CCN stretching fundamentals.

Address of Brazier and Carrick: Advanced Research in Energy Storage, Air Force Astronautics Lab./LSX, Edwards Air Force Base CA 93523.

Address of Oliphant and Bernath: Department of Chemistry, University of Arizona, Tucson AZ 85721.

MH9 (3:46) LATE PAPER MH11 PRESENTED HERE

THE ELECTRONIC AND GEOMETRIC STRUCTURES OF SEVERAL MOLECULAR STATES OF SCANDIUM NITRIDE

Kathryn L. Kunze and James F. Harrison

This abstract is for MH11

The electronic and geometric structures of fifteen scandium nitride species with formal σ, π, π -triple, σ, π -double, π, π -double, σ -single, and π -single two-electron bonds have been studied by ab initio MCSCF and multi-reference CI calculations techniques. All fifteen species are bound relative to the ground state atoms. In spite of the $a^2D\ 4s23d1$ ground state configurations of the bare Sc, the ground state ScN is the triply-bonded $1\Sigma^+$ with a $3d^3$ configuration dominant in situ. The π, π -doubly bonded $3\Sigma^+$ and the σ, π -doubly bonded 3Π are only 7.4 and 12.1 kcal/mol higher in energy, respectively. A Mulliken population analysis suggests the following: there is substantial ionic character in these bonds; regardless of the number of formal covalent bonds between N and Sc, the gross Sc to N charge transfer is relatively constant for all fourteen species with an in situ $4s13d^2, 4s13d14p1$, or $3d^3$ excited state Sc configuration dominate at equilibrium and is smaller for the one state with an in situ $4s23d1$. The term symbol, calculated bond length (R_{eq} , Å), vibrational frequency (ω_e , cm^{-1}), gross Sc to N charge transfer, and the absolute bond energy relative to the ground state fragments (D_e , kcal/mol) are as follows: Triply bonded species: $1\Sigma^+$; 1.768, 726, 0.59, 62.7. σ, π -Doubly bonded species: 3Π , 1.839, 802, 0.62, 50.6; 1Π , 1.845, 789, 0.62, 49.8; $3B_1$, 2.061, 566, 0.60, 17.8. π, π -Doubly bonded species: $3\Sigma^+$, 1.769, 861, 0.56, 55.3; 3Δ , 1.830, 790, 0.63, 11.7; 1Δ , 1.843, 785, 0.62, 10.5. σ -Singly bonded species: $3\Sigma^-$, 2.058, 577, 0.48, 27.3; $5\Sigma^-$, 2.250, 400, 0.60, 5.6; 5Π , 2.231, 438, 0.64, 10.3; 5Δ , 2.173, 489, 0.65, 21.1; 3Δ , 2.178, 491, 0.66, 18.9; 1Δ , 2.179, 496, 0.67, 17.3. π -Singly bonded species: $5\Sigma^+$, 2.102, 530, 0.58, 2.4; $5B_1$, 2.059, 576, 0.60, 13.7. We examine the effect of the interatomic spin couplings on the structures and we emphasize the structure of the calculations that we have been using for transition-metal containing species.

Address of Kunze and Harrison: Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322

MH10 (4:03)

The Resolved Emission and High Resolution Absorption Spectra of the $n-\pi^*$ Transition in Formyl Cyanide, CHOCN.

R.H. Judge, D.J. Clouthier and D.C. Moule

The pyrolysis of methoxyacetonitrile produces an abundance of simpler molecules as evidenced by the FT-IR spectrum⁽¹⁾. One of the more interesting molecules produced in the pyrolysis is formyl cyanide, CHOCN.

The origin band of formyl cyanide at $26291\ cm^{-1}$ was excited with a YAG pumped dye laser system and the resultant emission dispersed by a low resolution photodiode array spectrometer. An impurity free spectrum is obtained and a preliminary analysis has confirmed the tentative assignments from the weaker and molecule rich FT-IR spectra. Two new ground state frequencies have been observed and assigned. The results of this and the ongoing higher resolution work will be presented.

The high resolution absorption spectrum of the 0^0_0 band of the $X^1A'' \leftarrow X^1A'$ electronic transition in formyl cyanide has been recorded and is similar in appearance to that of the type C origin band of propynal. The results of the preliminary analysis of CHOCN has yielded only the symmetric rotor rotational constants due in part to the heavy congestion near the band origin. Work on a band contour fit and the supersonic jet spectrum is in progress and some of the recent results will be presented.

¹ D.J. Clouthier and D.C. Moule, J. Am. Chem. Soc., 109(21), 6259-61 (1987).

Address of Judge: Department of Chemistry, University of Wisconsin-Parkside, Kenosha, Wisconsin, 53403-2000.

Address of Clouthier: Department of Chemistry, University of Kentucky, Lexington, Kentucky, 40506.

Address of Moule: Department of Chemistry, Brock University, St. Catharines, Ontario, L2S 3A1.

MH12 (4:15)

RESONANCE RAMAN SPECTROSCOPY OF THE ALLYL RADICAL

J.D. GETTY, M.J. BURMEISTER, and P.B. KELLY

The first resonance Raman spectra of the allyl radical have been recorded. The structure and bonding of the allyl radical is of theoretical interest because it is the simplest delocalized pi electron system. The radical is also of interest as a possible combustion intermediate.

The gas phase allyl radical was produced by photolysis of allyl iodide and allyl bromide with the fourth and fifth harmonic of the Nd:YAG laser. The output of a DCM dye laser was frequency tripled to provide tuneable for ultraviolet Raman excitation. The probe laser was tuned to the allyl radical $X^2B_1 \rightarrow B^2B_1$ transition at 223 nm. The Raman scattered light was collected in standard backscatter geometry by a 2 inch f/0.67 spherical mirror and focussed onto the slits of a 1.0 meter Czerny-Turner monochromator. Spectra of the gas phase radical were recorded using blind photomultiplier tube and gated integrator.

The observed spectrum is comprised of four totally symmetric vibrations and several overtones. The observed frequencies will be compared to the theoretical predictions and data derived from infrared matrix isolation and multiphoton ionization methods. Vibrational relaxation of the allyl radical in different buffer gases will also be presented.

Address of Authors: Department of Chemistry, University of California, Davis, CA 95616

MH13 (4:32)

RESONANCE RAMAN SPECTROSCOPY OF THE METHYL RADICAL

S.G. WESTRE AND P.B. KELLY

Resonance Raman spectroscopy has been applied to the study of the gas phase methyl radical. Resonance enhancement allows selective examination of a minority species present in low concentration with minimum interference from other species. This technique has been used to elucidate the ground state vibrational structure of CH_3 and CD_3 . The information gained is complementary to infrared work in that the transitions that are observed are not infrared active. The results of this work compare well with literature values and theoretical predictions.

Vibrational progression of, ν_2 , have been observed. These new observations yield the anharmonic constants for CH_3 and CD_3 .

	CD_3	CD_3
X_{11}	$-22.7 \pm 1.5 \text{ cm}^{-1}$	$-9.1 \pm 1.3 \text{ cm}^{-1}$
X_{12}	$-9.8 \pm 1.5 \text{ cm}^{-1}$	$-4.3 \pm 1.4 \text{ cm}^{-1}$

In the resonance Raman spectrum, the pattern of relative intensities of the rotational lines is a sensitive function of laser excitation frequency and excited state linewidth. By fitting the resonance Raman spectrum the excited state lifetime can be determined.¹ An examination of the vibrational structure of observed absorption bands is also in progress.

¹L.D. Ziegler, J. Chem. Phys. 84 6013 (1986).

Address of Authors: Department of Chemistry, University of California, Davis, CA 95616

TA1 (8:30)

INFLUENCE OF THE AC STARK EFFECT ON MULTIPHOTON TRANSITIONS IN MOLECULES

W. LEO MEERTS, IRVING OZIER AND JON T. HOUGEN

A multiphoton mechanism for molecular beam transitions is presented which relies on a large first-order AC Stark effect to modulate the energy separation of the initial and final states of the multiphoton transition, but which does not require the presence of any intermediate level(s). The theoretical formalism uses ideas from the laser multiphoton literature for a two-level system interacting with a monochromatic electromagnetic radiation field, together with a close analog of the rotating wave approximation. The diagonal matrix elements of the Hamiltonian operator corresponding to the large AC Stark effect are removed by a mathematical substitution which in effect transforms appropriate differences of these diagonal elements into transition moments involving higher harmonics of the frequency of the monochromatic radiation field. The electric field strength of the true monochromatic radiation field is "distributed" among the higher harmonics of the effective field according to an expression involving Bessel functions. Because these Bessel functions are bounded, there exists for a given time t of exposure to the radiation, a threshold for the magnitude of the transition dipole matrix element coupling the two levels: Below this threshold, the transition probability in a traditional one-photon molecular beam electric resonance experiment cannot be made unity simply by increasing the amplitude of the radiation field. In fact, if the coupling matrix element is small enough, the molecular beam electric resonance signal cannot be detected within exposure time t . The algebraic formalism described above has been checked by computer solution of an initial value problem involving four real coupled linear differential equations. It was then used to explain the multiphoton transitions previously observed in molecular beam electric resonance studies on the two symmetric top molecules OPF_3 and CH_3CF_3 , where the number of photons involved in a given transition varies from 2 to 40.

Address of Meerts: Fysisch Laboratorium, Katholieke Universiteit Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Address of Ozier: Department of Physics, University of British Columbia, 6224 Agriculture Road, Vancouver, BC Canada V6T 2A6

Address of Hougén: Division of Molecular Spectroscopy, National Institute of Standards and Technology, Gaithersburg, MD 20899

TA2 (8:47)

GROUP-THEORETICAL TREATMENT OF SELECTION RULES FOR VIBRATIONAL TRANSITIONS IN MOLECULES EXHIBITING LARGE AMPLITUDE TUNNELING MOTIONS.

LAURENT H. COUDERT AND JON T. HOUGEN

As pointed out qualitatively by a number of authors, and as discussed quantitatively recently by Fraser¹, tunneling splittings may be significantly changed in excited vibrational states of van der Waals complexes when the tunneling motion necessitates transfer of vibrational excitation from one monomer to the other. For this and other reasons there is at present considerable interest in studies of vibrational transitions in such complexes and other molecules exhibiting tunneling motions.

In the present paper we examine from a group theoretical point of view methods for determining selection rules for transitions among the various tunneling-rotational components of the ground and excited vibrational states involved in such studies. For certain cases, which correspond physically to those where vibrational excitation need not be transferred, unambiguous group theoretical predictions, based on rather simple considerations, can be made for the selection rules. For other cases, where vibrational excitation must be transferred from one part of the molecule to another, the simple considerations mentioned above break down, and several different group theoretical "predictions" emerge, based on assumptions concerning the signs of the coupling matrix elements leading to the intramolecular energy transfer. These theoretical ideas will be illustrated for molecules like N_2H_4 , CH_3NH_2 , $(\text{HCCH})_2$ and $(\text{H}_2\text{O})_2$.

¹G. T. Fraser, J. Chem. Phys. in press.

Address of Coudert and Hougén: Molecular Spectroscopy Division, National Institute for Standards and Technology, Gaithersburg, MD 20899.

TA3 (9:04)

The Assignments And Analysis Of Near Infrared Spectra Of $(\text{H}_2\text{O})_2$ Based On Vib-Rotational Selection Rules Derived From A Partial PI Group

Z.S. Huang and R.E. Miller

The spectra of $(\text{H}_2\text{O})_2$ in the near infrared have been assigned and analyzed with the help of a partial group theoretical analysis. A partial PI group, which does not contain the tunneling motion involving the exchange of vibrational excitation, was used to derive tunneling-rotational selection rules. These selection rules, although not accounting for every feature observed in the spectra, offer considerable insight and understanding in assigning the high resolution spectra of $(\text{H}_2\text{O})_2$ observed in the near infrared.

Address: Dept. of Chemistry, Univ. of North Carolina, Chapel Hill, North Carolina 27599.

TA4 (9:21)

MICROWAVE ELECTRIC-RESONANCE OPTOTHERMAL SPECTROSCOPY OF $(\text{H}_2\text{O})_2$

G. T. FRASER, R. D. SUENRAM, AND L. H. COUDERT

The microwave spectrum of $(\text{H}_2\text{O})_2$ has been measured between 14 and 110 GHz using a newly developed electric-resonance optothermal spectrometer (EROS) described here. The reported measurements extend previous results on the \underline{a} -type $K_a=0-0$ and $1-1$ bands for the A_2^\pm , B_2^\pm , and E^\pm rotational-tunneling states and include the first observations of the \underline{c} -type $K_a=1-0$ band for the A_2^\pm and B_2^\pm states and the \underline{a} -type $K_a=0-0$ band for the A_1^\pm states. For the A_1^\pm states an interconversion tunneling splitting of 22.6 GHz is obtained, compared to the 19.5 GHz value found previously for the $K_a=0$ A_2^\pm and B_2^\pm states.

Addresses of Fraser, Suenram, and Coudert: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

TA5 (9:38)

MICROWAVE SPECTRUM OF THE D_2O DIMER

R. D. SUENRAM, G. T. FRASER, AND F. J. LOVAS

Extensive microwave measurements have been made on the $(\text{D}_2\text{O})_2$ using a pulsed-nozzle Fourier-transform microwave spectrometer and a recently developed electric-resonance optothermal spectrometer (EROS). The new measurements build on the previous spectroscopic work of Odutola *et al.*¹ and Coudert *et al.*² for the $K=0$ A_1^\pm , B_1^\pm , and E^\pm states. Spectra have been recorded between 9 - 110 GHz and include the first observation of the A_2^\pm and B_2^\pm states. The tunneling splitting for the $K=0$ A_2^\pm/B_2^\pm states is determined to be 1083.303(21) MHz, which is slightly lower than the 1172.115(14) MHz value found previously for the A_1^\pm/B_1^\pm states. In addition, we report the first $K=1$ measurements on $(\text{D}_2\text{O})_2$, giving a tunneling splittings of 1076.616(14) and 992.368(90) MHz for the A_1^\pm/B_1^\pm and A_2^\pm/B_2^\pm states, respectively. Searches have also been made for b or c -type $K=1-0$ transitions predicted near 100 GHz. A number of transitions have been observed but are presently unassigned.

¹J. A. Odutola, T. A. Hu, D. Prinslow, S. E. O'dell, and T. R. Dyke, J. Chem. Phys. **88**, 5352 (1988).

²L. H. Coudert, F. J. Lovas, R. D. Suenram, and J. T. Hougen, J. Chem. Phys. **87**, 6290 (1987).

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

TA6 (9:55)VIBRATIONAL EXCHANGE UPON INTERCONVERSION TUNNELING IN (HF)₂ AND (HCCH)₂G. T. FRASER

Model calculations are presented to interpret the large H-F and C-H stretching vibrational dependence of the interconversion tunneling splittings and the corresponding infrared vibrational-tunneling state selection rules in (HF)₂ and (HCCH)₂. The model consists of two potential curves in the tunneling coordinate, coupled by an interaction term that allows the vibrational excitation to be exchanged between the two monomer units, permitting tunneling to occur. The interaction term is approximated by resonant infrared transition-dipole coupling. The magnitudes of the calculated vibrational dependencies, their isotopic shifts, and the predicted selection rules are in agreement with previous experimental observations.

Address of Fraser: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Intermission**TA7 (10:30)**

THEORETICAL TREATMENT OF TUNNELING SPLITTINGS IN THE AMMONIA DIMER

JON T. HOUGEN AND LAURENT H. COUDERT

The ammonia dimer is generally believed to involve large amplitude motions which include nearly free internal rotation of each monomer unit about its symmetry axis, though the precise details of its large amplitude motions are far from understood at the present time. We have therefore decided to apply the relatively successful water dimer formalism to a determination of tunneling splitting patterns in the ammonia dimer. It should be noted at the outset, that this formalism is designed for large amplitude motions which are rather strongly hindered by high barriers in the potential surface, i.e. to tunneling motions, and the formalism may therefore not apply to (NH₃)₂. It may well apply to (ND₃)₂, however, and should certainly apply to still heavier species like (PF₃)₂.

In any case, inspired by the non-hydrogen-bonded structure proposed by Nelson et al.¹, which has two essentially antiparallel and inequivalent NH₃ units, we have considered a set of 18 frameworks for (NH₃)₂, which allow for internal rotation of each NH₃ unit about its C₃ axis, and for interchange of the two inequivalent NH₃ groups, but which excludes as non-feasible the inversion (umbrella) motion in each monomer. As is well known, this leads to the permutation-inversion group G₃₆, which is isomorphic to that used also for ethane, dimethylacetylene, dimethylether and acetone. By making assumptions (based primarily on intuition) about the relative ease of various tunneling motions, or, equivalently, assumptions about the relative magnitudes of various tunneling splittings, and by writing the appropriate computer program, we can generate predicted energy level splitting patterns for this molecule. We hope to try to match these various predicted patterns with experimental data, as more becomes available.

¹D. D. Nelson, Jr., G. T. Fraser and W. Klemperer, J. Chem. Phys. **83**, 6201-6208 (1985).

Address of Hougen and Coudert: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

TA8 (10:47)

TUNNELING - ROTATIONAL SPECTRUM AND STRUCTURE OF $(\text{H}_2\text{CO})_2$

F. J. LOVAS, R. D. SUENRAM, L. H. COUDERT, T. A. BLAKE, K. G. GRANT, AND Stewart E. NOVICK

The microwave spectra of $(\text{H}_2\text{CO})_2$ and $(\text{D}_2\text{CO})_2$ have been observed with a pulsed beam, Fabry-Perot cavity, Fourier transform microwave spectrometer. Both species exhibit a-type spectra which are split by tunneling motions involving internal rotation of each monomer unit and an interchange motion of donor-acceptor, analogous to motions in the water dimer.

Rotational analysis of the $(\text{H}_2\text{CO})_2$ species provides the constants $A = 18583.54$ MHz, $\frac{1}{2}(B + C) = 3272.105(34)$ MHz, and $B - C = 503.92(17)$ MHz. Stark effect measurements on this species yield dipole moment components $\mu_a = 0.858(4)$ D and $\mu_b = 0.027(10)$ D, and similar values are obtained for $(\text{D}_2\text{CO})_2$. The small value for μ_b has hampered observation of the expected b-type transitions.

The structure obtained from fitting the moments of inertia has the planes of the monomer units perpendicular in a nearly antiparallel orientation of the CO groups and the center-of-mass separation is $3.046(17)$ Å. Comparison of these results with other complexes containing H_2CO will be presented.

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

Address of Blake[†], Grant, and Novick: Department of Chemistry, Wesleyan University, Middletown, CT 06457.

[†]Current address: Department of Chemistry, University of Washington, Seattle, WA 98195.

TA9 (11:04)

ROTATIONAL SPECTRUM AND STRUCTURE OF THE $\text{H}_2\text{O}-\text{SO}_2$ COMPLEX

K. MATSUMURA, F. J. LOVAS, AND R. D. SUENRAM

The rotational spectrum of the $\text{H}_2\text{O}-\text{SO}_2$ complex has been measured in a pulsed molecular beam, Fabry-Perot cavity, Fourier transform microwave spectrometer. In addition to observation of the $\text{H}_2\text{O}-\text{SO}_2$ species, the ^{34}S isotopic form was observed in natural abundance, while $\text{HDO}-\text{SO}_2$ and $\text{D}_2\text{O}-\text{SO}_2$ spectra were obtained by employing D_2O seeded in the Ar carrier gas. For $\text{H}_2\text{O}-\text{SO}_2$ and $\text{D}_2\text{O}-\text{SO}_2$ two states are observed with a- and c-type spectra, while for the ^{34}S and HDO species only the a-type spectrum was assigned for the two states. Internal rotation of the water units is found to be the origin of the doubling observed through comparison of relative intensities and the expected spin weights.

The rotational constants for the $I=0$ state are: $A=8763.071(3)$ MHz, $B=3819.655(2)$ MHz, and $C=2900.899(2)$ MHz. Stark effect measurements yield electric dipole moment components $\mu_a = 1.984(2)$ D and $\mu_c = 0.488(4)$ D for $\text{H}_2\text{O}-\text{SO}_2$.

The geometry obtained from the derived moments of inertia has the planes of the monomer units tilted at -45° from parallel with the water O-atom closest to sulfur in SO_2 and a center-of-mass distance of $2.962(5)$ Å. Comparison of these results with the related complexes $\text{H}_2\text{O}-\text{O}_3^1$ and $\text{H}_2\text{S}-\text{SO}_2^2$ will be presented.

¹J. Z. Gillies, C. W. Gillies, R. D. Suenram, and F. J. Lovas, (to be published).

²R. E. Bumgarner, D. J. Pauley, and S. G. Kukolich, J. Chem. Phys. **87**, 3749 (1987).

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

TA10 (11:21)

STRUCTURE AND TUNNELING OF THE HYDROGEN BONDED COMPLEX WATER-CO

D. Yaron, K.I. Peterson, D. Zolanz, W. Klemperer, R.D. Suenram, and F.J. Lovas

The microwave spectrum of the water-CO complex has been observed using both molecular beam electric resonance and Fourier transform microwave spectroscopy. The water is hydrogen bonded to the carbon of the carbon monoxide. A tunneling motion between the two equivalent hydrogen bonded structures gives rise to two states. These states are unambiguously assigned based on hyperfine structure arising from either the proton spin-spin interaction (H_2O) or deuterium quadrupole hyperfine (D_2O). A barrier to the tunneling motion of about 200 cm^{-1} is obtained from the difference in the dipole moments of the two states using a simple one dimensional tunneling model. Although the water is hydrogen bonded to the CO, the O-H bond of water is tilted away from a linear hydrogen bonded configuration by about 12° . (The direction is such that the lone pairs on the oxygen, rather than the other hydrogen, are brought into the carbon.) Electrostatic models predict a linear hydrogen bonded structure, with a barrier to tunneling of between 400 and 900 cm^{-1} depending on the choice of distributed multipole model.

Address of Yaron, Zolanz, and Klemperer: Dept. of Chem., Harvard University, Cambridge, MA 02138.

Address of Peterson: Chemistry Department, Pastore Hall, University of Rhode Island, Kingston, Rhode Island, 02881.

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

TA11 (11:38)INTERNAL ROTATION IN WATER- N_2O and WATER- CO_2

D. Yaron, K.I. Peterson and W. Klemperer

Microwave spectra have been obtained for the complexes of water with CO_2 and N_2O using molecular beam electric resonance. Both complexes are planar with the oxygen of water binding to the center of the linear molecule, such that the heavy atoms form a T-shaped structure. In the CO_2 complex the water's C_{2v} axis is perpendicular to the CO_2 while in the N_2O complex it is tilted away from the a axis by 40° . Internal rotation occurs in both complexes, giving rise to two states with measurably different rotational constants. These differences cause splittings in the microwave transitions of water- N_2O , however in water- CO_2 only shifts are observed. (As the internal rotation exchanges the equivalent, zero spin oxygen nuclei of CO_2 only one internal rotation state is symmetry allowed for a given rotational state.) A recent fit of the transitions of water- CO_2 giving the rotational constant splittings for the isotopes H_2O , HDO, and D_2O will be presented. This allows for a detailed investigation of the two-fold internal rotation problem and comparison of the symmetric CO_2 complex with the asymmetric N_2O complex. The effects of paths more complex than a rotation about the C_{2v} axis of water are examined for water- N_2O . The interpretation of the centrifugal distortion constants will also be addressed. This is accomplished through a fast, simple implementation of the Eckart conditions to subtract overall rotation from an arbitrary rotation of the subunits.

¹K.I. Peterson and W. Klemperer, J. Chem. Phys. **80** (6), 2439 (1984).

Address of Yaron and Klemperer: Dept. of Chem., Harvard University, Cambridge, MA 02138.

Address of Peterson: Chemistry Department, Pastore Hall, University of Rhode Island, Kingston, Rhode Island, 02881.

TB1 (8:30)

DECOMP: A FOURIER TRANSFORM SPECTRUM DECOMPOSITION PROGRAM
M. C. ABRAMS AND J. W. BRAULT

Current techniques for processing high resolution Fourier transform spectra revolve around interactive graphical display of the spectrum on a computer. The DECOMP spectrum decomposition program, adapted to IBM PC-compatible computers, is designed explicitly for the reduction of Fourier transform spectra and focuses on reducing a spectrum into a list of line parameters. Basic methods of spectrum manipulation will be demonstrated, including background correction, line finding, line fitting to Voigt functions and atlas plotting of spectra. High resolution infrared emission and absorption spectra from the McMath Fourier transform spectrometer at the National Solar Observatory will be displayed.

Address of Abrams: Department of Physics, University of California at Berkeley, Berkeley, Ca. 94720, U.S.A.
Address of Brault: National Solar Observatory, Tucson, Az, 85726, U.S.A.

TB2 (8:47)

NEURAL NETWORK COMPUTATIONAL PARADIGMS IN HIGH RESOLUTION SPECTROSCOPY

W. E. BLASS

Neural network computational techniques¹ appear to hold considerable promise for useful applications in the realm of high resolution spectroscopy. The basis for such computational models will be briefly presented followed by a selection of examples of interest.

In particular, the use of backpropagation networks for resolution enhancement of spectra has been moderately successful. Examples of resolution enhancement using randomly generated network training data will be compared to ordinary (and successful) constrained deconvolution². Resolution enhancement of FTS spectra with sinc apodization is presently under study. The status of that study also will be reported.

¹D. E. Rumelhart and J. L. McClelland, **Parallel Distributed Processing, Vol.1**, MIT Press, Cambridge, Massachusetts, 1986.

Neural Networks for Computing, J. S. Denker, ed., AIP Conference Proceedings 151, American Institute of Physics, New York, 1986.

²W. E. Blass and G. W. Halsey, **Deconvolution of Absorption Spectra**, Academic Press, New York, 1981.

Deconvolution of Spectra, P. A. Jansson, ed., Academic Press, New York, 1984.

Address of Blass: Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200.

TB3 (9:04)

A NEW METHOD FOR COLLECTING DIGITIZED DIODE LASER SPECTRA WHICH PROVIDES A VERY ACCURATE FREQUENCY SCALE.

C. NICOLAS, A. W. MANTZ

A new method of Tunable Diode Laser (TDL) spectrum digitization is presented. While the TDL frequency is slaved to an internally coupled Fabry Perot Interferometer (icFPI)¹, this interferometer is tuned in a step by step manner. The extrema of a HeNe laser interference pattern trigger periodic temporary stabilization of the interferometer to the HeNe laser frequency. Thus at each step, the infrared spectroscopic data, characterized by a very stable and stationary frequency, are collected into a computer.

This technique is combined with a confocal Fabry Perot etalon, thus providing a frequency scale accuracy of about $3.5 \cdot 10^{-5} \text{ cm}^{-1}$ over a 1 cm^{-1} scan. The method is shown to be consistent with high resolution Fourier transform and heterodyne spectroscopy results, based on relative position measurements of N₂O absorption lines in the 2220 - 2240 cm^{-1} spectral region.

¹M. Reich, R. Schieder, H. J. Clar, and G. Winnewisser, Appl. Opt. 25, 130 (1986).

Address of Nicolas and Mantz: Laser Analytics, inc., 25 Wiggins Avenue, Bedford, MA 01730, USA.

TB4 (9:21)

CW OVERTONE CARBON MONOXIDE LASER EMISSION BETWEEN 2.8 AND 4.0 MICRON

WOLFGANG URBAN, MARTINA GROMOLL-BOHLE, WOLFRAM BOHLE, ANGELA WEIDENFELLER

A liquid nitrogen cooled CO plasma is used to drive overtone laser transitions $\Delta v = 2^1$. More than 160 single lines have been observed starting from $v = 15 \rightarrow 13$ up to $v = 37 \rightarrow 35$, at a maximum J distribution from 6 to 15. Line selection occurs via a gold coated grating in Littrow mounting. Single line power level on the strongest transitions is 120 mW, from 100 cm of cooled length.

The special features for optimum overtone lasing conditions of both discharge and cavity are presented and some possibilities of spectroscopic applications will be discussed.

¹M. Gromoll-Bohle, W. Bohle, W. Urban, Optics Comm. 69, 409 (1989)

Address: Institute fur Angewandte Physik, Universitat Bonn, Wegelerstrasse 8, D5300 Bonn 1, FRG.

TB5 (9:38)**"ANOMALOUS" RO-VIBRATIONAL INTENSITIES IN THE $\Delta v = 1$ BANDS OF SH ($X^2\Pi$)**A. Benidar, C. Chackerian, Jr., R. Farreng, and G. Guelachvili

Relative line intensities of p- and r- branch transitions of diatomic radical molecules (ClO, NH, OH) have recently¹⁻³ been used along with the theory of the Herman-Wallis effect to obtain estimates of electric dipole vibrational transition moments. Of the first and second row diatomic hydrides, *ab initio* calculations predict SH to exhibit the largest H.W. effect. Indeed, our spectra confirm a very large effect, and we present here an attempt at a quantitative analysis of the Herman-Wallis intensity perturbation in SH.

¹ J.B. Burkholder, P.D. Hammer, C.J. Howard, A.G. Maki, G. Thompson, and C. Chackerian, Jr., *J. Mol. Spectrosc.* **124**, 137 (1987).

² C. Chackerian, Jr., G. Guelachvili, A. Lopez-Pineiro, and R.H. Tipping, *J. Chem. Phys.* **90**, 641 (1989).

³ D.D. Nelson, Jr., A. Schiffman, D.J. Nesbitt and J.D. Yaron, *J. Chem. Phys.* (to be published).

Address of Benidar, Farreng and Guelachvili: Universite de Paris-Sud., Laboratoire d'Infrarouge, Campus d'Orsay Batiment 350, 91405 Orsay Cedex, France.

Address of Chackerian: NASA-Ames Research Center, Moffett Field, CA 94035.

TB6 (9:50)**DIODE LASER SPECTROSCOPY OF VIBRATIONALLY EXCITED SH⁺**

S. CIVIŠ, C. E. BLOM and P. JENSEN

We have detected rovibrational transitions of the $v = 2 \leftarrow 1$, $v = 3 \leftarrow 2$ and $v = 4 \leftarrow 3$ hot bands of SH⁺ in the $^3\Sigma^-$ electronic ground state. The signals were detected with velocity modulation in a high current discharge of He and H₂S. From the new and earlier data on SH⁺ a set of molecular constants was obtained.

On the basis of all available data for the electronic ground state of $^{32}\text{SH}^+$, $^{32}\text{SD}^+$ and $^{34}\text{SH}^+$ we have obtained a potential energy curve as an expansion in the Morse-type variable $y = 1 - \exp[-a(r - r_e)]$.

Address of S. Civiš, C. E. Blom and P. Jensen: Physikalisch-Chemisches Institut, Justus Liebig Universität, D-6300 Giessen, Federal Republic of Germany.

Intermission

TB7 (10:25)

PHOTOACOUSTIC MEASUREMENT OF DIFFERENTIAL BROADENING OF THE A DOUBLETS IN
 $\text{NO}(X^2\Pi_{1/2}, v=2-0)$ BY AR

A. S. PINE,

A differential broadening of the A doublets in the $v=2-0$ overtone band of the $^2\Pi_{1/2}$ ground electronic state of NO in an Ar buffer gas has been observed by photoacoustic spectroscopy using a tunable color-center laser. The broadening coefficients for the f symmetry components are larger than for the e symmetry components by up to ~6% for $J=16.5$. This differential depends on J and vanishes at low J , implicating the anisotropy of the unpaired electron Π orbital in the plane of rotation. The $^2\Pi_{3/2}$ transitions are slightly broader than the $^2\Pi_{1/2}$ as a result of spin-flipping collisional relaxation. The observed lineshapes also exhibit collisional or Dicke narrowing due to velocity-changing collisions.

Address of Pine: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

TB8 (10:42)

AIR-, NITROGEN-, AND OXYGEN-BROADENED HALFWIDTH COEFFICIENTS AND PRESSURE-INDUCED LINE SHIFTS IN THE ν_3 FUNDAMENTAL OF $^{13}\text{CH}_4$

V. MALATHY DEVI, D. CHRIS BENNER, M. A. H. SMITH, AND C. P. RINSLAND

Air-broadened, nitrogen-broadened, and oxygen-broadened halfwidths and pressure-induced line shift coefficients have been determined for transitions in the ν_3 fundamental band of $^{13}\text{CH}_4$ by analyzing room-temperature 0.01 cm^{-1} resolution absorption spectra recorded in the $2700\text{--}3200\text{ cm}^{-1}$ spectral region. These data were obtained with the McMath Fourier transform spectrometer of the National Solar Observatory on Kitt Peak. A 99% ^{13}C -enriched methane diluted to mixing ratios of 0.003 to 0.01 were used in 5 and 25 cm absorption path cells with total sample pressures ranging between 75 and 500 Torr. The halfwidth and pressure-shift coefficients were retrieved from the data using a non-linear least-squares fitting technique. The unshifted line positions were determined from the spectra of pure $^{13}\text{CH}_4$ at low pressure. The air- to nitrogen-broadened halfwidth ratio was almost one while the air-to-oxygen-broadened halfwidth ratio was found to be ~1.06. The derived halfwidth and pressure shift coefficients will be compared to values obtained for identical transitions in the ν_3 fundamental of $^{12}\text{CH}_4$ as well as to those in the ν_4 fundamental of $^{13}\text{CH}_4$.

Address of Malathy Devi and Benner: Department of Physics, College of William and Mary, Williamsburg, VA 23185

Address of Smith and Rinsland: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665-5225

TB9 (10:54)**TEMPERATURE DEPENDENCE OF COLLISION-INDUCED LINE SHIFTS IN THE ν_4 -FUNDAMENTAL OF $^{12}\text{C}^{1}\text{H}_4$ AT PLANETARY ATMOSPHERIC TEMPERATURES[†]**

S. CHUDAMANI, and P. VARANASI

Accurate knowledge of collision-induced line shifts is required at the relevant atmospheric temperatures in the analysis of the observed $^{12}\text{C}^{1}\text{H}_4$ spectra of the atmospheres of the major planets, the Saturnian satellite Titan, and Earth, in addition to intensity and line width data. The appropriate temperatures fall in the range between 90 and 288 K and the relevant perturbers are H_2 , He, N_2 , and air.

Using separate absorption cells for the reference and sample gases and placing them in series, we have been able to measure the pressure-induced shifts of the R(4) and R(7) multiplets located between 1330 and 1350 cm^{-1} in the ν_4 -fundamental of $^{12}\text{C}^{1}\text{H}_4$ at several temperatures between 100 and 296 K using a tunable diode laser. The temperature dependence of the shifts is presented for collisions of $^{12}\text{C}^{1}\text{H}_4$ with H_2 , He, Ar, N_2 , O_2 and air. The experiments have also yielded data on the intensities and collision-broadened half-widths at the various temperatures. The different variation with temperature of the line width and the line shift for each line measured is discussed.

[†]Supported by the Planetary Atmospheres Branch of the Solar System Exploration Division of NASA under Grant-in-Aid No. 33-015-139 and by the Upper Atmosphere Research Program of the Earth Sciences and Applications Division of NASA under Grant-in-Aid No. NAGW-1238

Address of the authors: Institute for Atmospheric Sciences, State University of New York, Stony Brook, NY 11794-2300

TB10 (11:11)**THE CH STRETCHING SPECTRUM OF GASEOUS CYCLOPENTANE-D9: COUPLING OF STRETCHING AND PSEUDOROTATION**

E. J. Variyar and R. A. MacPhail

It is well known that the lowest frequency vibration in cyclopentane corresponds to pseudorotation, a rapid puckering motion along a nearly barrierless phase-angle coordinate ϕ . This pseudorotational motion couples to the CH stretching vibrations and leads to pseudorotational structure in the CH stretching spectrum. We have obtained isotropic Raman spectra of gaseous $\text{C}_5\text{D}_9\text{H}$ which show this structure very clearly.

Most of the stretch-pseudorotation coupling can be accounted for by the adiabatic variation in the CH stretching frequency with ϕ . This frequency variation can then be used in an adiabatic approximation to simulate the CH stretching spectrum. We have calculated the frequency variation with ϕ by two methods, one using *ab initio* CH bond lengths and the other with a modified form of the Lifson-Stern empirical potential[1]. While both of these methods give simulated pseudorotational structure that is in qualitative agreement with the observed spectrum, the *ab initio* approach is significantly better at reproducing the spectral details. The effects of other perturbations on the spectrum have also been considered, including thermally excited radial levels and the variation of the zero point energy and reduced mass with ϕ .

1. S. Lifson and P. Stern, *J. Chem. Phys.* **77**, 4542 (1982).

Author's Address: Department of Chemistry, Duke University, Durham, NC 27706.

TB11 (11:28)**PSEUDOROTATIONAL DYNAMICS OF LIQUID CYCLOPENTANE FROM CH STRETCHING SPECTRA**

E. J. Variyar and R. A. MacPhail

Recent experimental and theoretical studies in our laboratory have shown that deuterium isolated CH stretching vibrations can be used to probe rapid conformational dynamics of molecules in condensed phases. These isolated CH stretching frequencies are sensitive to the local conformation of the CH bond, and thus to the conformational dynamics which interchange bond types on a fast enough timescale.

Our work has focused on the ultrafast internal dynamics of cyclopentane. This molecule undergoes a nearly barrierless conformational rearrangement called pseudorotation that interchanges the CH oscillators on the subpicosecond timescale. We have observed this motion as it is reflected in the partial motional collapse of the CH stretching bands in C5D9H. Analysis of these spectra should help us understand the effect of a solvent on low-barrier conformational dynamics in liquids.

To describe pseudorotation and its effects on the observed CH stretching spectrum, stochastic differential equations describing coupled vibration and pseudorotational motions are solved numerically and fit to isotropic Raman and FTIR spectra. The results of various stochastic models, in particular extended diffusion will be discussed. From fits to the experimental spectra we have obtained the temperature dependence of dynamical parameters such as the pseudorotation angular momentum relaxation time. We find the dynamical parameters to be independent of viscosity over the entire temperature range studied implying the dynamics along this coordinate cannot be described by a Stokes-Einstein model.

Author's Address: Department of Chemistry, Duke University, Durham, NC 27706.

TC1 (8:30)**ANALYSIS OF THE ROTATIONAL SPECTRUM OF METHANOL AND ITS ISOTOPIC VARIANTS TO MICROWAVE ACCURACY****T. ANDERSON, E. HERBST, F. C. DE LUCIA, AND P. HELMINGER**

A new method for the analysis and characterization of a large number of rotational-torsional transitions of methanol and its isotopic variants is presented which is based on our earlier work that used a direct diagonalization of an internal axis method Hamiltonian. In it the analysis of the *A* and *E* symmetry subspecies has been separated and selected cross terms between torsional and rotational operators have been added to the Hamiltonian.¹

Previous analyses of these molecules resulted in an overall rms deviation of 1-2 μ Hz for transitions with $J \leq 8$ in the first three torsional states. The data sets have now been expanded to include transitions of higher *J* and *K* in the first three torsional states without the introduction of systematic model error as was the case with the earlier model. The results presented here have an rms deviation of ~100 kHz, which is on the order of experimental error. As a consequence of this new approach, the predictive powers of this model have been greatly enhanced and now provide a means for the accurate characterization of the rotational-torsional spectrum of methanol and its isotopic variants.

¹ De Lucia, Herbst, Anderson, and Helming, *J. Mol. Spectrosc.* **134** (1989).

Address of Anderson, Herbst, and De Lucia: Department of Physics, Duke University, Durham, NC 27706
Address of Helming: Department of Physics, University of South Alabama, Mobile, AL 36688

TC2 (8:47)**SUBMILLIMETER LASER STARK SPECTROSCOPY OF CD₃OH WITH THE HCN LASER****J. C. SARKER, G. R. SUDHAKARAN, I. MUKHOPADHYAY, R. L. BHATTACHARJEE, AND L. H. JOHNSTON**

A submillimeter laser Stark spectrum of partially deuterated methyl alcohol, CD₃OH has been investigated at $\lambda = 311 \mu\text{m}$ of the HCN laser. The spectrum has been taken up to 60,000 volts/cm in both parallel and perpendicular polarizations. An R-branch K-doublet transition has been observed for the first time and assigned as $J_K = 14_4 + 13_3, A^-, v_t = 0$, and $J_K = 14_4 + 13_3, A^+, v_t = 0$ torsional state. Zero-field frequencies of this doublet are reported with an accuracy of about 10 MHz based on the contribution from the K-doublet interaction only. The accuracy should improve up to about 1 MHz when the other nearby levels interaction will be taken into account.

Address of Sarker: Department of Electrical Engineering, University of Idaho, Moscow, Idaho 83843.

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 Bhattacharjee: Department of Chemistry, University of Rochester, Rochester, NY 14627.

Address of Johnston: Department of Physics, University of Idaho, Moscow, Idaho 83843.

TC3 (9:04)**DIRECT MEASUREMENT OF $\Delta J = n$ PROCESSES IN METHYL FLUORIDE****H. O. EVERITT AND F. C. DE LUCIA**

A millimeter / submillimeter - infrared double resonance technique was used to study $\Delta J = n$ processes in ¹²CH₃F and ¹³CH₃F. In this experiment a Q-switched CO₂ laser populated a unique ro-vibrational level in the $V_3 = 1$ vibrational state of methyl fluoride. The time responses of the strengths of many rotational lines within the $V_3 = 1$ manifold were monitored. Outside the K-stack containing the pumped level, the time responses were well understood as being the result of the $\Delta K = 3n$, vibrational swap, and vibrational relaxation mechanisms. Within the same K-stack as the pumped level the early time responses displayed the additional effects of $\Delta J = n$ processes.

A numerical simulation of rotational energy transfer has been developed to describe rotational energy transfer in either isotope of methyl fluoride. The key experimentally verified assumption of this simulation was that all states within a given symmetry type are in rotational equilibrium. The lone exception to this rule involved those states within the same K-stack as the pumped level. Therefore, the simulation described energy transfer among two pools (one representing each symmetry type) and the many rotational levels of the K-stack containing the pumped level. The simulation was used as a basis for a nonlinear least squares fit of the experimental data in order to extract the rates of the $\Delta J = n$ processes. The $\Delta J = 1-5$ rates were measured for ¹³CH₃F, and the $\Delta J = 2-10$ rates were measured for ¹²CH₃F.

Address: Department of Physics, Duke University, Durham, NC 27706

TC4 (9:21)**ANALYSIS OF THE ROTATIONAL SPECTRUM OF DIMETHYL ETHER****S. L. SHOSTAK, T. M. GOYETTE, T. ANDERSON, E. HERBST AND F. C. DE LUCIA**

The spectrum of the ground torsional state of dimethyl ether has been measured in the frequency range 100-600 GHz covering rotational states up to $J=25$ and $K=5$. Over 700 torsional splittings from ~250 rotational lines were analyzed using a PAM Hamiltonian. A total of 4 parameters were varied in a least squares fit using higher order Van Vleck perturbation terms. The free parameters included the torsional barrier, V_3 , independent a- and b-type rotation-torsion interaction parameters Q_a and Q_b , and the C rotational constant. The RMS of the fit was < 200 kHz. Because of the parameterization of the Hamiltonian, this method should be applicable to other internal rotor molecules of this symmetry.

Address: Department of Physics, Duke University, Durham, NC 27706

TC5 (9:38)**ANOMALOUS BEHAVIOUR IN THE ROTATIONAL SPECTRUM OF THE $v_8 = 2$ AND 3 VIBRATION FOR THE $^{12}\text{CH}_3^{13}\text{C}^{15}\text{N}$ MOLECULE IN THE FREQUENCY RANGE 17-95 GHz****M. AL-SHARE, H.S. TAM, AND J.A. ROBERTS**

The methyl cyanide molecule was studied in the $v_8 = 2$ and 3 vibrations for rotational energy levels with $1 \leq J \leq 5$ to establish the trend in the energy level in the frequency range 17 to 95 GHz. Anomalous behaviour in the $^{12}\text{CH}_3^{13}\text{C}^{15}\text{N}$ rotational spectrum of the $v_8 = 3$ vibration for the $(K=\pm 1)$ ($\ell=\pm 1$) components with large frequency departures, $\approx 6(J+1)$ MHz, from a standard model were investigated to determine what interactions were at play which had been ignorable in $^{13}\text{CH}_3^{12}\text{C}^{15}\text{N}$ molecule.

The method of isotopic substitution enabled the molecular system to be "tuned" so that resonant interactions could be explored in more detail for each of the molecules.

These large departures are explained using a basic molecular model in which accidentally strong resonances (ASR) are at play.

*This work supported in part by grant B-842 of the Robert A. Welch Foundation, Houston, Texas.

Address of Al-Share and Roberts: University of North Texas, Denton, Texas.

Address of Tam: University of Kansas, Lawrence, Kansas

TC6 (9:50)

An IAM Theory for Internal Rotation in Completely Asymmetric Molecules.

Application to the Analysis of the Microwave Spectra of CH_2DOH and CHD_2OH .Mujian Liu and C. Richard Quade

An IAM theory has been developed for application in the spectral analysis of CH_2DOH ¹ and CHD_2OH ². Torsion-rotation term values are calculated with first principles from the molecular structure in a single degree of internal freedom model. A modified V and G structure³ gives the best fit to the data, even improving upon the phenomenological approach reported with the spectra.^{1,2} However, it is clear from the spectral fit that vibration-rotation-internal rotation interactions are also important.

1. Microwave detection of direct trans to gauche transitions in CH_2DOH .
C. F. Su and C. R. Quade, (To appear in *J. Mol. Spec.* spring '89).
2. Microwave detection of direct gauche to trans transitions in CHD_2OH .
C. F. Su and C. R. Quade, *J. Chem. Phys.* **90**, 1396(1989).
3. P. Venkateswarlu and W. Gordy, *J. Chem. Phys.* **32**, 1200(1955).

Department of Physics, Texas Tech University, Lubbock, Texas 79409

Intermission

TC7 (10:25)

MICROWAVE SPECTRUM OF meso-BISOXIRANE

C. F. SU, R. L. COOK, S. SUBRAMANIAM, AND V. F. KALASINSKY

The microwave spectrum of meso-bisoxirane has been recorded in the R-band, K-band, and X-band regions. Vibrational spectra of the gas, liquid, and solid phases indicate that the compound exists as a mixture of two conformations, but the more stable trans conformation (C_1 symmetry) has no dipole moment. Therefore, the very weak microwave spectrum was assigned to the gauche conformer (C_1 symmetry), and RF-MW double resonance was necessary to confirm some assignments. The following rotational constants (MHz) and dipole moment components (D) have been obtained:

$$\begin{array}{ll} A = 9187.45 & \mu_a = 1.08 \\ B = 2651.80 & \mu_b = 0.35 \\ C = 2608.92 & \mu_c = 2.80 \end{array}$$

A structure for meso-bisoxirane which is consistent with these data has been determined and will be discussed with regard to the structures and conformational stabilities of the related compounds d,l-bisoxirane and bicyclopropyl.

Address of Su and Cook: Department of Physics and Astronomy, Mississippi State University, Mississippi State, Mississippi 39762

Address of Subramaniam and Kalasinsky: Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762

TC8 (10:42)

MICROWAVE SPECTRUM, DIPOLE MOMENT, BARRIER TO INTERNAL ROTATION, AND MOLECULAR STRUCTURE OF GERMYLAZIDE

P. GRONER, J. F. SULLIVAN, AND J. R. DURIG

The microwave spectra of three isotopic Ge species of germyl azide, GeH_3N_3 , have been assigned. The splittings due to internal rotation of the germyl group have been analyzed yielding a threefold barrier of $86.6(1) \text{ cm}^{-1}$. An electric dipole moment of $2.58(2) \text{ D}$ has been determined from the Stark effect. The following refined structural parameters have been obtained with a fixed and slightly bent azide group: $r(\text{GeN}) = 1.866(12) \text{ \AA}$, $r(\text{GeH}) = 1.497(8) \text{ \AA}$, $\angle(\text{GeNN}) = 115.9(14)^\circ$, $\angle(\text{HGeH}) = 112.2(10)^\circ$, and a tilt of the symmetric germyl group of 4.0° away from the azide group. These results will be compared with the structures and barriers in other Group IVA-pseudohalides.

Address of Groner, Sullivan, and Durig: Department of Chemistry, University of South Carolina Columbia, South Carolina, 29208.

TC9 (10:54)

MICROWAVE SPECTRUM, STRUCTURE AND CONFORMATIONAL ANALYSIS OF CHLOROCYCLOPENTANE

M. J. LEE, P. GRONER, AND J. R. DURIG

In the microwave spectrum of chlorocyclopentane, the ground state and a series of vibrationally excited states of the axial conformer have been assigned by Loyd et al.¹ We reinvestigated the spectrum and were able to assign the ground state (both Cl isotopes) and two excited states (³⁵Cl isotope only) of the equatorial conformation. Rotational constants ($A = 6424.47(1)$, $B = 1832.301(5)$, $C = 1532.162(4) \text{ MHz}$ for ground state $c\text{-C}_5\text{H}_9^{35}\text{Cl}$), centrifugal distortion constants, and quadrupole coupling constants were determined, as well as improved constants for the axial conformers. The experimental rotational constants have been used to derive plausible structures for both conformations.

¹R. C. Loyd, S. N. Mathur and M. D. Harmony, *J. Mol. Spectrosc.* **72**, 359 (1978).

Address of Lee, Groner, and Durig: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

TC10 (11:06)

RAMAN AND INFRARED SPECTRA, NORMAL COORDINATE CALCULATIONS AND VIBRATIONAL ASSIGNMENT FOR 1,1,1,3,3,3-HEXAFLUORO-2-PROPANIMINE

J. R. DURIG, N. E. LINDSAY, AND T. G. SHEEHAN

The Raman (4000 to 10 cm^{-1}) and infrared (4000 to 50 cm^{-1}) spectra of gaseous and solid 1,1,1,3,3,3-hexafluoro-2-propanimine, $(\text{CF}_3)_2\text{C}=\text{NH}$, have been recorded. Additionally, the Raman spectrum of the liquid has been recorded and qualitative depolarization values obtained. A complete vibrational assignment for the normal modes utilizing C_s symmetry is proposed based on band contours, depolarization values, and group frequencies. The assignment is supported by a normal coordinate calculation utilizing a modified valence force field to calculate the frequencies and potential energy distribution of the normal modes. A CF_3 torsional mode is observed in the Raman spectrum of the liquid at approximately 60 cm^{-1} from which a periodic barrier of 5.0 kcal/mol has been calculated. The results of this investigation are compared with similar data on some corresponding molecules.

Address of Durig and Sheehan: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

Address of Lindsay: Ford Motor Company, 20000 Rotunda Drive, Dearborn, Michigan, 48121.

TC11 (11:18)

CONFORMATIONAL STABILITY, BARRIERS TO INTERNAL ROTATION, VIBRATIONAL ASSIGNMENT AND AB INITIO CALCULATIONS OF 2-FLUOROPROPENOYL FLUORIDE

J. R. DURIG, A. Y. WANG, T. S. LITTLE, P. A. BRLETIC, AND J. R. BUCENELL

The far infrared spectrum of gaseous 2-fluoropropenoyl fluoride, $\text{CH}_2\text{CF}=\text{CF}_2$, has been recorded at a resolution of 0.10 cm^{-1} in the 350 to 35 cm^{-1} region. The fundamental asymmetric torsional frequencies of the more stable *s-trans* (two double bonds oriented *trans* to one another) and the high energy *s-cis* conformation have been observed at 84.1 and 68.5 cm^{-1} , respectively, each with excited states falling to lower frequencies. From these data the asymmetric torsional potential function governing internal rotation about the C-C bond has been determined. From studies of the Raman spectrum at variable temperatures, the conformational enthalpy difference has been determined to be $220 \pm 34 \text{ cm}^{-1}$ ($629 \pm 97 \text{ cal/mol}$) and $370 \pm 82 \text{ cm}^{-1}$ ($1058 \pm 234 \text{ cal/mol}$) for the gaseous and liquid phases, respectively. A complete assignment of the vibrational fundamentals observed in the infrared (3500 to 50 cm^{-1}) spectra of the gas and solid and the Raman (3200 to 10 cm^{-1}) spectra of all three physical states is proposed. All of these data are compared to the corresponding quantities obtained from *ab initio* Hartree-Fock gradient calculations employing both the 3-21G and 6-31G* basis sets. Additionally, complete equilibrium geometries have been determined for both rotamers. The results are discussed and compared with the corresponding quantities obtained for some similar molecules.

Address of Durig, Wang, and Little: Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208.

Address of Brletic and Bucenell: Department of Chemistry, Washington and Jefferson College, Washington, Pennsylvania, 15301.

TC12 (11:35)

VIBRATIONAL SPECTRA OF SOME SUBSTITUTED VINYLIC COMPOUNDS

D. T. DURIG, T. S. LITTLE, G. A. GUIRGIS, AND J. R. DURIG

The infrared (3500-20 cm^{-1}) and Raman (3500-10 cm^{-1}) spectra of some substituted vinyl compounds of the form $\text{H}_2\text{C}=\text{C}(\text{X})\text{CH}_2\text{Y}$ where X, Y = F, Cl, and CH_3 , have been recorded in the gaseous, liquid, and solid phases. From the far infrared spectra of the gases, the asymmetric torsional fundamental has been observed and, in some cases, the torsional transitions for a second conformer have been identified. In these latter cases the potential function governing the asymmetric torsion has been determined. *Ab initio* calculations have also been carried out for this series of molecules and these results will be compared with the experimental results.

Address of D. T. Durig: Chemistry Department, University of the South, Sewanee, Tennessee, 37375.

Address of Guirgis: Mobay Corporation, Dyes and Pigment Division, Analytical and Environmental Department, Charleston, South Carolina, 29411.

Address of Little and J. R. Durig: Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

TD1 (8:30)

INTERATOMIC POTENTIALS FOR VAN DER WAALS COMPLEXES OF GROUP 13 METAL ATOMS WITH RARE GASES

C.L. CALLENDER, S.A. MITCHELL AND P.A. HACKETT

Interatomic potential parameters for the ground $X_{1,2} \ ^2\Pi_{1/2,3/2}$ and excited $B \ ^2\Sigma^+_{1/2}$ states of jet-cooled van der Waals complexes of Al and In atoms with rare gases have been determined from fluorescence excitation and emission spectra. Vibrational numbering in the B states is established from isotopic and rotational broadening of fluorescence excitation lineshapes. Bond distances are estimated by comparison with analogous states of alkali-rare gas molecules, and by modelling observed relative emission intensities with calculated Franck-Condon factors. Morse potentials are found to adequately describe the data for the ground states, but for the excited states there are indications of departures from Morse functions at large internuclear distances. Multiplet splittings in Al- and In-rare gas complexes are discussed in terms of an empirical treatment of spin-orbit coupling.

Address of Authors: Laser Chemistry Group, Division of Chemistry, National Research Council, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6.

TD2 (8:47)

LASER VAPORIZATION OF ALLOYS: FLUORESCENCE AND ELECTRONIC STRUCTURE OF AlCu

KOESUN PAK, MING-FANG CAI, SHANG-JIH TSAY, THOMAS P. DZUGAN, AND VLADIMIR E. BONDYBEY

Metals and alloys are among the key industrial materials and understanding of their properties and structure is of considerable importance. In this investigation, products of a laser vaporized copper-aluminum alloy are studied by time-resolved, laser-induced fluorescence. AlCu is identified among the products and three different electronic transitions of the molecule are analyzed. The electronic structure and bonding of the AlCu molecule will be discussed.

Address of Cai, Tsay, Pak, and Dzugan: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.
Present Address of Bondybey: Institut für Physikalische und Theoretical Chemie der Technischen Universität München, D-8046 Garching b. München, Deutschland - West Germany.

TD3 (9:04)

A LASER INDUCED FLUORESCENCE STUDY OF ELECTRONIC TRANSITIONS OF THE ALUMINUM DIMER

MING-FANG CAI, CHRISTOPHER C. CARTER, THOMAS P. DZUGAN, TERRY A. MILLER, AND VLADIMIR E. BONDYBEY

Currently there is great interest in the nature of the bonding in various types of metal dimers and clusters. Recently, the aluminum dimer has been observed in the products of laser vaporization of solid aluminum. The laser-induced fluorescence excitation spectra of the aluminum dimer reveal several electronic transitions.¹ Spectra of these transitions will be presented and the experimental molecular constants are compared with theoretical values.

¹M.-F. Cai, T. P. Dzugan, and V. E. Bondybey, in press.

Address of Cai, Carter, Miller, and Dzugan: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.
Present Address of Bondybey: Institut für Physikalische und Theoretical Chemie der Technischen Universität München, D-8046 Garching b. München, Deutschland - West Germany.

TD4 (9:21)**A HIGH RESOLUTION LASER SPECTROSCOPIC STUDY OF ELECTRONIC TRANSITIONS IN METAL DIATOMICS****CHRISTOPHER G. CARTER, MING-FANG CAI, THOMAS P. DZUGAN, SHANG-JIH TSAY, TERRY A. MILLER, AND VLADIMIR E. BONDYBEY**

The properties and structure of metal clusters, and in particular, both heteronuclear and homonuclear dimers, are of great interest and presently poorly known. Using laser vaporization techniques, the vibrational structure of several electronic transitions in Al_2 , $AlCu$, etc. has been observed.^{1,2} In recent work, we have obtained rotationally resolved spectra for some of these electronic transitions. We will present these spectra along with the rotational constants determined from them.

¹M.-F. Cai, T. P. Dzuga, and V. E. Bondybey, in press.

²M.-F. Cai, S.-J. Tsay, T. P. Dzuga, and V. E. Bondybey, in press.

Address of Carter, Cai, Dzuga, Tsay and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

Present Address of Bondybey: Institut für Physikalische und Theoretical Chemie der Technischen Universität München, D-8046 Garching b. München, Deutschland - West Germany.

TD5 (9:38)**PERMANENT ELECTRIC DIPOLE MOMENT MEASUREMENTS OF TRANSITION METAL OXIDES****J.E. Shirley, D.F. Nachman, T.C. Steimle**

The diverse and practically important chemical properties of transition metals have made them the focus of theoretical and experimental endeavors. Insight into the chemical properties of transition metals can be gained from an understanding of individual gas-phase transition metal containing molecules. The most relevant data for the elucidation of chemical bonding in these compounds are the permanent electric dipole moment and the magnetic hyperfine interactions. Because of the inherently transitory nature of these high temperature compounds there has historically been a lack of experimental information of this type.

With the use of intermodulated fluorescence (IMF)-Stark spectroscopy it has been possible to determine permanent electric dipole moments for the ground and excited electronic states of CuO , CuS , FeO , and CrO . The results of these high resolution spectroscopic studies and comparison with theoretical and semi-empirical models will be presented.

Address of Shirley, Nachman, and Steimle: Department of Chemistry, Arizona State University, Tempe, Arizona, 85287.

TD6 (9:55)**EXAMINATION OF SOME NEW SINGLET TRANSITIONS IN Li_2** **C. LINTON, F. MARTIN and R. BACIS**

Fluorescence spectra of 6Li_2 and 7Li_2 excited by the ultraviolet lines of Argon and Krypton ion lasers have been examined in the infrared region with a Fourier Transform Spectrometer. The various laser lines excited several $C^1\Pi_u + X^1\Sigma_g^+$ and $2^1\Sigma_u^+ + X^1\Sigma_g^+$ transitions and the resulting fluorescence was assigned to the $2^1\Sigma_u^+ - 2^1\Sigma_g^+$, $C^1\Pi_u - 1^1\Pi_g$, $C^1\Pi_u - 2^1\Sigma_g^+$ and $2^1\Sigma_u^+ - 1^1\Pi_g$ transitions. None of these transitions have been previously observed and this was the first experimental observation of the $2^1\Sigma_u^+$ "double minimum" state.

The assignment and analysis of the spectra will be presented for both isotopes and the results will be discussed in relation to ab-initio calculations. Several perturbations were observed and their assignment and analysis will be presented.

Address of Linton: Physics Department, University of New Brunswick, P.O. Box 4400, Fredericton, N.B. Canada, E3B 5A3.

Address of Martin and Bacis: Laboratoire de Spectrométrie Ionique et Moléculaire, Université Claude Bernard-Lyon I, 69622 Villeurbanne, France.

Intermission

TD7 (10:30)

SPECTROSCOPY OF RARE EARTH OXIDES: RECENT OBSERVATIONS

GUO BUJIN, C.H. CHENG and C. LINTON

The high resolution analysis of Samarium monoxide, presented last year, has continued. The spectra of ten transitions involving 5 low lying and 5 high lying states have been assigned and analyzed for six isotopes of samarium. The results of the analysis will be presented together with a discussion of observed perturbations and Ω doubling.

Some preliminary data has been obtained for Erbium Monoxide. Ligand Field Theory predicts that the low lying states are very close together and have low Ω which arise from projections on the internuclear axis of high angular momentum atomic states. This is expected to lead to some very strong perturbations and unusual spectra. The preliminary results will be discussed.

Address: Physics Department, University of New Brunswick, P.O. Box 4400, Fredericton, N.B., Canada, E3B 5A3

TD8 (10:47)

HIGH RESOLUTION SPECTROSCOPY AND PHOTOPHYSICS OF TRANSITION METAL CONTAINING DIATOMIC MOLECULES:

THE VISIBLE SPECTRUM OF VANADIUM NITRIDE

B. Simard and P. A. Hackett

The electronic spectrum of vanadium nitride has been studied in a molecular beam apparatus by laser-induced fluorescence. Rotational temperatures of ca. 25-30 K have been observed. Several electronic transitions have been observed at low resolution (0.1 cm^{-1}) in the 4000-7500 Å region. These have all been assigned. The (0,0) band of the $D^3\Pi(\pi_{3d}^1 \delta_{3d}^1) - X^3\Delta(\sigma_{4s}^1 \delta_{3d}^1)$ system is centered near 6240 Å and has been investigated at high resolution (120 MHz). The nuclear magnetic hyperfine structure which arises from the interaction of a metal centered unpaired electron (chiefly the σ_{4s} electron) with the magnetic nucleus of vanadium ($I=7/2$) has been resolved and a preliminary analysis will be presented. Besides the three case (a) allowed sub-bands, which are very prominent, three weak satellite bands could be observed at high resolution and their analyses permitted the triplet splittings to be determined. A transition centered near 6165 Å has been ascribed as the (0,0) band of the $d^1\Sigma^+ - X^3\Delta_1$ intercombination system. This band has been investigated at high resolution and a rotational analysis has been completed.

Laser Chemistry Group, Division of Chemistry, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6.

TD9 (11:04)

HIGH RESOLUTION SPECTROSCOPY AND PHOTOPHYSICS OF TRANSITION METAL CONTAINING DIATOMIC MOLECULES:
THE $C^4\Sigma^- - X^4\Sigma^-$ SYSTEM OF NIOBIUM SULPHIDE

B. Simard and P. A. Hackett

The $C^4\Sigma^- - X^4\Sigma^-$ system of niobium sulphide, NbS, has been studied in a molecular beam apparatus by laser-induced fluorescence. A vibronic analysis has been carried out and leads to the following constants: $\omega_e'' = 544.0 \text{ cm}^{-1}$, $\omega_e x_e'' = 1.7 \text{ cm}^{-1}$, $\omega_e' = 489.6 \text{ cm}^{-1}$, $\omega_e x_e' = 2.7 \text{ cm}^{-1}$. The data clearly show that the coupling scheme in both the C and X states are best described as case (a). A weak satellite band lying 62.7 cm^{-1} from the R-head of the $C^4\Sigma_{3/2}^- - X^4\Sigma_{3/2}^-$ sub-band could not be fitted to the C-X system. This band is tentatively assigned as a $^2\Sigma^+ - X^4\Sigma_{1/2}^-$ transition where the $^2\Sigma^+$ state contains a large admixture of $C^4\Sigma_{1/2}^-$ character. The dispersed emission spectrum resulting from the decay of the $^2\Sigma^+$ state leads to an energy separation of about 62 cm^{-1} between the $X^4\Sigma_{1/2}^-$ and the $X^4\Sigma_{3/2}^-$ components. The energy separation between the $C^4\Sigma_{1/2}^-$ and the $C^4\Sigma_{3/2}^-$ components is highly dependent of the vibrational energy content and is about 80, 77, 73, 63 and 62 cm^{-1} for the vibrational levels 0, 1, 2, 3 and 4 respectively. The (0,0) band has also been investigated at high resolution and this allowed the nuclear magnetic hyperfine structure, which arises from the interaction of a metal centered unpaired electron with the magnetic nucleus of niobium (I=9/2) to be resolved. A preliminary analysis will be presented.

Laser Chemistry Group, Division of Chemistry, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6.

TD10 (11:21)

THE ELECTRONIC SPECTRUM OF GAS-PHASE Nb_2

S.A. MITCHELL, C.L. CALLENDER AND P.A. HACKETT

Preliminary spectroscopic data for Nb_2 are reported. The dimer was produced by laser vapourization of a niobium rod, followed by supersonic expansion in helium. Several bands attributed to Nb_2 were observed by laser induced fluorescence in the region 670 - 680 nm. Analysis of the rotationally resolved structure observed in a strong band at around 674 nm allowed B values and bond lengths for the ground and upper states to be estimated. Further high resolution studies are currently underway. Resonant two-photon ionization spectroscopy gave rise to identical bands and provided an estimate of $51,330 \text{ cm}^{-1}$ for the first ionization potential of Nb_2 .

Address of Authors: Laser Chemistry Group, Division of Chemistry, National Research Council, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6.

TD11 (11:28)

VIBRONIC SPECTROSCOPY AND DYNAMICS IN THE JET-COOLED SILVER TRIMER

P. Y. Cheng and M. A. Duncan

Silver atom clusters are produced in a supersonic molecular beam with pulsed-nozzle laser vaporization. Mass-resolved resonant two-photon photoionization produces an electronic spectrum for the trimer (Ag_3) with an origin at $26,971 \text{ cm}^{-1}$ (3.34 eV). 17 vibronic bands are resolved. The vibronic level structure is consistent with a triangular ${}^2E''$ excited state undergoing dynamic Jahn-Teller distortion. Vibrational frequencies are obtained for the symmetric stretch (179 cm^{-1}) and the doubly degenerate bend (104 cm^{-1}).

Ongoing two-color experiments will attempt to measure the ionization potential and level specific lifetimes.

Address: Department of Chemistry, University of Georgia, Athens, Georgia, 30602.

TD12 (11:45)

DETERMINING DIATOM DISSOCIATION LIMITS AND LONG-RANGE POTENTIAL COEFFICIENTS FROM DIRECT FITS TO VIBRATIONAL ENERGIES AND ROTATIONAL CONSTANTS.

Mark R. Davies and Robert J. Le Roy

The usual method of analysing spectroscopic data for levels lying near dissociation in order to determine the dissociation energy and obtain estimates of the characteristic inverse-power long-range potential coefficients, involves first the determination of turning points for those levels, followed by least-squares fits of the outer turning points to the usual long-range potential form: $V(R) = D - \sum C_m/R^m$.¹ However, such fits are very highly correlated, leading to large statistical uncertainties in the resulting parameters, and more seriously, this approach offers no way of properly estimating the effect on these results of uncertainties in the experimental data.

This paper describes an alternate approach to this problem, in which the semiclassical expressions for the vibrational energies and rotational constants are fitted directly to the experimental data. This allows the effect of the experimental uncertainties to be directly reflected in the fitted parameter values and their uncertainties. Moreover, the effects of interparameter correlation are considerably reduced when one fits to the experimental quantities themselves, rather than to turning points derived from them.² Applications to both a model problem and to experimental data for real systems will be presented.

¹ See, e.g., S. Gerstenkorn and P. Luc, *J. Physique* 48, 1685 (1987).

² R.J. Le Roy, *J. Chem. Phys.* 73, 6003 (1980).

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

TE1 (1:30)**FTIR SPECTROSCOPY OF AEROSOLS****T.A. Dunder and R.E. Miller**

An experimental technique has been developed for the study of large clusters (aerosols) whose sizes are in the micron regime. The method is a variant of the technique developed by De Lucia¹ in which the gas of interest is injected into a helium-filled, liquid nitrogen cooled gas cell wherein rapid collisional cooling occurs. The diffusion time to the cell walls greatly exceeds the cooling time, such that the gas is "diffusion trapped" and may homogeneously condense to form clusters. The FTIR spectroscopy of the clusters reveals scattering and absorbance features. With the assumption of spherical clusters, Mie theory calculations have been performed using the bulk optical constants of the materials. From this analysis the size distribution has been determined. Results for C₂H₂, NH₃, and H₂O will be discussed, as well as applications of the technique to atmospheric studies.

¹J.K. Messer and F.C. De Lucia, Phys. Rev. Lett. 53, 2555 (1984).

Address of Authors: Dept. of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27599.

TE2 (1:47)**INFRARED INTENSITY ANALYSIS: APPLICATION TO THE SPECTRA OF MATRIX-ISOLATED THIOURACILS^a****WILLIS B. PERSON, K. KUBULAT, J. R. LESZCZYNSKI, AND K. SZCZEPANIAK**

Molecular orbital ab initio calculations (with a 3-21G* basis set) have been carried out for the infrared spectra of 2- and 4-thiouracil and of 2,4-dithiouracil. These calculated spectra compare very well with the experimental spectra from studies of these molecules isolated in an argon matrix at 15 K. Because this agreement is so good, we investigate the results from the calculation to determine just which bond displacements contribute to the intensity of each of the observed fundamentals. Such an "intensity analysis" gives a detailed picture of the source of the intensities in the observed spectra, and how these contributions change as a result of substitution of S atoms for O atoms in different positions in the parent uracil molecule.

^a Support from NIH Research Grant GM-32988 is gratefully acknowledged, as is support from the Alabama Supercomputing Network for the computations.

Address of Person, Kubulat, and Szczepaniak: Department of Chemistry, University of Florida, Gainesville, FL 32611.

Address of Leszczynski: Department of Chemistry, University of Alabama, Birmingham, AL 35294.

TE3 (2:04)

INTENSITIES OF ASYMMETRIC SPECIES BANDS AND HERMAN-WALLIS FACTORS FOR CARBON DIOXIDE CALCULATED BY DIRECT NUMERICAL DIAGONALIZATION

R. B. WATTSON, A. NEWBURGH, G. GALICA, and L. S. ROTHMAN

The transformation of the potential energy surface from normal coordinates to valence internal coordinates and back again, derived to seventh order, has been used to calculate band centers and intensities for the asymmetric species of carbon dioxide. The method used is an extension of the transformation in Hoy *et al.*¹ The calculation of the dipole moment function uses the same transformation. The results will be compared to experimental band parameters and to previously calculated parameters on the HITRAN database.²

Calculations of Herman-Wallis factors have been made by including the mixing of the perpendicular and parallel components of the dipole moment function resulting from the Coriolis diagonalization. Comparisons with experiment and recent calculations³ using perturbation theory will be presented.

The possibility of employing the formalism that has been used for linear molecules to non-linear molecules will be discussed. Convergence difficulties will be displayed and the method will be evaluated.

1. A.R. Hoy, I.M. Mills, and G. Strey, *Mol. Phys.* **24**, 1265 (1972).
2. L.S. Rothman, *et al.*, *Appl. Opt.* **26**, 4058 (1987).
3. J.K.G. Watson, *J. Mol. Spectrosc.* **125**, 428 (1987); **132**, 477 (1988).

Address of Wattson, Newburgh, and Galica: 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

TE4 (2:21)

REDUCING BACKGROUND EFFECTS IN NONLINEAR LEAST-SQUARES LINE INTENSITY ESTIMATES

R. L. HAWKINS

This paper proposes a method for reducing the effects of background (100% transmittance level) variations on line intensities measured by nonlinear least-squares fitting of transmittance spectra, without modelling the background.

Let f be a low-pass filter function, much wider than the lines in the spectrum. The spectrum is BT , where B is a slowly varying background and T the transmittance. The convolution $f*(BT)$ is then a lower-resolution version of the spectrum, with essentially the same background. The ratio $BT/(f*(BT))$ is a distorted version of T with the background cancelled out.

If T' is a calculated transmittance, then $T'/(f*T')$ can be fit to the distorted spectrum, obtaining line intensities without modelling B . This method reduces peak (observed-calculated) errors due to an unmodelled background by more than a factor of 10. Careful selection of the filter function f can yield error spectra which have almost zero correlation with the true spectrum, and therefore cause reduced errors in the retrieved intensities.

Lipkus¹ used this ratio, but with f a Legendre filter, to permit comparison between a sample spectrum containing a background and a background-free standard spectrum. Statham² and Atakan *et al.*³ used a similar method based on direct high-pass filtering of the spectrum. However, their filters produce error spectra which are highly correlated with the spectrum being fit.

¹A.H. Lipkus, *Appl. Spectrosc.* **42**, 395 (1988).

²P.J. Statham, *Anal. Chem.* **49**, 2149 (1977).

³A.K. Atakan, W.E. Blass and D.E. Jennings, *Appl. Spectrosc.* **34**, 369 (1980).

Address of Hawkins: Infrared Physics Branch, Optical Physics Division, Air Force Geophysics Laboratory, Hanscom AFB, MA 01731.

TE5 (2:33)

TEMPERATURE DEPENDENT MEASUREMENTS AND MODELING OF ABSORPTION BY
CO₂-N₂ MIXTURES IN THE FAR WING OF THE 4.3 μm CO₂ BAND

M.Y. Perrin, J.M. Hartmann, and L. Rosenmann

We present measurements of the absorption by CO₂-N₂ mixtures in the 4.3 μm region.

Experiments have been made in the 300-800 K and 0-60 bar ranges; they are in good agreement with previous determinations below 296 K. Frequency and temperature dependent factors χ are introduced in order to account for the sublorentzian behaviour of CO₂ far line-wings. Their dependences on temperature are deduced from experimental results beyond the 4.3 μm band-head in the 193-773 K range for both CO₂-CO₂ and CO₂-N₂ and fitted by simple analytical functions.

Comparisons between experimental and theoretical spectra in both sides of the band (2100-2600 cm⁻¹ range) are presented. It is shown that calculations using χ factors are inaccurate near line-centers at elevated pressure.

Address : Laboratoire E.M.2.C du CNRS (UPR 73) et de l'École Centrale des Arts et Manufactures, Ecole Centrale, Grande voie des Vignes, 92295 Châtenay-Malabry Cedex, France.

TE6 (2:45)

LINE POSITIONS OF HIGH TEMPERATURE CO₂ IN THE 15 μm REGION

MARK P. ESPLIN AND MICHAEL HOKE

A CO₂ sample of natural isotopic abundance has been heated to 800 K in a high temperature absorption cell of pathlength 1 3/4 meters. Spectra were taken using the AFGL (Air Force Geophysics Laboratory) high resolution Fourier transform spectroscopy with a resolution of 0.004 cm⁻¹. Many "hot bands" in the ν_2 region were observed. Effective vibration-rotation constants for these bands will be presented.

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.

TE7 (2:57)

MOLECULAR CONSTANTS AND INTENSITIES OF CARBON DIOXIDE BANDS IN THE 2395 TO 2760 CM⁻¹ SPECTRAL REGION

D. CHRIS BENNEK, V. MALATHY DEVI, C. P. RINSLAND, AND M. A. H. SMITH

Room temperature absorption spectra of ¹³C- and ¹⁸O-enriched carbon dioxide have been analyzed in the 2395-2760 cm⁻¹ spectral region. The data used in the analysis were recorded at low pressure (1 Torr) and 0.01-cm⁻¹ resolution with the Fourier transform spectrometer in the McMath solar telescope facility on Kitt Peak. Accurate positions and absolute intensities for over 900 unblended lines belonging to 11 bands of ¹⁶O¹³O¹⁸O, ¹⁶O¹³O¹⁷O, ¹⁶O¹²O¹⁸O, and ¹²C¹⁶O₂ have been determined using a nonlinear least-squares spectral fitting technique. For each band, the measured line positions were fitted to determine the band center and effective upper- and lower-state rotational constants and the absolute line intensities were fitted to determine the vibrational band intensity and F-factor coefficients. These results will be reported and compared with values available in the literature.

Address of Benner and Malathy Devi: Department of Physics, College of William and Mary, Williamsburg, VA 23185

Address of Rinsland and Smith: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665-5225

Intermission

TE8 (3:25)

MOLECULAR PARAMETERS FOR CARBON DIOXIDE BANDS IN THE 1820-2050 cm^{-1} SPECTRAL REGION

V. MALATHY DEVI, D. CHRIS BENNER, C. P. RINSLAND, AND M. A. H. SMITH

Line positions and intensities of carbon dioxide transitions between 1820 and 2050 cm^{-1} have been determined from long-path, low-pressure, room-temperature spectra recorded with 0.01 cm^{-1} resolution using the Fourier transform spectrometer in the McMath solar telescope facility on Kitt Peak. Several vibration-rotation bands belonging to the $^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{18}\text{O}_2$, $^{16}\text{O}^{12}\text{C}^{18}\text{O}$, $^{16}\text{O}^{13}\text{C}^{18}\text{O}$, and $^{16}\text{O}^{13}\text{C}^{17}\text{O}$ molecules were identified and unambiguous assignments made for more than 1200 lines.

Absolute intensities were derived for more than 1000 unblended lines belonging to 12 bands completely contained in this spectral region using a nonlinear least-squares spectral fitting technique. For each band, the accurately measured positions were fitted to determine the band center and effective upper- and lower-state rotational constants while the absolute intensities were fitted to determine the vibrational band intensity and F-factor coefficients. For this analysis, a CO_2 sample enriched in ^{13}C - and ^{18}O - was used in absorption path lengths of 48, 144 and 385 m with sample pressures of -1 Torr. The results will be presented and comparison made to values available in the literature.

Address of Malathy Devi and Benner: Department of Physics, College of William and Mary, Williamsburg, VA 23185

Address of Rinsland and Smith: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665-5225

TE9 (3:37)

THE $^{16}\text{O}_3$ ABSORPTION SPECTRUM NEAR 3.3 μm

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

Spectra of ozone generated from a 99.98% pure oxygen sample were recorded covering the 2800-3500 cm^{-1} at 0.010 cm^{-1} resolution with the McMath Fourier transform interferometer at the National Solar Observatory on Kitt Peak. The first extensive analysis of the 4 bands $3\nu_3$, $2\nu_3+\nu_1$, $2\nu_1+\nu_2$ and $3\nu_1$ absorbing in this spectral region has been performed leading to a precise set of rotational energy levels for the 4 vibrational interacting states $\{(003), (201), (102), (300)\}$. These experimental levels were then reproduced with the aid of a Hamiltonian taking into account the various resonances (Coriolis, Darling-Dennison) affecting the levels.

Moreover, using the equivalent width method, intensities of lines belonging to the four bands were measured with a relative uncertainty of about 10% and used to determine the corresponding transition moment constants.

Finally, from the vibrational energies, rotational and coupling constants as well as transition moment constants a complete and precise list of the line positions and intensities of the $3\nu_3$, $2\nu_3+\nu_1$, $\nu_3+2\nu_1$ and $3\nu_1$ bands of $^{16}\text{O}_3$ has been generated.

Address of 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

Address of Rinsland and Smith : Atmospheric Sciences Division, MS 401A, NASA Langley Research Center, Hampton, Virginia 23665-5225

Address of Malathy Devi : Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185

Address of Barbe : Groupe de Spectrométrie Moléculaire et Atmosphérique, Faculté des Sciences, 51062 Reims Cedex, France

TE10 (3:49)

IMPROVED LINE PARAMETERS FOR OZONE BANDS IN THE 4.8 AND 10 μm SPECTRAL REGIONS

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

In the present work, we report improved line parameters generated for ozone absorption bands in the 4.8 and 10 μm spectral regions. These parameters have been obtained by combining the results of recent analyses of room temperature laboratory absorption spectra of natural and ^{18}O -enriched ozone samples recorded at either 0.005 or 0.010 cm^{-1} resolution with the Fourier transform spectrometer operated on Kitt Peak by the National Solar Observatory. All of the parameters for the 4.8 and 10 μm bands have been updated as compared to those on the 1986 HITRAN compilation.

In the 10 μm region, the results reported by Flaud et al.^{1,2} and Camy-Peyret et al.³ have been used to compute positions, intensities, and lower state energies for the ν_1 and ν_3 bands of the $^{16}\text{O}_3$, $^{16}\text{O}^{16}\text{O}^{16}\text{O}$, and $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ isotopic species. The corresponding parameters for the $\nu_2+\nu_3-\nu_2$, $\nu_1+\nu_2-\nu_2$, $2\nu_3-\nu_3$, $\nu_1+\nu_3-\nu_1$, and $2\nu_1-\nu_3$ hot bands of $^{16}\text{O}_3$ were calculated using energy levels derived from studies of the 4.8, 5.7, and 14.3 μm spectral regions. The $2\nu_1-\nu_3$ band has been calculated for the first time; it is unexpectedly strong, with numerous lines observable between 1100 and 1250 cm^{-1} .

In the 4.8 μm region, the positions, intensities, and lower state energies of the $2\nu_1$, $\nu_1+\nu_3$, and $2\nu_3$ bands of $^{16}\text{O}_3$ were taken from Ref. 4. Corresponding parameters for the $\nu_2+2\nu_3-\nu_2$, $\nu_1+\nu_2+\nu_3-\nu_2$, and $2\nu_1+\nu_2-\nu_2$ hot bands of $^{16}\text{O}_3$ were calculated using energy levels determined from analysis of the 3.6 and 14.3 μm spectral regions.

For all bands, air-broadening coefficients at 296 K were calculated from a polynomial in J derived by fitting air-broadening measurements of individual lines in the ν_1 and ν_3 bands of $^{16}\text{O}_3$.⁵ Self-broadening coefficients at 296 K were calculated from a similar fit to the measurements reported by Smith et al.⁶

The new ozone line parameters yield considerable improvement in the accuracy of high resolution atmospheric transmission and emission calculations in 4.8 and 10 μm regions. Simulations generated with the new line parameters are compared with the laboratory spectra and 0.003 cm^{-1} resolution solar occultation spectra of the stratosphere to illustrate the quality of the new line parameters.

¹J.-M. Flaud et al., J. Mol. Spectrosc. **118**, 334-344 (1986).

²J.-M. Flaud et al., J. Mol. Spectrosc. **124**, 209-217 (1987).

³C. Camy-Peyret et al., J. Mol. Spectrosc. **118**, 345-354 (1986).

⁴C. P. Rinsland et al., J. Mol. Spectrosc. **130**, 204-212 (1988).

⁵M. A. H. Smith et al., J. Opt. Soc. Am. B **5**, 585-592 (1988).

⁶M. A. H. Smith et al., this session.

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.

Address of Goldman: Department of Physics, University of Denver, Denver, Colorado 80208.

TE11 (4:06)

MEASUREMENTS OF SELF-BROADENING OF OZONE

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

Self-broadened halfwidths have been determined for nearly 200 spectral lines of six different vibration-rotation bands of $^{16}\text{O}_3$ in the 4-14 μm region. These results were obtained from two series of room-temperature absorption spectra recorded at 0.005 cm^{-1} resolution using the McMath Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. The halfwidth values were obtained through a nonlinear least-squares spectral fitting procedure, and the resulting self-broadening coefficients lie within the range of 0.08 to 0.17 $\text{cm}^{-1}\text{atm}^{-1}$ at 296 K. These results are compared to previous measurements of ozone self-broadening, and the variation of the halfwidths with vibrational and rotational quantum numbers is examined.

Address of Smith and Rinsland: NASA Langley Research Center, Atmospheric Sciences Division, Mail Stop 401A, Hampton, Virginia 23665-5225.

Address of V. Malathy Devi: Physics Department, The College of William and Mary, Williamsburg, Virginia 23185.

TE12 (4:18)

NEW MEASUREMENTS AND ANALYSIS OF $H_2^{16}O$, $H_2^{17}O$, AND $H_2^{18}O$ IN THE 6.2 μm REGION

R. A. TOTH

The spectral region from 1000 to 2600 cm^{-1} was observed with the Kitt Peak FTS (McMath Solar telescope facility) at a resolution of 0.005 cm^{-1} . For $H_2^{17}O$ and $H_2^{18}O$, isotopically enriched samples of $H_2^{17}O$ (~60% $H_2^{17}O$ and ~40% $H_2^{16}O$) and $H_2^{18}O$ (~98% $H_2^{18}O$) were used.

Values of line positions and strengths were derived from measurements in the 010-000 and 020-010 bands of the three species. The line positions measurements were analyzed to obtain rotational energy level values in the (000), (010), and (020) states. The line strength analysis included transitions of which the minimum strengths were $5 \times 10^{-7} cm^2/atm$ for $H_2^{16}O$, and $\sim 10^{-6} cm^2/atm$ (normalized to 100% sample) for $H_2^{17}O$ and $H_2^{18}O$ at 296K.

Address of Toth: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109.

TE13 (4:35)

THE SPECTRUM OF $H_2^{16}O$ BETWEEN 9500 AND 11500 cm^{-1}

J.-P. Chevillard, J.-Y. Mandin, J.-M. Flaud and C. Camy-Peyret

The spectrum of water has been recorded between 9500 and 11500 cm^{-1} with the Fourier transform interferometer built by J.W. Brault, at NSO (Kitt Peak, AZ). The resolution is 0.015 cm^{-1} .

More than 530 accurate rotational energy levels have been determined for the following vibrational states: (041), (220), (121), (022), (300), (201), (102), and (003), belonging to the first decad of interacting states. About 750 intensities of well isolated lines have been accurately measured (typical uncertainty 7%) using the curve of growth method. The intensities of the remaining lines have also been obtained using the line depths measured from the spectra. The uncertainty in the intensities obtained by this faster method is on the average 15%.

Finally, a complete set of 2400 line positions and intensities is available between 9500 and 11500 cm^{-1} .

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

TE14 (4:47)

Low-Temperature Tunable Diode Laser Measurements of Line Positions, Intensities, and Air-Broadening Coefficients in the HNO_3 7.5 μm Band.

R.D. May and C.R. Webster

A computer-controlled tunable diode laser spectrometer has been used to measure line strengths, line positions, and air-broadening coefficients in selected regions of the HNO_3 7.5 μm band at 295 K and at 213 K. This spectral region is useful for atmospheric monitoring of HNO_3 , which is receiving increased attention due to the crucial role played by nitric acid in ozone depletion mechanisms active both in the north and south polar regions. Extraction of chlorine nitrate ($ClONO_2$) concentrations from atmospheric spectra using the strong Q-branch at 1292 cm^{-1} also relies on accurate line parameters for the overlapping HNO_3 subbands. The measurements reported here should result in improved $[HNO_3]$ and $[ClONO_2]$ retrievals from observed atmospheric spectra, and aid in the development of a better theoretical description of the interacting ν_3 and ν_4 bands.

Address: Jet Propulsion Laboratory, California Institute of Technology
Mail Stop 183 - 301
4800 Oak Grove Drive, Pasadena, California 91109

TE15 (5:02)

Far Infrared FT Spectroscopy of CHF_3

JOCHEN FRIES, DIETER HAUSAMANN, and VOLKER TANK

In the framework of atmospheric trace gas investigations the far infrared spectrum of CHF_3 has been observed with a high resolution (0.0013 cm^{-1}) Fourier transform spectrometer. In the $50 \leq J \leq 75$, $K \geq 10$ regime of the vibrational ground state, some 100 new rotational transitions ($J+1 \rightarrow J$, $K \rightarrow K$) were identified. These data help to improve the rotational constants obtained by Carlotti et al.¹⁾

1) M. Carlotti et al., J. Mol. Spectrosc. 123, 135 (1987)

Address: Institute of Optoelectronics, German Aerospace,
Research Est., D-8031 Oberpfaffenhofen, FRG

TF1 (1:30)

MICROWAVE AND INFRARED ELECTRIC-RESONANCE OPTOTHERMAL SPECTROSCOPY OF HF-HCl AND HCl-HF

G. T. FRASER AND A. S. PINE

Microwave and infrared spectra of HF-HCl and HCl-HF have been obtained using a molecular-beam electric-resonance optothermal spectrometer, which operates by quadrupole-field focusing of polar molecules onto a bolometer detector. The HF-HCl microwave measurements extend to $K_a=1$ the previous $K_a=0$ results of Janda, Steed, Novick, and Klemperer, allowing the determination of the K_a dependence and asymmetry of the Cl quadrupole coupling constant. For the metastable HCl-HF isomer no previous spectroscopic measurements have been reported. Here, microwave spectra are observed for the $K_a=0$ and 1 states and interpreted in terms of an L-shaped hydrogen-bonded structure for the complex, with a 3.235 Å center-of-mass separation between the HF and HCl subunits. The D_J distortion constants indicates that the harmonic stretching force constant for HCl-HF is ~35% larger than that of HF-HCl. Infrared spectra of the $K_a=0-0$ and 1-0 subbands of the H-F stretching band for HF-HCl and of the $K_a=0-0$ subband of the H-F stretch for HCl-HF are also reported. The vibrational predissociation linewidths depend on vibration, K_a state, isotopic species, and isomer excited.

Address of Fraser and Pine: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

TF2 (1:47)

ClO DIMER, ITS ROTATIONAL SPECTRUM, STRUCTURE, AND ATMOSPHERIC IMPORTANCE

M. BIRK, R. R. FRIEDL, E. A. COHEN, H. M. PICKETT AND S. P. SANDER

The products of the ClO self-reaction have been studied in a flowing chemical reactor using submillimeter wave spectroscopy. The region between 415 to 435 GHz was completely measured in the initial search for reaction products. The major products have been identified as one isomer of the ClO dimer and OClO. There is no evidence of a significant amount of additional dimer isomers. The observed ClO dimer has a b -type spectrum which has been shown definitively to arise from a peroxide structure, ClOOCl. The rotational constants as well as a complete set of quartic centrifugal distortion constants have been determined for the $^{35}\text{ClOO}^{35}\text{Cl}$ and $^{35}\text{ClOO}^{37}\text{Cl}$ isotopic species. Structural parameters have been derived from the ground state rotational constants and will be compared with *ab initio* results. In addition, the significance of the molecular structure with respect to ozone depletion in the polar stratosphere will be discussed.

Address of the authors: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

TF3 (2:04)

VAN DER WAALS COMPLEXES OF CHEMICALLY REACTIVE GASES: OZONE-ACETYLENE

J. Z. GILLIES, C. W. GILLIES, F. J. LOVAS, K. MATSUMURA AND R. D. SUENRAM

Pulsed beam Fourier transform microwave spectroscopy was used to investigate the rotational spectrum of the bimolecular complex formed between ozone and acetylene. The reactive gas mixture was sampled with a pulsed solenoid valve modified to allow the gases to be led separately into the high pressure side of the orifice through two ports. Two sets of rotational transitions were observed for $\text{O}_3\cdots\text{HC}\equiv\text{CH}$, $\text{O}_3\cdots\text{DC}\equiv\text{CH}$ and $\text{O}_3\cdots\text{DC}\equiv\text{CD}$. Nuclear spin statistics observed for the $\text{O}_3\cdots\text{HC}\equiv\text{CH}$ and $\text{O}_3\cdots\text{DC}\equiv\text{CD}$ isotopes indicate the splitting of the lines arises from internal rotation of acetylene about an axis perpendicular to the $-\text{C}\equiv\text{C}-$ axis. Both states for the three isotopes were fit to a Watson Hamiltonian giving the following rotational constants (in MHz) for the normal isotopic species: $A=9027.483(4)$, $B=2750.606(6)$ and $C=2184.160(6)$ for the excited state and $A=9030.074(3)$, $B=2750.588(8)$ and $C=2184.177(10)$ for the ground state. Stark effect measurements demonstrated the complex has a plane of symmetry with $\mu_a=0.041(1)$ and $\mu_c=0.473(1)$ Debyes. Least squares fits of the moment of inertia data were consistent with two structural forms. R_{cm} , the center of mass separation of ozone and acetylene was found to be 3.251(18)Å. Θ , the angle between the local C_2 axis of ozone and R_{cm} distinguishes the two forms. The moment of inertia data fit equally well to $\Theta=67(6)^\circ$ and $112(6)^\circ$.

Address of Gillies and Gillies: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180

Address of Lovas, Matsumura and Suenram: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

TF4 (2:21)

ROTATIONAL SPECTRA AND STRUCTURE OF ETHYLENE-OZONE COMPLEX

J. Z. GILLIES, C. W. GILLIES, R. D. SUENRAM, F. J. LOVAS AND W. STAHL

Microwave spectra of $\text{CH}_2=\text{CH}_2\cdots\text{O}_3$, $\text{CD}_2=\text{CH}_2\cdots\text{O}_3$ and *cis*- $\text{CHD}=\text{CHD}\cdots\text{O}_3$ were observed with a pulsed beam Fabry-Perot cavity Fourier Transform microwave spectrometer. Internal motions produced two components for each transition of the $\text{CH}_2=\text{CH}_2\cdots\text{O}_3$ and $\text{CD}_2=\text{CH}_2\cdots\text{O}_3$ complexes and only one component for each line of *cis*- $\text{CHD}=\text{CHD}\cdots\text{O}_3$. Nuclear spin statistics observed for $\text{CH}_2=\text{CH}_2\cdots\text{O}_3$ and $\text{CD}_2=\text{CH}_2\cdots\text{O}_3$ indicate the two states arise from internal rotation of ethylene about its C=C axis in the complex. The sets of lines for all three isotopes were independently fit to a Watson Hamiltonian. The rotational constants (in MHz) of $\text{CH}_2=\text{CH}_2\cdots\text{O}_3$ are $A=8246.841(2)$, $B=2518.972(4)$ and $C=2044.248(5)$ for the ground state and $A=8241.897(4)$, $B=2518.941(9)$ and $C=2044.287(11)$ for the excited state. Dipole moment measurements of $\text{CH}_2=\text{CH}_2\cdots\text{O}_3$ determined $\mu_a=0.017(1)$ and $\mu_c=0.466(2)$ Debye. The dipole and moment of inertia data show that the complex belongs to the C_s point group. Least squares fits of the isotopic moment data find the distance between the two centers of mass of $\text{CH}_2=\text{CH}_2$ and O_3 to be $3.279(27)\text{\AA}$. Four forms distinguished by tilts of the two planes containing the $\text{CH}_2=\text{CH}_2$ and O_3 subunits are consistent with the isotopic data. 1,3-dipolar cycloaddition theory and *ab initio* calculations are used with the structural results to argue that the $\text{CH}_2=\text{CH}_2\cdots\text{O}_3$ complex lies in a small minimum on the reaction coordinate prior to the transition state which produces ethylene primary ozonide $\overline{\text{CH}_2\text{CH}_2\text{OOO}}$.

Address of Gillies and Gillies: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180.

Address of Suenram and Lovas: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899.

Address of Stahl: Institut für Physikalische Chemie, Universität Kiel, Ludewig-Meyn-Str. 8, 230Kiel, Germany.

TF5 (2:38)

THE MICROWAVE SPECTRA OF THE ETHYLENE-SO₂ AND BENZENE-SO₂ DIMERS

A. M. ANDREWS, M. S. LABARGE, A. TALEB-BENDIAB, K. W. HILLIG II, AND R. L. KUCZKOWSKI

The rotational spectra of the $\text{C}_2\text{H}_4\text{-SO}_2$ and $\text{C}_6\text{H}_6\text{-SO}_2$ dimers have been observed with a FTMW spectrometer. Twenty-eight a and c dipole transitions have been assigned for $\text{C}_2\text{H}_4\text{-SO}_2$. The transitions occur as doublets of unequal intensity. The doublets presumably arise from internal rotation of the ethylene; the splittings are markedly affected by deuteration. The C_2H_4 and SO_2 planes are more or less parallel separated by $3.51(2)\text{\AA}$ (R_{cm}). The dipole moment of the dimer is $1.65(1)\text{ D}$, virtually unchanged from free SO_2 . Twenty-seven a and c dipole transitions have been assigned for the $\text{C}_6\text{H}_6\text{-SO}_2$ dimer. A number of additional transitions occur which are believed to arise from free or nearly free internal rotation states. The C_6H_6 and SO_2 planes are approximately parallel separated by $3.48(2)\text{\AA}$ (R_{cm}). The dipole moment of the complex is $2.05(1)\text{ D}$.

Address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

TF6 (2:55)

THE MICROWAVE SPECTRA OF THE TRIMETHYLAMINE-SO₂ AND PYRIDINE-SO₂ DIMERS

J.-J. OH, M. S. LABARGE, J. MATOS, K. W. HILLIG II, AND R. L. KUCZKOWSKI

The rotational spectra of TMA-SO₂ and C₅H₅N-SO₂ have been observed in a FTMW spectrometer. Twenty-five a and c dipole transitions have been assigned for the TMA-SO₂ charge transfer complex. The C₃ axis of the TMA points toward the sulfur atom and makes an angle of 101° with the SO₂ plane. The N-S distance is 2.28(3) Å. The dipole moment of the complex is 4.80(4) D. Forty-one a and c dipole transitions have been assigned for the pyridine-SO₂ dimer. Two structures fit the rotational constants. The most likely structure is similar to TMA-SO₂ with the nitrogen end of the pyridine pointing at the sulfur atom. The pyridine and SO₂ planes are approximately perpendicular and the N-S distance is 2.54(3) Å. The dipole moment is 4.81(3) D. No evidence for internal rotation or tunneling has been observed for either complex.

Address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

Intermission

TF7 (3:30)

SPECTROSCOPIC DETERMINATION OF THREE STABLE ISOMERS OF THE MIXED BINARY COMPLEX N₂O-HCN

D.C. Dayton and R.E. Miller

The optothermal detection method has been used to obtain the first spectroscopic results for the mixed binary complex N₂O-HCN. Three distinctive spectra were recorded in the C-H stretching region of HCN monomer which are attributed to three isomeric forms of N₂O-HCN. To date, only a handful of weakly bound species have exhibited more than one stable form. In particular, N₂O-HF^{1,2} and CO₂-HCN^{3,4} are each known to have two stable isomers. Two of the isomers of N₂O-HCN have structures which are similar to the isomers of N₂O-HF, namely linear and bent. In addition, a third isomer with a parallel structure has also been discovered. Ab initio calculations have also been performed and are in agreement with the experimental results. N₂O-HCN is the first binary complex to display three stable isomeric forms and should provide greater insights into the detailed nature of these potential energy surfaces.

¹C.H. Joyner, T.A. Dixon, F.A. Baiocchi and W. Klemperer, J. Chem. Phys. 74 6550 (1981).

²C.M. Lovejoy and D.J. Nesbitt, J. Chem. Phys. 87 1450 (1987).

³K.R. Leopold, G.T. Fraser and W. Klemperer, J. Chem. Phys. 80 1039 (1984).

⁴T.D. Klotts, R.S. Ruoff and H.S. Gutowsky, in press.

Address of Authors: Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599

TF8 (3:47)

THE EFFECTS OF NON-RIGIDITY ON THE HYPERFINE STRUCTURE OF $(C_2D_2)_2$

L. H. COUDERT

In $(C_2D_2)_2$ the hyperfine structure arises mainly from the quadrupole coupling of the four deuterium atoms. This dimer also exhibits a large amplitude motion consisting of a geared rotation of the two acetylene subunits, during which each deuterium atom is put in turn into the hydrogen bond, thus leading to a change of the electric field gradient tensor for any given deuterium nucleus. The hyperfine structure of $(C_2D_2)_2$ should therefore give us important information on the interaction of the quadrupole coupling with the large amplitude motion.

The theoretical approach involves setting up a complete quadrupole Hamiltonian for the four deuterium atoms, which is allowed to depend upon the large amplitude coordinate necessary to fully describe the various configurations of the molecule. The mean value of this operator is then evaluated for each of the tunneling levels, which for acetylene dimer¹ take the form of nondegenerate A or B type levels, or doubly degenerate E type levels. The unexpected result is that for nondegenerate tunneling levels the calculation of the mean value leads to an effective hyperfine Hamiltonian which is the sum of four one-deuterium hyperfine Hamiltonians, each with the same effective coupling constant. The group S_4 of the permutations of 4 identical particules can be used to classify the hyperfine energy levels, and symmetry adapted wavefunctions can be constructed prior to the diagonalisation of the hyperfine Hamiltonian. Such an approach is similar to the one used by Wolf, Williams and Weatherly² for $CFCl_3$ and $CHCl_3$, except that the number of identical particules is increased by one in the present problem. The particular symmetry properties of the effective hyperfine Hamiltonian will be discussed, and we hope to be able to compare predicted hyperfine patterns with data.

¹G. T. Fraser, R. D. Suenram, F. J. Lovas, A. S. Pine, J. T. Hougen, W. J. Lafferty, and J. S. Muenter, *J. Chem. Phys.* **89**, 6028-6045 (1988).

²A. A. Wolf, Q. Williams, and T. L. Weatherly, *J. Chem. Phys.* **47**, 5101-5109 (1967).

Address: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.

TF9 (4:04)

THE ISOMERIC STRUCTURES AND VAN DER WAALS VIBRATIONAL FREQUENCIES OF $(GLYOXAL)_n \cdot (Ar)_m$ COMPLEXES

Luc Lapierre, Donald Frye, and Hai-Lung Dai

Using laser induced fluorescence (LIF) and stimulated emission pumping (SEP), we have characterized the $(glyoxal)_n \cdot (Ar)_m$ complexes generated in a supersonic expansion of He (100 psi)/Ar (0.1-10%)/glyoxal(70-700 mTorr). More than 20 spectral features near the band origin of the glyoxal $\tilde{A} \leftarrow \tilde{X}$ transition were observed in the LIF spectrum. From 1) the band type, 2) the rotational constants obtained from the band contour analysis, 3) the intensity dependence on Ar and glyoxal concentrations and 4) the fluorescence lifetime, these features are assigned to the van der Waals vibrational series of 5 complexes. These are 1) a glyoxal-Ar complex with the Ar on the C_2 axis perpendicular to the glyoxal plane, 2) a glyoxal-Ar complex with Ar in the HCO gulf of the glyoxal plane, 3) a glyoxal-Ar₂ complex with both Ar's on the same side of the molecular plane, 4) a staggered $(glyoxal)_2$ complex, and 5) a $(glyoxal)_2 \cdot Ar$ complex. The Ar position in one of the glyoxal-Ar complex shifts from the C_2 axis position in the \tilde{X} state to a position tilted away from the axis in the \tilde{A} state. The van der Waals vibrational frequencies of some of the complexes were obtained for the \tilde{A} state from LIF and the \tilde{X} state from SEP.

Address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104

TF10 (4:21)

A PAIR-POTENTIAL MODEL FOR THE STRUCTURES AND VAN DER WAALS VIBRATIONAL FREQUENCIES OF GLYOXAL·Ar_n COMPLEXES.

Donald Frye, Luc Lapierre, Hai-Lung Dai

A naive pair potential model is used to calculate the intermolecular potential energy surface between glyoxal and argon. The glyoxal molecule is assumed to be composed of fragments (2 H and 2 CO) and the interaction potential is a sum of the individual pair wise potentials, Ar·H and Ar·CO, which has been determined by previous molecular beam scattering experiments.¹ The overall success of this model calculation in comparison with the experimental observations is surprisingly good: (1) The model accurately calculates the two isomeric structures of the glyoxal·Ar complex, and the structure of the glyoxal·Ar₂ complex; (2) The calculated binding energies are consistent with the experimentally observed spectral shifts; (3) The model can account for the experimentally observed large structural change that occurs upon electronic excitation of glyoxal in one of the glyoxal·Ar complex structures. A normal mode analysis of the van der Waals vibrational frequencies based on the model potential will also be discussed and compared to experimental results.

1. J.P. Toennies, W. Welz, and G. Wolf, J. Chem. Phys. 71, 614 (1979); K. Mirsky, Chem. Phys. 46, 445 (1980).

Address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104.

TF11 (4:38)

Electronic Structure via Simulated Annealing Techniques: Solvent Shifts of Guest Atom Transition Frequencies in Rare Gas Clusters

Chiachin Tsou and Sherwin J. Singer

The spectroscopic shifts of guest species in rare gas clusters are studied as a model for solvation in condensed phases, and as a probe of the cluster structure. These clusters are thought to exist in both fluid and solid-like forms, depending upon experimental conditions, and the observation of several spectroscopic peaks has been interpreted as arising from several distinct cluster isomers.

We report preliminary results of a simulated annealing calculation for guest atoms in argon clusters. Cluster configurations are sampled by standard molecular dynamics simulation of the nuclear coordinates. Quenches at regular intervals identify locally stable cluster arrangements. Use of simulated annealing techniques permits calculation of the Born-Oppenheimer surface for nuclear motion and transition frequencies in configurations of low symmetry.

Address: Department of Chemistry, Ohio State University, Columbus, Ohio.

TF12 (4:50)

Al IONIZATION POTENTIALS FROM EFFECTIVE POTENTIAL QMC WITH CORE POLARIZATION

P.A. Christiansen

In preliminary studies effective potential quantum Monte Carlo techniques were used to compute the first three ionization potentials of Al. Although core polarization was found to be negligible for the first ionization potential, corrections of about 0.2 and 0.4 eV respectively were found for the second and third. With core polarization included, the relativistic effective potential QMC procedure reproduces all three ionization energies to within 0.05 eV.

Department of Chemistry, Clarkson University, Potsdam, N.Y. 13676

TG1 (1:30)

OBSERVATION OF FINE STRUCTURE IN THE $Q_{1-0}(1)$ TRANSITION OF ORTHOHYDROGEN IMPURITY IN SOLID PARAHYDROGEN

MAN-CHOR CHAN, MITSUO OKUMURA, BRENT D. REHFUSS, AND TAKESHI OKA

Hundreds of very sharp spectral lines with typical linewidth of ~ 20 MHz have been observed around the $Q_{1-0}(1)$ transition (at $4146.5673 \text{ cm}^{-1}$) of $o\text{-H}_2$ impurity in a sample of solid $p\text{-H}_2$ ($\sim 99.8\%$) at 4.2 K. The spectrum from 4137 to 4154 cm^{-1} was recorded using a 115 mm long cell and a difference frequency laser spectrometer with tone-burst modulation. Transition frequencies are reproducible but the intensity changes as $o\text{-H}_2$ concentration varies. The complexity of the spectrum may be ascribed to orientational splittings of pairs of $o\text{-H}_2$ molecules by EQQ interactions.¹ The preliminary analysis will be discussed.

¹W.N. Hardy and A.J. Berlinsky, *Phys. Rev. Lett.* **34**, 1520 (1975).

Address of Chan, Rehfuss, and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

Address of Okumura: Division of Chemistry, California Institute of Technology, Pasadena, California 91125

TG2 (1:47)

INFRARED STUDIES OF HD AND D_2 IMPURITIES IN SOLID PARAHYDROGEN

MAN-CHOR CHAN AND TAKESHI OKA

We report measurements of infrared transitions of HD and D_2 impurities ($\sim 1\text{-}2\%$) in a parahydrogen sample of 0.7 cm long at 4.2 K. Spectra from 1800 to 8000 cm^{-1} recorded by a Bomem FTIR spectrometer show the double transitions between a $p\text{-H}_2$ and an impurity molecule and also the single transitions of impurity molecules. The sharpness of the latter indicates the possibility of accurate measurement of linewidth and line position of transitions of HD and D_2 using laser spectroscopy.

Address: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

TG3 (2:04)

OBSERVATION OF THE ν_3 AND ν_4 FUNDAMENTALS OF METHANE IMPURITY EMBEDDED IN SOLID PARAHYDROGEN

MAN-CHOR CHAN, SZETSEN LEE, AND TAKESHI OKA

Our recent observation of very sharp spectral lines in solid hydrogen¹ has suggested the possibility of conducting high resolution spectroscopy in molecular solids. Following this idea, rotationally resolved spectrum of ν_3 and ν_4 bands of CH_4 impurity ($\sim 0.01\%$) in a $p\text{-H}_2$ crystal have been studied using a 0.7 cm long cell at 4.2 K. Spectra were first recorded by a Bomem FTIR spectrometer at 0.1 cm^{-1} resolution. The major features agree well with earlier work on CH_4 in solid N_2 and noble-gas matrices.²⁻⁴ Higher resolution studies of the ν_4 band using a diode laser spectrometer, however, have revealed a great many sharp lines with typical linewidth of $\sim 0.01 \text{ cm}^{-1}$. The observed spectrum and preliminary analysis will be discussed.

¹M. Okumura, M.-C. Chan, and T. Oka, *Phys. Rev. Lett.* **62**, 32 (1989); M.-C. Chan, M. Okumura, B.D. Rehfuss, and T. Oka, this Conference.

²B. Nelander, *J. Chem. Phys.* **82**, 5340 (1985).

³F.H. Frayer and G.E. Ewing, *J. Chem. Phys.* **48**, 781 (1968).

⁴A. Chamberland, R. Belzile, and A. Cabana, *Can. J. Chem.* **48**, 1129 (1970).

Address: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

TG4 (2:21)

INFRARED TRANSITIONS IN SOLID HYDROGEN INDUCED BY THE BOMBARDMENT OF 3 MeV ELECTRON BEAM

MAN-CHOR CHAN, MITCHIO OKUMURA, AND TAKESHI OKA

Several new features have been observed in the infrared spectrum of solid hydrogen when it was ionized by the bombardment of 3 MeV electrons from a van der Graaff accelerator at Argonne National Laboratory. The spectrum from 1800 to 7000 cm^{-1} of a 2 cm long crystal of hydrogen was recorded using a Bomem FTIR spectrometer at 4 cm^{-1} resolution. The observed lines have a very long lifetime similar to the features reported earlier in deuterium species subject to tritium β ionization¹ and high energy proton bombardment.² The interpretation of these features will be discussed based on the *ab initio* calculations³ and earlier experiments⁴ on ionic hydrogen clusters.

¹P.C. Souers, E.M. Feason, P.E. Roberts, R.T. Tsugawa, J.D. Poll, and J.L. Hunt, *Phys. Lett.* **A77**, 277 (1980)

²R.L. Brooks, M.A. Selen, J.L. Hunt, J.R. MacDonald, J.D. Poll, and J.C. Waddington, *Phys. Rev. Lett.* **51**, 1077 (1983)

³Y. Yamaguchi, J.F. Gaw, and H.F. Schaefer III, *J. Chem. Phys.* **78**, 4074 (1983)

⁴M. Okumura, L.I. Yeh, Y.T. Lee, *J. Chem. Phys.* **88**, 79 (1988)

Address of Chan and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

Address of Okumura: Division of Chemistry, California Institute of Technology, Pasadena, California 91125

TG5 (2:38)

PREDICTED INTENSITIES FOR NEW RAMAN TRANSITIONS IN SOLID HD

M. Attia, M. Ali, R. H. Tipping, and J. D. Poll

The scattering efficiencies for the zero-phonon and phonon branches associated with predicted new Raman transitions in solid HD are calculated. These transitions arise from the interaction-induced polarizability of a pair of molecules expressed in terms of the vector separation between the centers of mass, and satisfy different rotational selection rules from those of allowed Raman transitions. For single transitions in which only one molecule of the pair is excited by the incoming photon, one expects an R branch, while for double transitions in which both molecules are excited, one expects R + S and T + S branches. A previously obtained experimental Raman spectrum of solid HD does have spectral features similar in shape and intensity to those predicted for the R_R phonon branch, although this feature was tentatively assigned as a two-phonon Raman-active transition. We conclude that a new Raman study of solid HD carried out with higher sensitivity and over a greater frequency region would be of interest to determine the correct assignment of this feature.

Address of M. Attia, M. Ali and R. H. Tipping: Department of Physics, University of Alabama, Tuscaloosa, AL 35487-0324.

Address of J. D. Poll: Department of Physics, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

TG6 (2:55)INTENSITIES OF $R_{\nu}(0)$ TRANSITIONS IN SOLID HD

R. H. Tipping, J. D. Poll, S. Y. Lee, S-i. Lee, T. W. Noh and
J. R. Gaines

Experimental values of the integrated intensity of the zero-phonon $R_2(0)$ and $R_3(0)$ transitions in solid HD are reported for the first time. Three distinct dipole components, the allowed dipole and the shifted isotropic and anisotropic overlap induced-dipoles, in conjunction with their associated interferences, all play an important role in the absorption process. A two-parameter model describing the dependence of the induced dipoles on the internuclear separation is constructed. The parameters in this model are then determined by fitting to the previously observed $R_1(0)$ and the newly measured $R_2(0)$ intensities. The $R_3(0)$ transition intensity predicted by our model agrees well with the experimental value, and the present model also enables us to refine the theoretical calculation of the intensity of the $R_0(0)$ transition published previously.

Address of R. H. Tipping: Department of Physics, University of Alabama, Tuscaloosa, AL 35487-0324.

Address of J. D. Poll: Department of Physics, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

Address of S. Y. Lee: Applied Optics Laboratory, Korea Advanced Institute of Science and Technology, Cheongryang, Seoul, South Korea.

Address of S-i. Lee: Department of Physics, Pohang Science and Technology Institute, P. O. Box 125, Pohang, South Korea.

Address of T. W. Noh: LASSP, Cornell University, Ithaca, N. Y. 14853.

Address of J. R. Gaines: Department of Physics, University of Hawaii at Manoa, Honolulu, Hawaii 96822.

TG7 (3:12)

INFRARED SPECTRA OF HYDROGEN DIMERS

A.R.W. MCKELLAR

Hydrogen dimers are being studied using a Bomem Fourier transform spectrometer together with long absorption paths (112 m) at very low temperature (20 K) and moderate pressures (10 to 200 torr). Last year at this conference, spectra of $(H_2)_2$ and $(D_2)_2$ in the regions of the monomer fundamental bands ($3000-5000\text{ cm}^{-1}$) were presented.

New results have now been obtained for $(HD)_2$ and for the mixed species H_2-D_2 , and $HD-D_2$. The region studied has been extended to the monomer first overtone bands at 6000 to 9000 cm^{-1} and to the pure rotational transitions of H_2 in the far infrared. Theory has still not developed to the point of being able to use these data to refine the hydrogen intermolecular potential energy surface, but promising work is in progress by J. Schaefer (Garching) and G. Danby (London).

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

TG8 (3:29)

IMPROVED POTENTIAL ENERGY SURFACES FOR THE INTERACTION OF H₂ WITH Ar

Claudio Chuaqui and Robert J. Le Roy

The best existing potential energy surfaces for the H₂-rare gas systems were determined from an analysis based largely on the discrete infrared spectra associated with the $v=1-0$ fundamentals of the H₂ or D₂ components of these complexes.¹ However, McKellar has now observed transitions of H₂-Ar involving excited van der Waals stretching states, as well as spectra associated with the component diatom undergoing pure rotational ($S_0(0)$, $S_0(1)$) and first overtone vibrational ($Q_2(1)$, $S_2(0)$ and $S_2(1)$) transitions.² The present paper describes our use of these new data, in conjunction with microwave spectra, and elastic and inelastic differential cross section measurements, to determine an improved potential energy surface for the H₂-Ar system.

The present analysis is the first to take account of the excited stretching states of the van der Waals bond; hence it should yield an improved characterization of the shape of the potential along the atom-diatom separation coordinate. In addition, the inclusion of data involving the hydrogen overtone transitions should lead to a better representation of the diatom-stretching dependence of the potential energy surface, while the far infrared data should better characterize the stretching-dependence of the potential anisotropy. The current status of this analysis, as well as the applicability of the methods developed to other more strongly-anisotropic systems, will be discussed.

¹ R.J. Le Roy and J.M. Hutson, *J. Chem. Phys.* **86**, 837 (1986).

² A.R.W. McKellar, in *Structure and Dynamics of Weakly Bound Molecular Complexes* (NATO ASI Series C, Vol. 212, D. Reidel, Dordrecht, A. Weber, editor, 1987), pp. 141-147; A.R.W. McKellar, paper RA9 at the 42nd Symposium on Molecular Spectroscopy (Columbus, June 15-19, 1987); A.R.W. McKellar (private communication, 1988).

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

TH1 (1:30)

STIMULATED EMISSION SPECTROSCOPY OF SINGLET CH₂: THE BENDING BARRIER HEIGHT AND THE \bar{a} - \bar{b} SPLITTING

Wei Xie, Carmel Harkin, and Hai-Lung Dai

Stimulated Emission Pumping (SEP) has been used to detect the bending vibrational overtones of \bar{a}^1A_1 CH₂ ($v_2=2, 3$, and 4). The vibrational term values and rotational constants were determined. Comparison between the bending potential model calculations^{1,2} and experimental results places the barrier height of the bending motion for \bar{a}^1A_1 CH₂ at about 9800 cm⁻¹ and the \bar{a} and \bar{b} state splitting at 8300 cm⁻¹. As a result, the numbering of the \bar{b}^1B_1 bending vibrational levels needs to be changed from v_2 to v_2-2 . Furthermore, abnormally strong $\Delta K_a=3$ transitions in the $\bar{a} \leftarrow \bar{b}$ band and the tunneling effect in the high bending overtones will be discussed.

1. P.R.Bunker and T.J.Sears J. Chem. Phys. **83** 4866 (1985)
2. G.Duxbury and Ch.Jungen Molec. Phys. **63** 981 (1988)

Address: Department of Chemistry University of Pennsylvania, Philadelphia PA 19104

TH2 (1:47)

An Isotopic Substitution Test for Orbiting H Atoms in Vibrationally Highly Excited $\tilde{X}^1\Sigma_g^+$ Acetylene

Yit-Tsong Chen, J. K. Lundberg, J. P. Pique, Y. Chen and R. W. Field

A Statistical Fourier Transform (SFT) analysis of the Stimulated Emission Pumping (SEP) spectrum of acetylene (at $\sim 26,500$ cm⁻¹ above the zero-point energy of the $\tilde{X}^1\Sigma_g^+$ state) revealed recurrences at 6 ps. A speculative assignment [J. P. Pique, M. Lombardi, Y. Chen, R. W. Field and J. L. Kinsey, *Ber. Bunsenges. Phys. Chem.*, **92**, 422 (1988)] of these recurrences as a free orbiting motion of one H about CCH can be tested by isotopic substitution. We are recording SEP spectra of DCCD. Well isolated and rotationally assigned intermediate rovibronic levels for SEP have been selected from rotationally-resolved fluorescence excitation spectra ($\tilde{A} \leftarrow \tilde{X}, 3^4_0$) of C₂D₂ observed at different temperatures ($\sim 10K \rightarrow 400K$). SEP spectra of vibrationally highly excited ($> 26,000$ cm⁻¹ in $\tilde{X}^1\Sigma_g^+$ state) C₂D₂ are currently being obtained through several low-J intermediate states. Each of these SEP spectra belongs to a nearly "pure sequence" of all rigorous quantum numbers (J, ortho/para etc.). The vibrational features in the congested spectral region sampled by SEP, however, are intrinsically unassignable in terms of the nonrigorous vibrational quantum numbers. We have applied a Statistical Fourier Transform technique to decode the short-time (<ps.) molecular dynamical information embedded in the raw SEP spectra. The orbiting period together with the orbital radius of the hypothetical free-rotation of H/D atom(s) in acetylene, revealed from this new statistical technique, will be discussed.

Address of Y. T. Chen, Lundberg and Field: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Address of Pique: Laboratoire de Spectrometrie Physique Universite Scientifique et Medicale de Grenoble BP87, 38402 Saint Martin d'Heres, Cedex.

Address of Y. Chen: Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089.

TH3 (2:04)

U.V. OPTICAL DOUBLE RESONANCE STUDY OF THE PREDISSOCIATED \tilde{C}^1A_g STATE OF ACETYLENE

J. K. LUNDBERG, J. P. PIQUE, Y. CHEN, R. W. FIELD

A predissociated vibronic progression in the trans-bending (v_3) mode of HCCH with vibrational origin at 61,340 cm⁻¹ has been observed using the $\tilde{C}^1A_g \leftarrow \tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g^+$ excitation scheme. We have determined the \tilde{C} state to be a strongly bent valence state with electron configuration $(1a_g)^2(1b_u)^2(2a_g)^2(2b_u)^2(3a_g)^2(3b_u)^2(4a_g)^2$, and electronic symmetry 1A_g . Analysis of the J and K resolved spectra have allowed us to determine the $B \equiv C$ and A rotational constants of this state to be 0.85(6) cm⁻¹ and 7.5(6) cm⁻¹ respectively.

We are currently recording the spectra of DCCD to obtain bond lengths and angles for this state. The results of these experiments will be presented and the vibrational and J, K- dependence of the predissociation rate will be discussed.

Address of Field and Lundberg: Department of Chemistry, Massachusetts Institute of Technology, Cambridge MA 02139

Address of Pique: Laboratoire de Spectrometrie Physique BP87 38402 Grenoble, France

Address of Chen: Department of Chemistry, University of Southern California, Los Angeles CA 90089-0482

TH4 (2:21)

THE FIRST SINGLET ELECTRONIC STATE IN ACETYLENE.

T.R.HUET and M.HERMAN

Litterature and new data concerning the $\tilde{A}-\tilde{X}$ band system in C_2H_2 , C_2D_2 and C_2HD are put together in order to derive information on the \tilde{A} electronic state in acetylene. Full sets of vibrational frequencies are determined for the three isotopomers (a). The last original rotational sets of constants characterizing vibrational levels of this state will be also presented. The geometrical structure (r_0) is calculated from the results of the rotational analysis. this latter information will be combined with intensity calculations to discuss the axis-switching phenomenon in acetylene.

(a) in collaboration with J. Vander Auwera, C. Hamilton, J.L. Kinsey and R.W. Field.

Address : Laboratoire de Chimie Physique Moléculaire, CP. 160, Université Libre de Bruxelles, Ave. Roosevelt 50, 1050 Brussels, Belgium.

TH5 (2:38)THE BENDING VIBRATIONAL LEVELS IN C_2D_2 .T.R.HUET, M.HERMAN and J.W.C.JOHNS

The rotational analysis of the $\tilde{A}-\tilde{X}$ band system in C_2D_2 put forward rovibrational perturbations in the ground electronic state (1), arising because of the proximity of the two bending frequencies, ν_4'' (trans-bend at 511.5 cm^{-1}) and ν_5'' (cis-bend at 538.6 cm^{-1}) through Darling-Dennison, rotational and vibrational l -doubling interactions (2). The far infrared ($20\text{-}150\text{ cm}^{-1}$) and infrared ($400\text{-}600\text{ cm}^{-1}$) absorption spectrum, recorded with the modified Bomem DA 3.002 Fourier Transform Spectrometer of the Herzberg Institute of Astrophysics, is analyzed with the aim to bring information on the excited bending levels. Preliminary results will be presented.

1. T.R.Huet and M.Herman, J. Mol. Spectrosc. 132, 361-8 (1988).
2. J.Pliva, J. Mol. Spectrosc. 44, 145-65 (1972), 44, 165-82 (1972) ; J.K.G.Watson, J. Mol. Spectrosc. 101, 83-93 (1983).

Address of Huet and Herman : Laboratoire de Chimie Physique Moléculaire, CP. 160, Université Libre de Bruxelles, Ave. Roosevelt 50, 1050 Brussels, Belgium.

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

Intermission

TH 6 (3:05)

ROTATIONAL ANALYSIS OF LASER INDUCED FLUORESCENCE SPECTRA OF AROH AND AROD

Wafaa M. Fawzy

A theoretical model for the rotational energy levels and rotational line intensities for complexes formed from an open-shell diatomic molecule in a ${}^2\Sigma$ or ${}^2\Pi$ electronic state and a rare gas atom or a closed shell diatomic molecule was presented last year at this meeting.¹⁻² This model allows the line connecting the rare gas atom to the center of mass of the diatomic open-shell fragment to be at any angle θ relative to the diatomic axis. This theoretical model has now been applied to the observed rotational structure of the laser induced fluorescence spectra of ArOH/ArOD.³⁻⁵ Results of fitting the experimental data to the theoretical model show that the rotational structure of the observed lower energy vibrational bands fits a parallel type transition whereas rotational structure of the higher energy vibrational bands fits a perpendicular type transition. Results of fitting also show that the equilibrium structure of ArOH/ArOD is bent with a bond angle θ of 20-30 degrees.

The theoretical model and its application to analysis of the rotational structure of ArOH and ArOD will be presented.

1. Wafaa M. Fawzy and Jon T. Hougen, 43 Symposium in Molecular Spectroscopy, Paper ME11, OSU, (1988)
2. Wafaa M. Fawzy and Jon T. Hougen, in preparation for publication
3. M. T. Berry, M. R. Brustin, J. R. Adamo and M. I. Lester, J. Phys. Chem. 92, (1988) to be published.
4. M. T. Berry, Mitchell R. Brustin and Marsha I. Lester, Chem. Phys. Lett. 153, 17 (1988)
5. Wafaa M. Fawzy and Michael C. Heaven, J. Chem. Phys. 89, 7030 (1988)

Address-Fawzy: Brookhaven National Laboratory, Chemistry Department, Upton, NY 11973

TH7 (3:22)

ELECTRONIC SPECTRA OF AROH/AROD AND CHARGE TRANSFER

Wafaa M. Fawzy and M. C. Heaven

Laser induced fluorescence spectra of ArOH associated with electronic excitation of the A-X($v'=0-v''=0$) of the OH radical was previously reported.¹⁻³

An extensive search in the vicinity of the OH/OD A (${}^2\Sigma$)-X (${}^2\Pi$) system ($v'=0-v''=0$ and $v'-1-v''=0$) led to the observation of thirty six vibronic bands which were identified as belonging to ArOH and ArOD complexes. All of the bands were found to originate from the ground electronic state of the OH/OD radical (${}^2\Pi_{3/2}$), $v''=0$. Two distinguishable vibronic structures were identified. A lower energy vibrational progression was assigned as the Van der Waals stretch. This band system is designated as the "A" bands. A higher energy set of bands shows a different vibrational structure and does not fit a simple vibrational mode progression. These bands are labeled as "U" system. The label "U" was chosen to indicate that the origin of these bands could not be identified. Partially resolved rotational structure for all of the observed ArOH/ArOD bands was recorded. The "A" and "U" systems were also distinguished by their different rotational structure and effect of H/D substitution on the vibrational and rotational parameters.

Results of preliminary rotational analysis give a ground state constant (\bar{E}_0) of 0.100 cm^{-1} for ArOH and 0.098 cm^{-1} for ArOD. \bar{E}_0 constants for the $v'=0$ band of the "A" system excited state were determined to be 0.178 cm^{-1} for ArOH and 0.168 cm^{-1} for ArOD. These rotational constants and the observed large shift of the ArOH/ArOD complex band origin to the red of the OH/OD radical band origin show that the Ar-OH/Ar-OD Van der Waals bond has been considerably shortened upon electronic excitation. This suggests that charge transfer might considerably contribute to the stability of ArOH and ArOD complexes in the excited electronic state.

Observed spectra and results of vibronic analysis will be presented.

1. Wafaa M. Fawzy and M. C. Heaven, J. Chem. Phys. 89, 7030 (1988)
2. M. T. Berry, Mitchell R. Brustin, Joseph R. Adamo, and Marsha I. Lester, J. Phys. Chem. 92, 5551 (1988)
3. M. T. Berry, Mitchell R. Brustin and Marsha I. Lester, Chem. Phys. Lett. 153, 17 (1988)

Address-Fawzy: Brookhaven National Laboratory, Department of Chemistry, Upton, NY 11973

Address-Heaven: Emory University, Department of Chemistry, Atlanta, GA 30324

TH8 (3:39)**ZERO FIELD LEVEL CROSSING IN THE CLEMENTS E BAND OF SO₂****J. S. Muentzer** and John Deutsch

The observation of zero electric field level crossing, the electric analog of the Hanle effect, permits the measurement of electric dipole moments in excited electronic states. We have applied this technique to the Clements E band of SO₂. A free jet expansion of SO₂ seeded in argon was crossed with the output of a doubled, Nd:YAG pumped, dye laser. SO₂ fluorescence was collected along the third orthogonal direction. The electric field was established by two transparent electrodes located above and below the plane defined by the molecular beam and the laser beam. The laser was polarized parallel to the external field. The electric field was applied during alternate laser pulses, and the boxcar integrator used to process the photomultiplier output averaged the difference between the fluorescence intensity with and without the field.

Initial data were obtained for the Clements E band. The laser frequency was fixed at the $1_{10} - 0_{00}$ excitation, so only fluorescence from the $1_{10}, M=0$ state was detected in strong field conditions. As the electric field was reduced, the Stark splitting between the $1_{10}, M=0$ and the $1_{10}, M=\pm 1$ levels first became comparable to the homogeneous linewidth and then the detected fluorescence approached the zero field value. The electric field corresponding to the half height of this level crossing signal was observed to be 138 v/cm. Using this value, and the known radiative lifetime, produced an excited state dipole moment of 0.76 D.

Address of Muentzer: Dept. of Chemistry, University of Rochester, Rochester, N.Y. 14627.

Address of Deutsch: Dept. of Chemistry, SUNY at Geneseo, Geneseo, N.Y. 14454.

TH9 (3:56)**FLUORESCENCE EXCITATION SPECTRUM OF CCl₂ IN A SUPERSONIC FREE JET****J.-I. CHOE, S. TANNER AND M.D. HARMONY**

Dichlorocarbene (CCl₂) has been produced in a continuous supersonic free jet by pyrolysis of (CH₃)₃SiCCl₃ seeded in argon using a nozzle heated to 400°C. Laser excitation spectra of several bands of the $\Lambda \ ^1B_1 + X \ ^1A_1$ electronic system have been obtained for the cold carbene ($\approx 20^\circ\text{K}$) in the 500-540 nm spectral region. Partial rotational resolution of several $(v_1, v_2, 0) + (0, 0, 0)$ progressions has yielded an assignment based on a perpendicular-band of a near-prolate symmetric rotor with clearly assignable $R_{R_K}(J)$ band-head structure. Analysis of the band-head positions in conjunction with spectral band shape simulations leads to rotational constant information for the ground vibronic state and the various observed vibrational states of the 1B_1 excited electronic state. Although the data are not complete, they provide reliable inferences to be made about the ground and excited electronic state structures.

Address of Choe, Tanner, and Harmony: Department of Chemistry, University of Kansas, Lawrence, KS 66045.

TH10 (4:13)**The High Resolution Electronic Absorption Spectrum of the HCN₂ Free Radical****B. R. SWEETING** and C. W. Mathews

The rotational structure of one band in the electronic transition of the HCN₂ free radical near 3170 Å has been measured. This spectrum was first reported by Herzberg and Travis¹ in their paper on the NCN radical.

The complexity of the fine structure required an iterative approach. First and second differences were used in the assignments of J values and a correlation performed with the computed line diagram. The observed transitions were subjected to a least squares fit to calculate a new theoretical spectrum. This was repeated until the best fit of the molecular constants was achieved.

The resulting geometries for both the upper and lower electronic states are then compared with the results of *ab initio* calculations for HCNN.

¹ G. Herzberg and D. N. Travis, Can. J. of Phys. 42, 1658 (1964).

Address of authors: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

TH11 (4:30)

SF₂ observed from 280 to 500 nm by Resonance Enhanced Multiphoton Ionization Spectroscopy

R. D. Johnson III, J. W. Hudgens

Spectra of the SF₂ radical have been observed from 295 to 495 nm by Resonance Enhanced Multiphoton Ionization (REMPI). Three new electronic states have been observed. Their assignments and origins are : 4s ¹B₁ 54400 cm⁻¹, 4p ¹B₁ 62000 cm⁻¹, and 4p ¹A₁ 63800 cm⁻¹. The 4s state is observed by a 2+1 REMPI process and the 4p states are observed by both 2+1 and 3+1 REMPI processes. Progressions involving ν₁ (symmetric SF stretch) and ν₂ (bend) modes are observed and assigned. The values obtained are 4s : ω₁ = 999 cm⁻¹ and ω₂ = 400 cm⁻¹, 4p ¹B₁: ω₁ = 964(2) cm⁻¹, 4p ¹A₁ 967(30) cm⁻¹.

Address: Chemical Kinetics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

WE1 (1:00)**ELECTRONIC STRUCTURE AND MECHANISM FOR HIGH T_c SUPERCONDUCTORS**WILLIAM A. GODDARD

To understand the superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{Cu}_1\text{O}_4$, $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$, and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_6$, we carried out quantum chemical (generalized valence bond) calculations on various clusters to obtain information about the electronic states of the oxidized systems and about the magnetic interactions. In addition, on these we used the recently developed valence-bond band theory to calculate the energy bands for these systems. These results indicate that (i) all copper sites have a Cu^{II} (d^9) oxidation state with one unpaired spin that is coupled antiferromagnetically to the spins of adjacent Cu^{II} sites; (ii) oxidation beyond the cupric (Cu^{II}) state leads not to Cu^{III} but rather to oxidized oxygen atoms, with an oxygen p hole bridging two Cu^{II} sites; (iii) the hopping of these oxygen p holes (in CuO sheets) from site to site is responsible for the conductivity in these systems; and (iv) the oxygen p hole at these oxidized sites is ferromagnetically coupled to the adjacent Cu^{II} d electrons despite the fact that this is opposed by the direct dd exchange. Using these ideas, we derived the magnon pairing mechanism to explain the high-temperature superconductivity of all three systems. Critical features include (i) a one- or two-dimensional lattice of linear Cu-O-Cu bonds that contribute to large antiferromagnetic (superexchange) coupling of the Cu^{II} (d^9) orbitals; (ii) holes in the oxygen p bands [rather than Cu^{II} (d^9)] leading to high mobility hole conduction; and (iii) strong ferromagnetic coupling between oxygen p holes and adjacent Cu^{II} (d^9) electrons. The ferromagnetic coupling of the conduction electrons with copper d spins induces the attractive interaction responsible for the superconductivity. The disordered Heisenberg lattice of antiferromagnetically coupled copper d spins serves a role analogous to the phonons in a conventional system. This theory has been used to solve self-consistently for the k-dependent energy gap as a function of temperature. In addition, we have calculated the critical magnetic fields, the specific heat, and the tunneling as a function of temperature.

This model leads to suggestions concerning modifications of current materials to improve T_c and suggests limits to the T_c for current materials.

Address of Goddard: Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91109.

WE2 (1:30)**ON THE PHOTOEMISSION AND OPTICAL SPECTRA OF La_2CuO_4** RICHARD L. MARTIN

Ab Initio quantum chemistry calculations for a number of cluster models of the superconducting cuprates will be discussed. It will be argued that the optical gap in La_2CuO_4 is that of a "traditional" Mott insulator. Parameters describing an effective single band model will be suggested, and the close correspondence between the electronic excitations of the cuprates and those of the alternant polyenes in the narrow band limit will be stressed.

Address of Martin: Los Alamos National Laboratory, Los Alamos, New Mexico 87545.

WE3 (2:00)**BAND-LIKE ELECTRONIC STRUCTURE AND FERMI EDGE OF $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ SINGLE CRYSTALS AS DETERMINED BY PHOTOEMISSION SPECTROSCOPY**

A.J. Arko*, R.S. List*, R.J. Bartlett*, S.-W. Cheong* Z. Fish*, J.D. Thompson*, C.G. Olson#, A.-B. Yang#, R. Liu#, C. Gu# B.W. Veal+, J.Z. Liu+, A.P. Paulikas+, K. Vandervoort+, J.C. Campuzano+, J.E. Schirber**, and N.D. Shinn**

We have re-examined the electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ single crystals via photoemission spectroscopy, making the measurements at 20 K in order to maintain surface oxygen stoichiometry. We find that typical spectra display a large sharp (resolution limited) Fermi edge consistent with metallic behavior. $N(E_F)$ per Cu atom is very roughly estimated to be as large as 20% of that of Cu metal and contains about 20-80 mix of Cu-3d and O-2p orbitals. Dispersion and final state enhancements, phenomena associated with well defined bands, are observed at E_F and throughout the valence bands. We find excellent agreement with a calculated DOS if the DOS is shifted to higher binding energies by ~ 0.5 eV (except for the feature at E_F). Not only peak positions, but also line shapes of the spectra appear to agree with previous calculations, which would indicate that the calculations contain the correct mix of 3d and 2p orbitals throughout the valence bands. Thus much of the O-2p intensity is peaked in a narrow, 2eV wide band near E_F with a long tail extending to -7 eV, while the Cu-3d band is centered at -4 eV and has a width of about 4 eV. Our results complement well the angle - resolved measurements of Takahashi, which likewise point to a hybridized band-like behavior of the superconducting oxides. The very large resonance of the -12 eV satellite, which decreases in intensity relative to the valence bands as the surface deteriorates, is probably a result of a SCK autoionization process and points to the existence of empty Cu-3d states.

Work supported by the U.S. Dept. of Energy

*Los Alamos National Laboratory, P-10 Group, Los Alamos, NM, 87545

Ames National Laboratory - USDOE Iowa State University, Ames, Iowa 50011

+Materials Science Division Argonne National Laboratory, Argonne, IL 60439

** Sandia National Laboratories, Albuquerque, NM 87185

WE4 (2:30)**SPECTROSCOPY OF HIGH TEMPERATURE SUPERCONDUCTORS**

N. W. WINTER, R. M. PITZER, C. I. MERZBACHER, D. K. TEMPLE, AND C. E. VIOLET

In order to develop and test theories of high temperature superconductors and to understand the influence of crystal structure, atomic valence, and chemical composition on the superconducting properties, it is necessary to have an accurate description of their electronic structure. We are investigating the copper-oxide based high temperature superconductors by calculating the NMR, NQR, photoemission, Raman, and Mossbauer spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ using first-principles cluster methods. This allows for the inclusion of the correct electron-exchange potential and configuration mixing in determining the gradients, chemical shifts, one-electron energies and total energies that can be compared to experiment.

Address of Winter, Merzbacher, Temple, and Violet: Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550.

Address of Pitzer: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

Intermission

WE5 (3:15)

MANY-BODY HAMILTONIAN PARAMETERS AND SPECTROSCOPY OF La_2CuO_4

R.M. Martin, J.F. Annett, A.K. McMahan, and S. Satpathy.

Key spectroscopic features of the high T_c superconductor parent compound La_2CuO_4 are not described by conventional band theory in the local (spin) density approximation, namely: the insulating gap at the Fermi level, the antiferromagnetism and a prominent Cu $d^9 \rightarrow d^8$ photoemission satellite. These features can be understood, however, by using constrained density functional theory to construct *ab initio* values for parameters in a many-body Hamiltonian^{1,2}. The comparison with experiment can then be used to refine the calculated values, especially the key parameter the copper-oxygen energy difference, $\epsilon_p - \epsilon_d$, which is difficult to determine accurately *ab initio*.

The solutions to this many-body Hamiltonian, found either in an Anderson impurity approximation or by diagonalising clusters, do describe the important spectroscopic features giving a 2--3eV energy gap an antiferromagnetic exchange energy of 0.15--0.2eV, and a photoemission satellite corresponding to $U_d=8\text{eV}$, all consistent with experimental data. The ground state consists of x^2-y^2 symmetry holes at each copper site, with neutral excitations to the $3z^2-r^2$ state at $\approx 1\text{eV}$ and the xy , xz , and yz states at $\approx 2\text{eV}$; the latter are consistent with the NMR chemical shift tensor. The holes introduced by doping are in primarily d^9_L states, where we find two competing low energy states for the ligand hole with either x^2-y^2 or $3z^2-r^2$ symmetry about the copper sites³.

1. A.K. McMahan, R.M. Martin and S. Satpathy, Phys. Rev. B. **38** 6650 (1988).
2. M.S. Hybertsen, M. Schluter and M.E. Christensen, preprint.
3. J.F. Annett, R.M. Martin, A.K. McMahan and S. Satpathy, submitted for publication.

Address of Annett and Martin: Dept. of Physics, University of Illinois,
1110 W. Green St., Urbana, IL. 61801

WE6 (3:45)

ELECTRONIC STRUCTURE STUDIES OF HIGH- T_C SUPERCONDUCTORS BY HIGH-ENERGY SPECTROSCOPIES

J. Fink, N. Nücker, H. Romberg, S. Nakai, M. Alexander, R. Manzke*, T. Buslaps*, and R. Claessen*

Kernforschungszentrum Karlsruhe, INFP, P.O. Box 3640, D-7500 Karlsruhe, FRG;

*Institut für Experimentalphysik, Universität Kiel, FRG

The electronic structure studies of the high-temperature superconductors $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ and $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ by high-energy spectroscopies are reviewed. Electron energy-loss spectroscopy in transmission (EELS), angle-resolved photoemission (ARUPS) and inverse angle-resolved photoemission (ARIPES) have been used. Low energy-loss spectra ($0.1 < E \leq 50\text{eV}$) yield the orientation dependent dielectric function over a wide energy range. Information on d-d excitations, charge-transfer excitations, charge-carrier plasmons and interband transitions is obtained. Absorption edges of the O 1s and the Cu 2p levels provide information on the symmetry and the character of holes in these materials. In addition, the electronic states of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ at the Fermi level had been studied by high resolution ARUPS and ARIPES. Temperature-dependent measurements indicate below T_c an opening of a gap of about 60 meV yielding a ratio $\Delta(0)/k_B T_c$ about twice as large as the BCS value. Recent EELS results on the electron high- T_c superconductor $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_{4-y}$ are reported.

WE7 (4:15)**ABSORPTION AND PHOTOINDUCED ABSORPTION STUDIES OF SEMICONDUCTING $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.***

R.P. MCCALL, J.M. GINDER, J.M. LENG, H.J. YE, A.J. EPSTEIN, W.E. FARNETH, E.M. MCCARRON, and S.I. SHAH

Optical and infrared absorption and photoinduced absorption (PA) spectroscopies have been applied to the high- T_c families of materials. These techniques give insight into the types of charged excitations existing in these materials, as well as the nature of their ground states and mechanisms for superconductivity. Near-steady-state optical PA spectra on thin films and pressed pellets of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for $\delta \sim 0.7$ show PA peaks around 1 eV and a crossover to photoinduced bleaching (PB) at higher energies. Variability of the data from sample to sample may indicate the glassy nature of these materials. The infrared PA spectra reveal several photoinduced infrared active vibrational (IRAV) modes and a broad electronic transition centered at $\sim 1000 \text{ cm}^{-1}$. The presence of the photoinduced IRAV modes and the higher-lying absorptions and bleachings shows that charged defect states lying within the energy gap are created upon photoexcitation. Several of the photoinduced IRAV modes indicate a loss of symmetry and a tetragonal-to-orthorhombic transition that occurs upon photoexcitation, involving a possible charge transfer from the CuO_2 plane layers to the CuO chain layers. The variation of the IR and photoinduced IRAV modes with oxygen isotope substitution is in accord with expectations of the usual mass effects for vibrational modes.

* Work supported in part by DARPA through a contract monitored by US ONR.

Address of McCall, Ginder, Leng, Ye, and Epstein: Department of Physics, The Ohio State University, Columbus, Ohio 43210, U.S.A.

Address of Farneth, McCarron, and Shah: Central Research and Development Department, Experimental Station, E.I. du Pont de Nemours, Inc., Wilmington, Delaware 19808, U.S.A.

WF1 (1:30)**MOLECULAR STRUCTURE, FORCE FIELD, AND CORIOLIS INTERACTION OF HBO**

Y. Kawashima, Y. Endo, K. Kawaguchi, T. Suzuki, M. Fujitake, and E. Hirota

The vibrational frequencies and the rotational, vibration-rotation, ℓ -type doubling, and centrifugal distortion constants determined for the six isotopic species, $H^{11}BO$, $H^{10}BO$, $D^{11}BO$, $D^{10}BO$, $H^{11}B^{18}O$, and $H^{10}B^{18}O$, were simultaneously analyzed to derive the equilibrium molecular structure and the harmonic and third-order anharmonic potential constants of the HBO molecule. The equilibrium bond lengths thus obtained are $r_e(H-B)=1.16667(41)\text{\AA}$ and $r_e(B-O)=1.20068(10)\text{\AA}$, and the substituted, average, and effective structures were also calculated for comparison. We found the ν_1 and $\nu_2 + \nu_3$ states of DBO being coupled by a Coriolis interaction, and analyzed the coupling by observing the vibration-rotation and rotational spectra associated with the ν_1 state.

Address of Kawashima: Kanagawa Institute of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa 243-02, Japan

Address of Endo: College of General Education, the University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

Address of Kawaguchi, Suzuki, Fujitake, and Hirota: Institute for Molecular Science, Okazaki, 444, Japan.

WF2 (1:47)**DIODE LASER SPECTROSCOPY OF METAL OXIDES IN LOW PRESSURE FLAMES**

H. G. HEDDERICH and C. E. BLOM

Recently, we have reported the first gas-phase infrared spectrum of an alkaline earth metal oxide, CaO^1 . Substantial improvement has been made by multipassing the infrared radiation through the low pressure flame in which the oxides are formed. More than 40 rovibrational transitions of the fundamental band and the first and second hot band have been measured. By comparing the relative intensities of nearby fundamental and hot band transitions, the state distribution of CaO in the flames has been monitored. Depending on the flame conditions, the vibrational temperature varied between 500 and 1500 K, whereas the rotational temperature was always close to 350 K.

New results for barium oxide include spectra for a number of hot bands of ^{138}BaO , ^{137}BaO , ^{136}BaO , ^{135}BaO and ^{134}BaO . Using the isotopic dependence of the constants, a set of Dunham-coefficients was obtained from these data.

¹ C. E. Blom and H. G. Hedderich, Chem. Phys. Lett. **145**, 143 (1988).

Address of H. G. Hedderich and C. E. Blom: Physikalisch-Chemisches Institut, Justus Liebig Universität, D-6300 Giessen, Federal Republic of Germany.

The paper will be presented by M. Winnewisser.

WF3 (2:04)**THE INFRARED SPECTRUM OF THE LiO RADICAL**

Chikashi Yamada and Eizi Hirota

The vibrational spectrum of the 7LiO radical ($v=1-0$) was observed by infrared diode laser spectroscopy. The LiO radical was produced in a heat pipe cell by the reaction of N_2O and Li vapor, as in the microwave measurement. Analysis of the present infrared data combined with the microwave results gave precise values for band origin and spin-orbit interaction constants.

Address: Institute for Molecular Science, Okazaki 444, Japan.

WF4 (2:16)**LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF NCS IN A FREE JET EXPANSION**

E.J. Northrup and Trevor J. Sears

A laser-induced fluorescence spectrum (355-450 nm) has been recorded for the $A^2\Pi-X^2\Pi$ and $B^2\Sigma^-$ band systems of the radical NCS rotationally cooled in a supersonic free jet expansion. A detailed analysis has been carried out for the A-X system. The linear radical NCS is of interest because of the Renner-Teller interaction in both the A and X states and because of the large spin-orbit coupling constant ($A=323.4\text{ cm}^{-1}$) in the ground electronic state relative to the Renner-Teller splitting ($\epsilon\omega_r=69\text{ cm}^{-1}$). The detailed information available from this study for all three vibrational modes provides a good test of the ability of the current Renner-Teller models to describe the spectrum of such a species. A detailed vibronic analysis has been carried out for the A and X electronic states for the two stretching modes excited by up to three quanta and for excited bending levels. Rotational analyses were conducted for the stronger bands involving each of the three vibrational modes. Results of these analyses will be presented at the meeting. Problems with the use of the Renner-Teller models to fit the excited bending levels will be discussed.

This research was carried out at Brookhaven National Laboratory under Contract No. DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Address of Northrup and Sears: Department of Chemistry, Brookhaven National Laboratory, Upton, N.Y., 11973.

WF5 (2:33)**THE INFRARED SPECTRUM OF THE ETHYL RADICAL AROUND 18.9 μ m**

TREVOR J. SEARS AND JOAN M. FRYE

An infrared absorption spectrum of C_2H_5 has been observed by diode laser spectroscopy in the region 520-550 cm^{-1} . The radical was formed by excimer laser photolysis of C_2H_5I at 248 nm or $(C_2H_5)_2CO$ at 193 nm. Both precursors showed the same transient absorption spectrum and the spectrum is close to the position of the strongest infrared absorption band assigned to C_2H_5 in low temperature matrix spectra¹. The gas phase spectrum is very complicated, however 5-6 rotational progressions can be identified. The complexity of the spectrum seems most likely due to strong interaction between the ν_9 (pyramidal distortion) vibration and the low frequency torsional (internal rotation) mode. Another possibility is that the radical center is non-planar and the spectral complexity is due to inversion doubling, however this seems a less likely explanation at present. Progress on the analysis of the spectrum will be reported at the meeting.

This research was carried out at Brookhaven National Laboratory under Contract No. DE-AC02-76CH00016 with the U. S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

¹ J. Pacansky and M. Dupuis, J. Amer. Chem. Soc. **104**, 415, (1982)

Address of Sears : Department of Chemistry, Brookhaven National Laboratory, UPTON, N.Y., 11973.

Address of Frye : Department of Chemistry, Building 200C-157, Argonne National Laboratory, ARGONNE, IL., 60439

WF6 (2:45)**INFRARED SPECTRUM OF $SiH_2 \nu_2$ BAND BY DIODE LASER KINETIC SPECTROSCOPY**

Chikashi Yamada, Eizi Hirota

Hideto Kanamori,

Nobuki Nishiwaki, Naoshi Itabashi, Kozo Kato, and Toshio Goto

The infrared spectrum of the ν_2 band of the silylene, SiH_2 (X^1A_1), was observed for the first time in the gas phase. The SiH_2 was generated by the photolysis of phenylsilane with an ArF excimer laser. The absorption spectra were recorded by diode laser kinetic spectroscopy. The rotational and centrifugal distortion constants were determined accurately, in addition to the band origin, $998.6241(3)\text{ cm}^{-1}$. Force field calculation was carried out to derive the Coriolis coupling constant between the ν_1 and ν_3 modes.

Address of Yamada and Hirota: Institute for Molecular Science, Okazaki 444, Japan.

Address of Kanamori: The University of Tokyo, Komaba, Japan

Address of Nishiwaki, Itabashi, Kato, and Goto: Nagoya University, Nagoya 460, Japan.

WF7 (3:02)**DETERMINATION OF REACTION RATE AND DIFFUSION CONSTANTS OF THE SiH₃ RADICAL IN SILANE PLASMAS**

Chikashi Yamada, Eizi Hirota,
Naoshi Itabashi, Kozo Kato, Nobuki Nishiwaki, and Toshio Goto

Time resolved infrared spectra of SiH₃ were observed in pulsed discharge silane plasmas using diode laser kinetic spectroscopy. The rate of recombination plus disproportionation reactions was determined for the first time, together with the diffusion constants of SiH₃ in hydrogen and argon. These fundamental quantities will be useful in discussing CVD mechanisms leading to amorphous silicon.

Address of Yamada and Hirota: Institute for Molecular Science,
Okazaki 444, Japan.

Address of Nishiwaki, Itabashi, Kato, and Goto: Nagoya
University, Nagoya 460, Japan.

Intermission**WF8 (3:30)****INFRARED SPECTROSCOPY OF LARGE CO₂ CLUSTERS**

R. Disselkamp and G.E. Ewing

Carbon dioxide clusters were formed by admitting monomeric CO₂, diluted in an inert gas, into a large cell cooled to 77K¹. The resulting suspension of clusters, each containing of the order of 10² molecules, were spectroscopically studied through FTIR techniques. The cluster size is such that the number of molecules in the interior is comparable to the number on the exterior (faces, edges and corners). Spectroscopic features associated with vibrational motions of these interior and exterior molecules are observed. Quantum mechanical and electromagnetic classical descriptions of the experimental results will be presented.

¹ G. Ewing and De T. Sheng, *J. Phys. Chem.* **92** (1988) 4063.

Address of Disselkamp and Ewing: Department of Chemistry, Indiana University,
Bloomington, IN 47405

WF9 (3:47)**VIBRATION-TUNNELING ENERGY LEVELS OF (HF)₂ FROM CLOSE-COUPPLING CALCULATIONS ON AN *AB INITIO* POTENTIAL SURFACE**

M. D. MARSHALL, P. R. BUNKER, P. C. GOMEZ, M. KOFRANEK,
H. LISCHKA, AND A. KARPEN

Using the analytical expression developed by Bunker, *et. al.*¹ for the *ab initio* potential energy surface of HF dimer,² close-coupling calculations are performed giving the energies of excited vibration and vibration-tunneling states. These results are compared with experiment when possible and with the results of approximate methods of calculation. The large number of channels required for convergence indicates that in some ways the HF dimer resembles a "normal" strongly-bound molecule more closely than a weakly-bound complex such as (H₂)₂.

¹P.R. Bunker, M. Kofranek, H. Lischka, and A. Karpfen, *J. Chem. Phys.* **89**, 3002 (1988).

²M. Kofranek, H. Lischka, and A. Karpfen, *Chem. Phys.* **121**, 137 (1988).

Address of Marshall: Department of Chemistry, Amherst College, Amherst, MA 01002.

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

Address of Kofranek, Lischka, and Karpfen: Institut für Theoretische Chemie und Strahlenchemie der
Universität, Wien, A-1090 Wien, Währingerstrasse 17, Austria.

WF10 (4:04)

AN AB INITIO SEMIRIGID BENDER CALCULATION OF THE ROTATION AND TRANS-TUNNELLING SPECTRA OF (HF)₂ AND (DF)₂

P.R. BUNKER, P.C. GOMEZ, M.D. MARSHALL, M. KOFRANEK, H. LISCHKA, AND A. KARPFFEN

Using a purely ab initio minimum energy path¹ for the trans-tunnelling motion in the HF dimer the energy levels for the K-type rotation and trans-tunnelling motion for (HF)₂ and (DF)₂ are calculated with a one-dimensional Semirigid Bender Hamiltonian and no adjustable parameters. The transition moments for rotation-tunnelling transitions are calculated, using our ab initio value for the dipole moment of an isolated HF molecule, and we also calculate \bar{B} values. The energy levels we obtain are in close agreement with experiment;² for example the K=0 tunnelling splitting in (HF)₂ is calculated as 0.65 cm⁻¹ compared to the experimental value of 0.65869 cm⁻¹. As well as showing that our ab initio minimum energy path is very good, the calculation demonstrates that the Semirigid Bender formalism is able to account quantitatively for the unusual K-dependence of the rotational energies resulting from the quasilinear behaviour,³ and that the trans-tunnelling motion is separable from the other degrees of freedom. We use the results to predict the locations, and transition moments, of the $\Delta K=0$ and ± 1 subbands in the tunnelling spectra of (HF)₂ and (DF)₂, many of which have not yet been observed.

¹P.R. Bunker et al., J. Chem. Phys. 89, 3002 (1988).

²W.J. Lafferty et al., J. Mol. Spectrosc. 123, 434 (1987).

³A.S. Pine et al., J. Chem. Phys. 81, 2939 (1984).

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

Address of Marshall: Department of Chemistry, Amherst College, Amherst, MA 01002.

Address of Kofranek, Lischka, and Krapfen: Institut für Theoretische Chemie und Strahlenchemie der Universität Wien, Währingerstrasse 17, A-1090 Wien, Austria.

WF11 (4:21)

A CALCULATION OF THE ROTATION-TORSION ENERGY LEVELS OF (HF)₂ AND (DF)₂

P.R. BUNKER, P.C. GOMEZ, M.D. MARSHALL, M. KOFRANEK, H. LISCHKA, AND A. KARPFFEN

The energy levels for torsion and K-type rotation for the HF dimer are calculated using an ab initio potential surface.¹ The symmetry of the levels are determined using the Molecular Symmetry Group, and a correlation diagram is obtained that shows how levels split (and how they do not split) as the torsional barrier is raised or lowered at the cis-position. The experimental results that have been obtained for the torsional fundamental band² will also be discussed.

¹P.R. Bunker et al., J. Chem. Phys. 89, 3002 (1988).

²K. von Puttkamer and M. Quack, Mol. Phys. 62, 1047 (1987).

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

Address of Marshall: Department of Chemistry, Amherst College, Amherst, MA 01002.

Address of Kofranek, Lischka, and Krapfen: Institut für Theoretische Chemie und Strahlenchemie der Universität Wien, Währingerstrasse 17, A-1090 Wien, Austria.

WF12 (4:38)

INVERSION-ROTATION SPECTRUM OF HF DIMER

S.P. BELOV, E.N. KARYAKIN, I.N. KOZIN, A.F. KRUPNOV, O.L. POLYANSKY, M.YU. TRETYAKOV,
N.F. ZOBOV, R.D. SUENRAM and W.J. LAFFERTY

The inversion-rotation spectrum of HF--HF has been investigated with the RAD-3 spectrometer at Gorky (1) in the frequency range 180-380 GHz at 210 K and pressures from 0.5 to 1.5 Torr. The spectrum was reexamined in the range 60-125 GHz with a conventional Stark spectrometer at pressures of 0.1 to 0.2 Torr and at temperatures near 195 K at NIST. Altogether 10 P-, Q-, and R-branch lines of the K=3 a-type inversion-rotation subband have been observed. The rotational constants of this subband are somewhat anomalous as compared with the previously observed lower K subbands (2). For example, B'-B" for this subband is positive while this difference is negative for the lower K transitions, and the Q-branch degrades to lower frequencies. The assignment, however, is well established by the missing lines in the Q- and P-branches. The inversion frequency for K=3 is 114 307.04(46) MHz which is in good agreement with the value of 114 790(150) MHz obtained by von Puttkamer et al. (3) from far IR studies. High J R-branch lines of the K=0 through K=2 subbands which fall in the higher frequency region have also been identified and improved rotational constants for these states obtained.

- (1) S.P. Belov and M.Yu. Tretyakov, IX Int. Conf. on High Res. IR Spectrosc., Prague, **68** (1986).
(2) W.J. Lafferty, R.D. Suenram, and F.J. Lovas, J. Mol. Spectrosc. **123**, 434 (1987).
(3) K. von Puttkamer, M. Quack, and M.A. Suhm, Mol. Phys., in press.

Address of Belov, Karyakin, Kozin, Krupnov, Polyansky, Tretyakov, Zobov: Institute of Applied Physics, Academy of Sciences of the USSR, Gorky, USSR
Address of Suenram and Lafferty: Molecular Spectroscopy Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

WF13 (4:55)

State-to-State Vibrational Predissociation

K.W. Jucks, D.C. Dayton, E.B. Bohac and R.E. Miller

Using a variation of the optothermal detection method, photofragment angular distributions for several HF containing van der Waals complexes have been measured. These distributions show resolved structure which can be assigned to individual fragment dissociation channels. This data can be used to establish correlations between the rotational states of the two fragments. The relative state-to-state cross sections for (HF)₂ are determined and compared with unimolecular dissociation theories. This comparison clearly shows that the predissociation dynamics of (HF)₂ is highly non-statistical. In addition to this information, the experiment also yields an accurate zero point dissociation energy (D₀) for (HF)₂.

Address: Dept. of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599.

WG1 (1:30)**THE QUADRATIC VIBRATIONAL FORCE FIELD OF *n*-BUTANE****W. F. MURPHY**

Ab initio quadratic vibrational force fields have been calculated at the Hartree-Fock level for the *trans* and *gauche* conformers of *n*-butane. Gas phase Raman and infrared spectra have been observed and assigned for several isotopically substituted species.

The *ab initio* force fields must be scaled appropriately to reproduce the frequency assignments for the observed spectra. However, the scaled force fields reported last year at this conference were not able to reproduce observed frequencies and Raman trace scattering cross sections in an entirely satisfactory manner.

Since the quadratic *ab initio* force field calculates harmonic frequencies, scaling such a force field to reproduce observed (anharmonic) frequencies involves the drastic assumption of negligible anharmonicity. In cases where a detailed vibrational analysis is not possible, harmonic frequencies may be estimated by an empirical 'harmonization' procedure, as has been done, for example, in the case of ethane¹. The application of such a procedure in the cases of *n*-propane, previously investigated by us², and *n*-butane is being investigated.

Secondly, *ab initio* force fields which incorporate electron correlation contributions have been more successful in reproducing vibrational frequencies in many cases, especially for modes involving skeletal motions. However, the direct calculation of such force fields for *n*-butane is not currently feasible, especially for the lower symmetry *gauche* conformer. Differences between force constant matrix elements calculated for benzene with and without electron correlation were recently reported to be independent of the basis set³. In an extension of this idea, the two types of force fields available for *n*-propane² may be used to estimate corrections to the *n*-butane force fields, in an attempt to account for the effects of electron correlation in this more complicated case.

The effectiveness of these measures to obtain improved force fields for *n*-butane will be discussed.

¹J. L. Duncan *et al.*, *J. Mol. Spectrosc.* **98**, 87 (1983).

²K. M. Gough *et al.*, *J. Chem. Phys.* **87**, 3332 (1987).

³H. Guo and M. Karplus, *J. Chem. Phys.* **89**, 4235 (1988).

Address: Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6.

WG2 (1:47)**AB INITIO MOLECULAR ORBITAL CALCULATIONS OF THE INFRARED SPECTRUM OF THE HYDROXYLAMINE DIMER****G.A. YEO and T.A. FORD**

The Gaussian-80 computer program has been used to calculate the structures, dimerization energies, infrared band wavenumbers and intensities of two hydrogen bonded dimers of hydroxylamine, at the restricted Hartree-Fock level of theory and employing the 6-31G** basis set. The calculated properties are compared with those of the monomer, reported earlier, and are rationalized on the basis of the natures of the two dimers. The calculated intensity changes are interpreted in terms of changes in some of the atomic polar tensor elements resulting from dimer formation.

Address: Department of Chemistry, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa.

WG3 (2:04)**VIBRATIONAL SPECTRA OF 1-FLUOROCYCLOBUTENE****NORMAN C. CRAIG, STEVEN S. BORICK and THOMAS R. TUCKER**

Gas-phase infrared spectra and liquid-phase Raman spectra have been recorded for 1-fluorocyclobutene, a new substance. For this molecule of C_s symmetry we propose a complete assignment of vibrational fundamentals. They are in cm^{-1} : (a) 3111, 2954, 2948, 1667, 1464, 1437, 1306, 1214, 1189, 1154, 972, 911, 866, 651, 412; (a') 2982, 2969, 1140, 1076, 1020, 855, 764, 436, 264. These assignments correlate well with those of 1-chlorocyclobutene¹ but not so well with some of the out-of-plane modes in the published assignments of unsubstituted cyclobutene.²

The ring puckering frequency of 264 cm^{-1} for 1-fluorocyclobutene will be compared with values for related cyclobutenes.

¹N. C. Craig and S. S. Borick, 43rd Symposium on Molecular Spectroscopy, The Ohio State University, June 13-17, 1988, p. 185.

²J. E. Baggott, H. J. Clase and I. M. Mills, *Spectrochim. Acta* **42A**, 319 (1986).

Address: Department of Chemistry, Oberlin College, Oberlin OH 44074

WG4 (2:16)

REVISED VIBRATIONAL ASSIGNMENT FOR CYCLOBUTENE

NORMAN C. CRAIG and STEVEN S. BORICK

Lord and Rea¹ and Aleksanyan and Garkusha² observed the infrared and Raman spectra of cyclobutene and proposed assignments of its vibrational fundamentals. Baggott, Clase and Mills³ contributed a higher resolution, FT-infrared study and reevaluated the assignments. For this molecule of C_{2v} symmetry with 24 fundamentals, they left ν_{20} (in-plane ring bend) unassigned and gave provisional assignments for three of the five a_2 modes based on indirect evidence.

Our assignments of the out-of-plane modes for 1-chlorocyclobutene and 1-fluorocyclobutene raised doubts about some of the assignments for the a_2 modes of cyclobutene and about the previous characterizations of some of the a_2 and b_2 modes of this molecule. We have examined the Raman spectrum of liquid cyclobutene at -100°C . We confirm $\nu_{10}(a_2)$ at 1142 cm^{-1} and propose $\nu_{11}(a_2)$ at 1011 cm^{-1} , $\nu_{12}(a_2)$ at 816 cm^{-1} , and $\nu_{20}(b_2)$ at 888 cm^{-1} . We concur with Baggott, Clase, and Mills on all of the other fundamentals. $\nu_{12}(a_2)$ and $\nu_{24}(b_2)$ are more appropriately characterized as out-of-plane modes of vinylic CH bonds than as CH_2 modes, in accord with the normal coordinate calculations of Sverdlov and Krainov.⁴

¹R. C. Lord and D. G. Rea, J. Am. Chem. Soc. **79**, 2401 (1957).

²V. T. Aleksanyan and O. G. Garkusha, Izv. Akad. Nauk SSSR Ser. Khim. 2227 (1976).

³J. E. Baggott, H. J. Clase and I. M. Mills, Spectrochim. Acta **42A**, 319 (1986). ($b_1 \leftrightarrow b_2$)

⁴L. M. Sverdlov and E. P. Krainov, Opt. Spectrosc. (Engl. Transl.) **6**, 94 (1962).

Address: Department of Chemistry, Oberlin College, Oberlin, OH 44074

WG5 (2:28)

FERMI RESONANCE ANALYSIS OF VIBRATIONAL OVERTONE SPECTRUM OF PYRROLE

F. ZHU, Y. RANASINGHE, AND D. L. SNAVELY

The vibrational overtone spectrum of gaseous pyrrole was obtained by laser photoacoustic spectroscopy. A quantitative analysis of this spectrum was conducted modelling the stretch-bend coupling in the N-H oscillator.

The seven bands from the fundamental¹, and third and fourth overtone absorptions of the N-H oscillator. The pure stretch localmode model did not yield satisfactory values for the mechanical frequency and the anharmonicity. The bands were globally fitted to the tridiagonal Fermi resonance model developed by Quack². The transition frequencies were in good agreement with experiment.

The magnitude of stretching parameter, ν_s , correlates with the N-H bondlength in pyrrole (99 pm). The value of the stretch-bend interaction parameter, k_{sbb} , indicates that the Fermi resonance is weak compared to the C-H stretch-bend interaction.

¹R. Navarro and J. M. Orza, Anales de Quimica **79**, 557-570 (1970).

²H-R. Dubal and M. Quack, J. Chem. Phys., **81**(9), 3779(1984).

Address of Zhu and Snavely: Department of Chemistry, Bowling Green State University, Bowling Green, Ohio, 43403.

Address of Ranasinghe: Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907.

WG6 (2:45) Paper MG4 is presented here. See page 59 for abstract of MG4.

WG 1 (3: 10)**ELECTRONIC TRANSITION MOMENT DIRECTIONS IN BIPHENYLENE**

Robert Herczegh and Leigh B. Clark

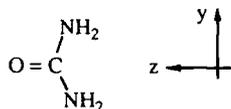
Polarized reflection spectra of the *ab*-face of crystalline biphenylene have been measured between 400 and 155 nanometers, and the corresponding absorption spectra have been calculated from the reflection spectra using the Kramers-Kronig transformation. The vapor spectrum of biphenylene between 400 and 130 nanometers has been measured. The vapor spectrum reveals the presence of eight excited electronic states, and the symmetry of six of these excited states has been deduced from the polarized crystal absorption spectra. Exciton calculations have been carried out to help confirm the symmetry assignments.

Address of Herczegh and Clark: Department of Chemistry, University of California at San Diego, La Jolla, CA 92093-0342.

WG 2 (3: 22)**POLARIZED VACUUM UV SPECTRA OF CRYSTALLINE UREA**

Blair F. Campbell and Leigh B. Clark

Polarized reflection spectra of single crystals of urea and a urea-hexadecane adduct have



been measured to 135 nm. Absorption spectra obtained by Kramers-Kronig analysis of the reflection data indicate the presence of three strong bands at $56,000\text{ cm}^{-1}$, $62,000\text{ cm}^{-1}$ and $65,000\text{ cm}^{-1}$. The transition moment directions are unambiguously found to be *y*, *z* and *y* and correspond to transitions with excited state symmetries of B_2 , A_1 and B_2 , respectively.

In spite of the fact that urea is a fairly small molecule of reasonably high symmetry and is closely related to the heavily studied amide grouping, little previous work on urea has been found. The only prior report of its electronic spectrum showed a single broad band centered at $58,800\text{ cm}^{-1}$, while the predictions of an extensive *ab-initio* calculation of the electronic states published in 1974 are completely inadequate.

Present address of Campbell: Rocketdyne Division, Rockwell International Corp., 6633 Canoga Avenue, Canoga Park, CA 91303.

Address of Clark: Department of Chemistry, University of California at San Diego, La Jolla, CA 92093-0342.

WG 3 (3: 34)**PRERESONANCE RAMAN EXCITATION PROFILES: COMPARISON WITH MORE DIRECT PROBES OF DIPOLE-FORBIDDEN EXCITED ELECTRONIC STATES***

L. SZTAINBUCH AND G. E. LEROI

For centrosymmetric chromophores, such as linear polyenes, approximately half of the electronic excited state manifold is inaccessible from the ground state by conventional absorption spectroscopy because of parity selection rules. Such "hidden" states are typically studied by two-photon induced fluorescence spectroscopy, or by high resolution absorption and fluorescence excitation spectroscopy of samples placed in a Shpolskii matrix environment. In cases where these techniques are not applicable, (e.g. non-fluorescent molecules), preresonance Raman spectroscopy may be a suitable alternative. The preresonance Raman excitation profile is determined point-by-point from the ratio of the scattered intensity of a sample vibrational band to that of a nearby solvent mode as a function of the excitation energy, and the hidden states manifest themselves as interference features.¹

However, the interpretation of the interference features, and their relationship to the hidden state origin, which is not active in the excitation profile, rely on self-consistency arguments. In an effort to establish more firmly the utility of preresonance Raman profiles, we have chosen diphenyldodecapentaene (DPDP) as a model compound. The low-lying, hidden 2^1A_g state origin of DPDP has been located at low temperatures by both two-photon excitation² and matrix absorption/emission³ spectroscopy. We present here the preresonance Raman excitation profile of DPDP in the region just below the allowed 1^1B_u electronic state, in the $20000\text{--}22700\text{ cm}^{-1}$ energy range. The results are in excellent accord with those of the more direct methods, and establish preresonance Raman excitation as a viable technique for locating parity-forbidden electronic states.

*Research supported in part by the U.S. National Science Foundation

¹J. Friedman and R. M. Hochstrasser, *Chem. Phys. Lett.* **32**, 414 (1975)

²R. R. Birge and H. L. Fang, private communication

³J. S. Horwitz, T. Itoh, and B. E. Kohler, *J. Chem. Phys.* **87**, 2433 (1987)

Address of Authors: Department of Chemistry and the LASER Laboratory, Michigan State University, East Lansing, MI 48824-1322

WG'4 (3:51)**TWO-PHOTON EXCITATION SPECTRUM OF PERYLENE IN SOLUTION*****JEONG-A YU, DANIEL G. NOCERA AND GEORGE E. LEROI**

The selection rules for two-photon absorption often permit one to generate excited states that cannot be accessed by one-photon transitions. In particular, for molecules with a center of symmetry the parity selection rules for two-photon transitions are g-g and u-u, instead of g-u.

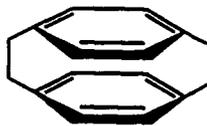
The two-photon excitation spectra of perylene in *n*-hexane at room temperature and 77 K have been obtained using both linear and circular polarized light over the excitation energy range 23,530 cm⁻¹ - 35,700 cm⁻¹. The dipole-forbidden S₀ - S₂ transition, which is uncertain in the one-photon absorption spectrum, is observed at ~27,000 cm⁻¹. From measurement of the linear/circular polarization ratio, Ω , as a function of excitation energy and comparison with previous experimental and calculated values, we have assigned several low-lying "g" symmetry excited states of perylene.

*Research supported in part by the U.S. National Science Foundation

Address of Authors: Department of Chemistry and the LASER Laboratory, Michigan State University, East Lansing, MI 48824-1322

WG'5 (4:08)**SPECTROSCOPY OF [2,2]PARACYCLOPHANE COMPLEXES WITH BENZENE*****JEONG-A YU, GEORGE E. LEROI AND DANIEL G. NOCERA**

Paracyclophanes are aromatic hydrocarbons with unique steric and electronic properties. The structure of paracyclophanes consists of the cofacial disposition of benzene rings (which may be substituted) tethered with hydrocarbon side chains. The intercavity distance between the rings can systematically be manipulated by judicious choice of the side chain. For example, the short ethylene tether in [2,2]paracyclophane causes the π -clouds to interpenetrate (intraannular distance ~3.1 Å). This transannular interaction of π -electron clouds can be reduced by simply increasing the length of the tether. As model cavity-containing molecules, paracyclophanes provide the opportunity to investigate specific complexation effects or the excited state properties of cofacial systems. We have initiated our studies with investigation of the laser induced fluorescence excitation spectra of [2,2]paracyclophane in a continuous wave supersonic free jet expansion. Complexation of the [2,2]paracyclophane with benzene has been investigated and the results of this work will be discussed.



[2,2]paracyclophane

*Research supported by the U.S. National Science Foundation

Address of Authors: Department of Chemistry and the LASER Laboratory, Michigan State University, East Lansing, MI 48824-1322

WG'6 (4:25)**PRESSURE EFFECT ON THE ZERO-FIELD SPLITTINGS OF AROMATIC TRIPLETS**I. Y. Chan and Xiugi Qian

Optically detected magnetic resonance experiments under pressure in excess of 40 kbar have been performed in several triplet state aromatic molecules. The sample is contained in a small hole in a metal gasket in a diamond anvil high pressure cell. A judiciously designed hairpin effectively couples microwave magnetic field to the sample.

Data will be reported for p-dichlorobenzene (DCB) in p-xylene, s-tetrachlorobenzene (TCB) in durene and quinoxaline (Q) in durene. The zero-field parameter D decreases linearly with increasing pressure, whereas E has more subtle changes. These results are interpreted in terms of the mesomeric effect in chlorobenzenes and the inductive effect in azaromatics. The quadrupolar field gradient of the Cl^{35} isotope has been measured as a function of pressure. Its decreasing trend corroborates the above picture.

Address of Chan and Qian: Department of Chemistry, Brandeis University, Waltham, MA 02254-9110

WG'7 (4:42)**PRESSURE EFFECT ON ZERO-FIELD SPLITTINGS IN TRIPLET CARBONYLS: $\pi\pi^*$ - $n\pi^*$ COUPLING**I. Y. Chan and Xiugi Qian

Optically detected magnetic resonance under high pressure was first reported by us using benzophenone (BP) as an example [1]. We have since investigated other triplet carbonyls with the aim of understanding the dominant factor in determining the pressure effect of the zero-field parameter D in this class of molecules. We will present data on biacetyl and benzil neat crystals, as well as on acetophenone doped in dibromobenzene. The D-value for BP increases some 13% over 40 kbar; whereas it decreases substantially for all the other carbonyls examined.

These results are comprehensible if we recognize the important contribution of spin-orbit coupling (SOC) to the zero-field parameters of triplet carbonyls. The second order perturbation of SOC connect the $\pi\pi^*$ and $n\pi^*$ triplets in a spin-specific manner. As pressure affects the energy of the $\pi\pi^*$ state, it changes the D-value of the lowest triplet. All our data may be rationalized this way. In contrast the pressure effect on spin-spin dipolar interaction becomes unimportant.

 [1] C.J. Sandroff, I.Y. Chan and W.M. Chung, J. Chem. Phys. 84, 2424 (1987).

Address of Chan and Qian: Department of Chemistry, Brandeis University, Waltham, MA 02254-9110

WG'8 (4:59)**SOLVENT RELAXATION EFFECTS ON THE LUMINESCENCE PROPERTIES OF 7-HYDROXYFLAVONE:--STEADY STATE AND TIME RESOLVED STUDIES****MUNNA SARKAR and P.K.SENGUPTA**

7-Hydroxyflavone (7HF) gives a blue fluorescence ($\lambda_{max}=450$ nm) at 77K and a green fluorescence ($\lambda_{max}=537$ nm) at 298K when $\lambda_{exc}=365$ nm in ethanol-methanol (1:1 vol/vol) solvent. The blue and green fluorescence have been found to originate from the same ground state species namely the conjugate anion of 7HF (7HFA). Large change in the excited state dipole moment of 7HFA takes place and has been calculated to be 13.7D using the solvatochromic shift method. The large blue shift of the steady state emission maximum when the temperature is decreased from 298K to 77K, is rationalised in terms of solvent relaxation around excited fluorophore. When the relaxation time of the solvent (τ_r) is comparable to the fluorescence lifetime (τ_f), the reorientation of the solvent dipoles around the excited solute manifest in a time dependent shift of emission maximum as well as temperature dependent shift of the steady state emission maximum.

Time resolved studies (in the nanosecond time domain) have been carried out in order to obtain further insight into the solvent relaxation process involved here.

Address : Nuclear Chemistry Division
Saha Institute of Nuclear
Physics, 1/AF Bidhannagar,
Calcutta 700 064, India

RA1 (8:30)

SUB-DOPPLER DIRECT IR LASER ABSORPTION SPECTROSCOPY IN FAST ION BEAMS: THE FLUORINE HYPERFINE STRUCTURE OF HF⁺

J.V. COE, J.C. OWRUTSKY, E.R. KEIM, D.C. HOVDE, N.V. AGMAN, AND R.J. SAYKALLY

Using a newly developed technique for measuring vibration-rotation spectra of molecular ions with sub-Doppler resolution, Direct Laser Absorption Spectroscopy in Fast Ion Beams (DLASFIB), hyperfine-resolved vibration-rotation transitions of HF⁺ have been measured.¹ Along with optical combination differences and laser magnetic resonance data, these have been analyzed to yield the fluorine hyperfine parameters, a, b, c and d, for both v=0 and v=1 in the X²Π state. Comparisons with many body perturbation theory results are presented.

¹J. V. Coe, J. C. Owrutsky, E. R. Keim, N. V. Agman, and R. J. Saykally, *J. Chem. Phys.*, (in press).

Address of Owrutsky, Keim, Agman and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720.

Address of Coe: Department of Chemistry, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210.

Address of Hovde: Department of Chemistry, Princeton University, Princeton, NJ 08544.

RA2 (8:47)

ASSIGNMENT OF THE 2ν₂ BAND OF THE H₃⁺ ION IN EMISSION

W. A. MAJEWSKI, P. A. FELDMAN, J. K. G. WATSON, S. MILLER, AND J. TENNYSON

In a search for the 2ν₂ band of the H₃⁺ ion in emission the region 4500–5200 cm⁻¹ of the spectrum was recorded in 1985, employing the hollow-cathode electrical discharge cell previously used to observe the ν₂ fundamental in emission¹. However, the high rotational temperature of the H₃⁺ ions prevented a rotational analysis until high-quality *ab initio* predictions became available in 1988² and were tested against the difference band 2ν₂ – ν₂ by Bawendi, Rehfuß and Oka³. These *ab initio* calculations have now been extended⁴ to higher values of J, and have made it possible to assign more than 50 of the observed lines to rotational transitions of this band. The rotational temperature is found to be approximately 1800 K. By a comparison with the laboratory spectrum, more than 20 emission lines observed from one of the polar 'hot spots' in the auroral zone of Jupiter⁵ have been assigned as belonging to this band, giving the first definitive observation of extraterrestrial H₃⁺.

1. 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).
2. S. Miller and J. Tennyson, *J. Mol. Spectrosc.* **128**, 530–539 (1988).
3. M. G. Bawendi, B. D. Rehfuß, and T. Oka, Paper RA10, 43rd Symposium on Molecular Spectroscopy, Columbus, Ohio (1988).
4. S. Miller and J. Tennyson, *J. Mol. Spectrosc.*, to be published.
5. J.-P. Maillard and P. Drossart, personal communication.

Address of Majewski, Feldman and Watson: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6

Address of Miller and Tennyson: Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, England

RA3 (9:09)

INFRARED STUDIES ON VIBRATIONALLY EXCITED H₃⁺

LI WEI XU, MOUNGI BAWENDI, BRENT D. REHFUSS, CHARLES GABRYS, AND TAKESHI OKA

Recently Watson¹ identified the 2ν₂ (z=2)–0 overtone emission band of H₃⁺ in a Fourier transform infrared spectrum discovered by astronomers in Jupiter.² In order to better understand the spectrum we are extending our earlier studies³ to more observation of hot bands and overtone bands. A difference frequency spectrometer using a LiIO₃ crystal as the non-linear optical element is used to cover the wide wavelength region of 2–5.5 μm. A liquid-nitrogen cooled H₂-He plasma is used to produce vibrationally hot H₃⁺. The observation and analysis of the spectrum based on the first principle calculation of Miller and Tennyson⁴ will be reported.

¹J.K.G. Watson, private communication

²J.P. Maillard and Drossart, *CFHT Bulletin* **20**, 13 (1989)

³M.G. Bawendi, B.D. Rehfuß, and T. Oka, this Symposium, 1988

⁴S. Miller and J. Tennyson, private communication

Address of Xu, Rehfuß, Gabrys and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

Address of Bawendi: AT&T Bell Laboratories, Murry Hill, New Jersey 07974

RA4 (9:26)**MICROWAVE SPECTRA OF THE HD⁺ AND D₂⁺ IONS AT THEIR DISSOCIATION LIMITS.**

ALAN CARRINGTON, IAIN R. McNAB, CHRISTINE A. MONTGOMERIE AND JOHN M. BROWN

We have observed microwave transitions in the HD⁺ and D₂⁺ ions involving energy levels very close to their dissociation limits. In HD⁺ the spectrum detected arises from a rotational transition between the two highest bound vibration-rotation levels in the 1σ ground state (v=21 and v=22)¹. D₂⁺ has seven vibration-rotation levels supported by the van der Waals minimum in the first excited 2pσ_u electronic state² and we have detected microwave electronic transitions between these and high-lying vibration-rotation levels of the ground 1σ_g electronic state.

¹A. Carrington, I.R. McNab and C.A. Montgomerie, *Mol. Phys.*, **65**, 751 (1988).²A. Carrington, I.R. McNab and C.A. Montgomerie, *Phys. Rev. Lett.* **61**, 1573 (1988).

Address of Carrington, McNab and Montgomerie: Department of Chemistry, Southampton University, Southampton SO9 5NH, United Kingdom.

Address of Brown: Physical Chemistry Laboratories, South Parks Road, Oxford OX1 3QZ, United Kingdom.

RA5 (9:43)**OBSERVATION OF HIGHLY EXCITED VIBRATIONAL STATES OF X³Σ⁻ OH⁺**

B. D. REHFUSS, M.-F. JAGOD, L.-W. XU and T. OKA

The hot band progression (v=2←1, v=3←2, v=4←3 and v=5←4) as well as high J transitions of the fundamental of the ³Σ⁻ ground electronic state of OH⁺ have been observed using He-dominated plasmas in the infrared between 3250-2400 cm⁻¹. Our difference frequency spectrometer was used as the infrared source with velocity modulation for detection. OH⁺ was produced in an AC glow discharge of 50 mtorr O₂, 50 mtorr H₂ and 10 torr He. Because of its high ionization potential and low proton affinity, He is very effective in raising the electronic temperature of plasmas without reducing ion concentration.

270 transitions (v=0-5) have been simultaneously fit by a non-linear least-squares program for the appropriate linear molecule Hamiltonian for a ³Σ state. B_v, D_v, H_v, as well as the spin-spin and spin-rotation λ_v, γ_v constants have been determined for nearly all states. The data have also been fit to the Dunham¹ model potential where the vibration-rotation coefficients Y_{kl}'s are expressed as:

$$E_{vJ} = \sum_{kl} Y_{kl} (v+1/2)^k [J(J+1)]^l$$

The vibrational and rotational temperatures will also be discussed.

¹J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).

Address of Rehfuss, Jagod, Xu and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637.

RA6 (10:00)**OBSERVATION OF HIGHLY EXCITED STATES OF PROTONATED NITROGEN, N₂H⁺**

B. D. Rehfuss, L.-W. XU and T. OKA

Each of the fundamental vibration bands of N₂H⁺ has been previously observed¹⁻⁴ as well as the first hot band⁴ ν₁ + ν₂ ← ν₁. In this paper we report the observation of a very dense spectrum in the infrared region between 3240 - 3120 cm⁻¹ corresponding to hot bands in each vibrational mode (2ν₁ ← ν₁, ν₁ + ν₃ ← ν₃ and ν₁ + nν₂ ← nν₂ {n=2,3}).

The spectrum was taken using our difference frequency spectrometer with the velocity modulation technique for detection. N₂H⁺ was produced in a liquid-nitrogen cooled AC glow discharge with a mixture of 60 mtorr N₂, 120 mtorr H₂ and 7 torr He. The intensity of the lines had only a slight dependence on the amounts of N₂ and H₂, whereas the hot bands decrease dramatically with the exclusion of He. Discussion of the vibrational and rotational temperatures will also be presented.

¹C. S. Gudeman, M. H. Begemann, J. Pfaff and R. J. Saykally, *J. Chem. Phys.* **78**, 5837 (1983).²T. J. Sears, *J. Opt. Soc. Am. B.* **2**, 786 (1985).³S. C. Foster and A. R. W. McKellar, *J. Chem. Phys.* **81**, 3424 (1984).⁴J. C. Owrutsky, C. S. Gudeman, C. C. Martiner, L. M. Tack, N. H. Rosenbaum and R. J. Saykally, *J. Chem. Phys.* **84**, 605 (1986).

Address of Rehfuss, Xu and Oka: Department of Chemistry and Astronomy and Astrophysics, University of Chicago, Chicago, Illinois 60637.

Intermission

RA7 (10:30)

THE INTERNAL ROTATION SPLITTINGS IN $C_2H_3^+$

P.R. BUNKER AND P.C. GOMEZ

Splittings that are believed to result from the 'internal rotation' of the three hydrogen atoms around the C-C core in the $C_2H_3^+$ molecule have been assigned¹ in what is believed to be the antisymmetric CH stretching band. These results show that the splittings are negligible in the vibrational ground state, in agreement with results² based on an ab initio potential surface,³ but that they are significant in the vibrationally excited state. By fitting to these splittings we determine the 'effective' internal rotation potential in the antisymmetric CH stretching band. The relation of this potential to the ab initio potential is discussed in terms of the way in which the antisymmetric stretching frequency changes with the internal rotation geometry.

¹M.W. Crofton, M.-F. Jagod, B.D. Rehfuss and T. Oka, to be published.

²R. Escribano, P.R. Bunker, and P.C. Gomez, Chem. Phys. Letters 150, 60 (1988).

³R. Lindh, B.O. Boos, and W.P. Kraemer, Chem. Phys. Letters 139, 407 (1987).

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

RA8 (10:47)

THE LABORATORY DETECTION OF H_2COH^+ .

T. Amano and H. E. Warner

Formaldehyde is one of the most abundant interstellar molecules. Protonated formaldehyde is a precursor of H_2CO and at the same time is formed from H_2CO through proton transfer reactions with ions such as H_3^+ , HCO^+ , HN_2^+ , H_3O^+ . In early theoretical models of the formation of interstellar molecules, H_3CO^+ was assumed to be the most stable form of protonated formaldehyde. Several recent *ab initio* calculations, however, have predicted that H_2COH^+ is the most stable isomeric form, and have predicted the rotational transition frequencies to assist in astronomical searches. Nevertheless, the predictions have not been accurate enough to warrant astronomical searches.

The ν_1 fundamental band (O-H stretch) of H_2COH^+ has been observed in the 3- μ m region with a difference frequency laser as a radiation source. Protonated formaldehyde was generated in a hollow cathode discharge through a gas mixture of H_2CO (~ 10 mTorr) and H_2 (~ 1 Torr). The band was found perturbed, and only the $K_a = 0$ and $K_a = 1$ lines have been assigned at the present stage. The spectroscopic parameters for the ground state, however, have been derived from the combination differences. The rotational transition frequencies, that are relevant for search for the interstellar lines, are calculated from these molecular constants.

Address of T. Amano and H. E. Warner: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

RA9 (11:04)

INFRARED SPECTROSCOPY OF AN H_2/O_2 DISCHARGE: I - THE H_3O^+ ION

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

In an effort to observe and identify the long-time elusive infrared spectrum of the HO_2^+ ion, we undertook a thorough investigation of an H_2/O_2 glow discharge. A high resolution tunable infrared laser (color center laser) spectrometer along with high sensitivity velocity modulation detection was used. An AC glow discharge of 50 mtorr H_2 , 50 mtorr O_2 , and 1-10 torr He was studied between 3100 - 3600 cm^{-1} . The majority of the spectrum can be attributed to the H_3O^+ ion. The hot band, $\nu_2 + \nu_3 \leftarrow \nu_2$, has been studied along with a complete analysis of the ν_3 fundamental.^{1,2} Upon changing the He pressure from 1 to 10 torr the S/N of the fundamental decreased fourfold while that of the hot band stayed the same. This greatly helped in the identification and assignment of the two bands. The alchemy of the discharge along with the assignment of the spectra will be presented.

1. M. H. Begemann, and R. J. Saykally, *J. Chem. Phys.* **82**, 3570 (1983).

2. A. Stahn, H. Solka, H. Adams, and W. Urban, *Mol. Phys.* **60**, 121 (1987).

Address: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637.

RA10 (11:21)

INFRARED SPECTROSCOPY OF AN H₂ / O₂ DISCHARGE: II - THE H₂O⁺ ION

C. J. PURSELL, W. C. HO, B. M. DINELLI, and T. OKA

During a thorough investigation of an H₂ / O₂ glow discharge, conditions which favored the formation of the H₂O⁺ ion over the more abundant H₃O⁺ ion were discovered. A high resolution tunable infrared laser (color center laser) spectrometer along with high sensitivity velocity modulation detection was used to study an AC glow discharge between 3100 - 3600 cm⁻¹. The ν_3 fundamental of the H₂O⁺ ion which had been identified earlier¹ was observed using 50 mtorr H₂, 50 mtorr O₂ and 10 torr He. But, it was discovered that the S/N increased considerably in just a pure He discharge, owing to a small water impurity in the He tank². This also had the effect of reducing, in fact almost eliminating completely, the signals due to H₃O⁺. This greatly helped in the identification of many more transitions from the ν_3 , and also made possible the identification of the ν_1 fundamental. The alchemy of the discharge along with assignment of the ν_1 and ν_3 of the H₂O⁺ ion will be presented.

1. B. M. Dinelli, M. W. Crofton, and T. Oka, *J. Mol. Spectrosc.* **127**, 1-11 (1988).
2. This result was also observed by Urban's group at Bonn; *private communication* - H. Solka.

Address of Pursell, Ho, Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637.

Address of Dinelli: Istituto di Spettroscopia Molecolare, Via de'Castagnoli 1, 40126 Bologna, Italy.

RA11 (11:38)

THE INFRARED DETECTION OF HOSi⁺ AND DOSi⁺

H. E. WARNER, T. AMANO, A. FOX, D. BOHME, N. MOAZZEN-AHMADI,
AND A. R. W. MCKELLAR

The ν_1 (O-H stretch) and ν_3 (O-Si stretch) bands of HOSi⁺ have been observed, and 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 Rosmus.¹

We employed the difference frequency laser system to observe the ν_1 band, whose origin is approximately 3660 cm⁻¹ and the diode laser to observe the ν_3 band, whose origin is approximately 1130 cm⁻¹. Both bands were observed in a hollow cathode discharge, with approximately 15 kHz discharge modulation. The initial detection of the ion was made by discharging (CH₃)₃SiOH in a buffer of H₂ and He, with high discharge current and water cooling. Later, it was discovered that better results could be obtained by mixing SiH₄ and N₂O with either H₂ or H₂ and He, with dry-ice and methanol cooling. It was not possible to observe HOSi⁺ with mixtures of SiH₄ and H₂O.

We have observed several lines of the ν_1 band of DOSi⁺ around 2700 cm⁻¹, but have no definitive assignment or molecular constants. This was produced in a similar manner to HOSi⁺, initially with (CH₃)₃SiOD in a buffer of D₂ and He, and subsequently with SiH₄ in a buffer of D₂ and He. Attempts to observe the ν_3 band of DOSi⁺ were unsuccessful.

¹ P. Botschwina and P. Rosmus, *J. Chem. Phys.* **82**,1420 (1985).

Address of Warner, Amano, Moazzen-Ahmadi, and McKellar: Herzberg Institute of Astrophysics, National Research Council, Ottawa, Ontario, Canada K1A 0R6

Address of Fox and Bohme: Department of Chemistry, York University, North York, Ontario, Canada M3J 1P3

RB1 (8:30)NEW MEASUREMENTS OF THE IONIZATION POTENTIAL AND DISSOCIATION ENERGY OF H₂

E.E. Eyler, E. McCormack, and J.M. Gilligan

The accuracy of theoretical work on the ground state of H₂ has improved dramatically in the past few years, considerably surpassing the accuracy of existing measurements. The calculations are now sufficiently good that new experimental measurements can sensitively test the quantum electrodynamic corrections in this simple molecular system, predicted to be 0.378 cm⁻¹ with an uncertainty of a few times 0.01 cm⁻¹. This talk will describe progress in a new program of measurements at Yale, in which both the ionization potential and the dissociation limit are being determined with much improved accuracy.

To determine the ionization potential we have extrapolated the Rydberg np series, the same basic approach used in the classic experiment by Herzberg and Jungen,¹ and the more recent laser experiment by Glab and Hessler.² Our new measurement is a two-part effort: first two-photon intervals from the ground state to the E,F(2sσ) state near 100,000 cm⁻¹ are determined, then transitions from the E,F state to the high Rydberg states are measured. For both measurements, a pulse-amplified cw dye laser is used in conjunction with a collimated molecular beam to provide Doppler-free spectra with linewidths of order 100 MHz. Four rotational branches to Rydberg np states with n=42-88 have been studied. One- and two-channel quantum defect theory analyses describe the results within experimental uncertainties, and yield four consistent results for the ionization potential. The result of 124417.524 ± 0.015 cm⁻¹ agrees with the theoretical value of 124417.503 cm⁻¹ and is 7 times more accurate than previous experiments.

The dissociation energy can be determined either from direct observation of the dissociative continuum or from extrapolation of the highest bound vibrational levels. We are trying both approaches, using stepwise laser excitation from the E,F state to the region of the second dissociation limit. Our current results indicate that the spectrum just below threshold is unexpectedly complex, so that a careful treatment of non-adiabatic couplings and a modification of existing line assignments may be required.

These experiments were supported by the National Science Foundation.

¹G. Herzberg and Ch. Jungen, *J. Mol. Spec.* **41**, 425 (1972).

²W.L. Glab and J.P. Hessler, *Phys. Rev. A* **35**, 2102 (1987).

Address: Department of Physics, Yale University, P.O. Box 6666, New Haven, CT 06511-8167

RB2 (9:05)DISSOCIATION AND IONIZATION OF EXCITED STATES OF H₂⁺

D. L. HUESTIS, R. KACHRU, AND H. HELM

The bound excited states of molecular hydrogen can decay in three ways: through radiation, ionization, and dissociation. Which decay path the molecule chooses depends on symmetry and the available energy, but most importantly on the region of internuclear distance sampled by the vibrational wavefunction, which controls the extent of interaction with the dissociative doubly-excited configurations.

We report experimental studies of competition between ionization and dissociation in both singlet (EF¹Σ_g⁺, B¹Σ_u⁺, and C¹Π_u intermediate) and triplet (c³Π_u, g, h³Σ_g⁺, i, 2³Π_g, and j³Δ_g final) excited states. A special feature of this work is control of the internuclear distance (i.e. high vibrational levels) in the final state by selecting a specific intermediate state by multiphoton excitation (singlets) or by double-resonance labeling (triplets). Predissociation occurs by barrier penetration, rotational, spin-orbit and spin-spin, and radial coupling mechanisms. Both rotational and vibrational autoionization are investigated, in the latter case with large Δv changes mediated by doubly-excited states.

* Research supported by AFOSR and NSF

Address of authors: Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

RB3 (9:40)**UNDERSTANDING HIGH-L STATES OF H₂: EXPERIMENT AND THE POLARIZATION MODEL*****S.R. LUNDEEN**

The high-L, non-penetrating, Rydberg states of H₂ can be understood with a physical picture which would be quite inappropriate for low-L states. The structure of high-L states is dominated by long-range, rather than short range, interactions, with inter-series mixing playing only a minor role. These physical ideas are incorporated into the "polarization model" which gives a rather successful a-priori theoretical description of such states.¹

The most precise experimental studies of high-L structure have been obtained using fast beam microwave/optical methods.² In separate experiments, both the (0,1)10L states with $4 \leq L \leq 7$, and the (0,1)nL states, with $26 \leq n \leq 30$ and $4 \leq L \leq 6$ have been studied with precision of $< 10^{-5} \text{ cm}^{-1}$. The most recent experimental results obtained with these techniques will be reviewed and compared with the predictions of the polarization model.

*Supported by NSF under Grant PHY-87-09707

¹W.G. Sturuss, E.A. Hessels, P.W. Arcuni, and S.R. Lundeen, Phys. Rev. A **38**, 135 (1988)

²W.G. Sturuss, E.A. Hessels, P.W. Arcuni, and S.R. Lundeen, Phys. Rev. Lett. **61**, 2320 (1988)

Address of Lundeen: Dept. of Physics, Univ. of Notre Dame, Notre Dame, IN 46556

Intermission**RB4 (10:35)****LASER STUDIES OF AUTOIONIZATION PROCESSES IN MOLECULAR HYDROGEN¹****S. T. PRATT, P. M. DEHMER, J. L. DEHMER, F. S. TOMKINS, AND M. A. O'HALLORAN**

Recent results of optical-optical double resonance studies of rotational and vibrational autoionization in molecular hydrogen will be reported. In the experiments on rotational autoionization, one laser was used to excite a two-photon transition to the E,F $^1\Sigma_g^+$, $v^+=E0$, $J^+=0-4$ levels, and a second laser was used to probe single photon transitions to the rotationally autoionized, np Rydberg series converging to the X $^2\Sigma_g^+$, $v^+=0$, $N^+=1-6$ rotational levels of the ion.² Of the five dipole allowed Rydberg series converging to $v^+=0$ excited from each intermediate J^+ level ($J^+ > 2$), two are allowed to rotationally autoionize in a coupling scheme that assumes ejection of pure p-waves in the ionization process and singlet coupling of the spins of the ion core and the outgoing electron. As expected, members of these Rydberg series have large half-widths. Ionization is also observed for the series that are forbidden to rotationally autoionize according to this simple coupling scheme, and the possible decay mechanisms will be discussed. In experiments on vibrational autoionization, rotationally resolved photoelectron spectra were recorded for members of the np Rydberg series converging to the X $^2\Sigma_g^+$, $v^+=1$, $N^+=1$ and $N^+=3$ levels of the ion. The results will be compared with a simple model and the significant deviations from this model will be discussed.

¹Work supported by the U.S. Department of Energy, Office of Health and Environmental Research, under Contract W-31-109-Eng-38.

²M. A. O'Halloran, P. M. Dehmer, S. T. Pratt, J. L. Dehmer, and F. S. Tomkins, J. Chem. Phys. **90**, 930 (1989).

Address of Pratt, Dehmer, Dehmer, and Tomkins: Argonne National Laboratory, Argonne, Illinois 60439.

Address of O'Halloran: Department of Physics and Astronomy, University of Oklahoma, Norman, Oklahoma 73019.

RB5 (11:10)**ROTATIONAL AND VIBRATIONAL DISTRIBUTIONS IN RESONANCE ENHANCED MULTIPHOTON IONIZATION OF MOLECULES.**

V. McKOY, M. BRAUNSTEIN, S. N. DIXIT, D. L. LYNCH, H. RUDOLPH, AND J. A. STEPHENS

Resonance enhanced multiphoton ionization (REMPI) coupled with high-resolution photoelectron spectroscopy is an important *state-specific* probe of the photoionization dynamics of molecular excited states. In this talk we will discuss results of studies of ion rotational and vibrational distributions for REMPI of several small molecules such as H₂, O₂, NO, CH, and OH. Some highlights of these results include (i) non-Franck-Condon ion vibrational distributions arising from the presence of autoionizing (H₂) and shape resonances (O₂) and from orbital evolution in the resonant state (OH), and (ii) rotational distributions of ions and the associated photoelectron angular distributions (NO and CH) with emphasis on their non-atomic-like behavior.

Address of McKoy, Braunstein, Rudolph, and Stephens: Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125.

Address of Dixit: Lawrence Livermore National Laboratory, L-446, Livermore, CA 94550.

Address of Lynch: Department of Chemistry, University of Nevada, Reno, NV 89557.

RC1 (8:30)

PREDISSOCIATION LINE WIDTHS OF THE SCHUMANN-RUNGE BANDS OF O₂

A.S.-C. CHEUNG, S.S.-I. CHIU, K. YOSHINO, J.R. ESMOND, D.E. FREEMAN and W.H. PARKINSON

A non-linear least squares method of retrieving predissociation line widths from experimental absorption cross sections¹ has been applied to the (0,0) to (12,0) Schumann-Runge bands of oxygen. Predissociation line widths deduced, for the upper state of the Schumann-Runge bands, are larger than theoretical predictions and the latest measurements of Lewis et al.² Systematic variation of predissociation line widths with respect to rotation was not confirmed except in v=6, 9, 11 and 12. These larger line widths will have an impact on calculations of solar flux penetration into the earth's atmosphere and of the photodissociation rates of trace species in the upper atmosphere.

This work is supported by NASA grant NAG 5-484 to Smithsonian Astrophysical Observatory.

¹K. Yoshino, D.E. Freeman, J.R. Esmond and W.H. Parkinson, *Planet. Space Sci.* **31**, 339-353, (1983).

²B.R. Lewis, L. Berzins, J.H. Carver and S.T. Gibson, *J. Quant. Spectrosc. Radiat. Transfer* **36**, 187-207, (1986).

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

RC2 (8:42)

PHOTOABSORPTION COEFFICIENTS FOR CARBON MONOXIDE ABSORPTION BANDS BETWEEN 94.0 nm AND 100.4 nm

G. STARK, K. YOSHINO, P.L. SMITH, D. ZUCKER, W.H. PARKINSON and K. ITO

Theoretical descriptions of the abundance and excitation of CO in interstellar clouds require accurate and complete information on many molecular properties. In particular, data such as line positions, line widths, and photoabsorption coefficients, which will allow the photodissociation rate for CO to be determined, are needed. We have measured photoabsorption cross sections for CO at a resolving power more than 20 times greater than that used in previous work.¹ Most of the measurements were made with 6.65-m vertical-dispersion spectrograph/spectrometer at the Photon Factory of the National Laboratory for High Energy Physics, Japan.² The theoretical resolution was less than 3×10^{-4} nm, but we believe that the actual value was about 7×10^{-4} nm. Our integrated cross section values will be compared to those of ref. 1.

This work is supported by NASA grant NSG-7304 to Harvard University and by JSPS Fellowship program.

¹C. Letzelter, M. Eidelsberg, F. Rostas, J. Breton and B. Thieblemont, *Chem. Phys.* **114**, 273-288 (1987).

²K. Ito, T. Namioka, Y. Morioka, T. Sasaki, H. Noda, K. Goto, T. Katayama, and M. Koike, *Appl. Opt.* **25**, 837-847 (1986).

Address of Yoshino, Smith, Zucker, and Parkinson: Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138

Address of Stark: Dept. Physics, Wellesley College, Wellesley, MA 02181

Address of Ito: Photon Factory, National Laboratory for High Energy Physics, Tsukuba 305, Japan.

RC3 (8:54)

FOURIER TRANSFORM SPECTROSCOPY IN THE VACUUM ULTRAVIOLET REGION, THE FOURTH POSITIVE BANDS OF CO

A.P. THORNE, K. YOSHINO and W.H. PARKINSON

Fourier Transform Spectroscopy is, in the IR, visible and near UV regions, a well-established technique for observing high resolution absorption and emission spectra with quantitative intensities. To our knowledge, only one FTS exists at the Imperial College, London for operation in the VUV region. The design of that high-resolution VUV instrument has been discussed by Thorne et al.¹, and its performance has been demonstrated by atomic line emission spectra showing a resolution of 0.03 cm^{-1} near 42650 cm^{-1} . We present the results of the Fourth Positive bands of CO in the resolution of 0.08 cm^{-1} in the wavelength region 177-215 nm. The observed linewidths are around 0.15 cm^{-1} which is slightly larger than the Doppler widths 0.12 cm^{-1} at 300 K.

This work is supported by NSF grant ATM-87-17875 to Harvard College Observatory.

¹A.P. Thorne, C.J. Harris, I. Wynne-Jones, R.C.M. Learner and G. Cox, *J. Phys. E: Sci. Instrum.* **20**, 54-60, (1987).

Address of Thorne: Imperial College of Science and Technology, London SW72BZ, England

Address of Yoshino and Parkinson: Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138

RC4 (9:06)

ULTRAVIOLET SPECTROSCOPY OF CARBON MONOXIDE

J. E. MAYHUGH AND K. C. JANDA

One photon resonant and two photon resonant multiphoton ionization techniques are used to study carbon monoxide, carbon monoxide dimers, and complexes of carbon monoxide with rare gases.

Address of Mayhugh and Janda: Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, U.S.

RC5 (9:23)

FOURIER TRANSFORM SPECTROSCOPY OF BC, BD, CuD AND ZnD

W. T. M. L. FERNANDO, L. C. O'BRIEN AND P. F. BERNATH

Gas phase BC was made in a composite wall Cu/B₂C hollow cathode discharge operated with a flow of Ar gas. The emission from the discharge was observed with the Fourier transform spectrometer associated with the National Solar Observatory at Kitt Peak. The observed lines near 17900 cm⁻¹ are assigned to the 0-0 band of the B⁴Σ⁻-X⁴Σ⁻ transition of BC.

The BD and CuD molecules were produced by passing D₂ gas through the Cu/B₂C hollow cathode. The A¹Π-X¹Σ⁺ transition of BD and the A¹Σ⁺-X¹Σ⁺ transition of CuD were analysed. The rotational structure of the two main isotopes of Cu, ⁶³Cu and ⁶⁵Cu, was resolved.

ZnD was produced in a Zn/Ni/C hollow cathode operated with D₂ and argon gases. All the branches of the A²Π-X²Σ⁺ transition were observed in our spectrum. The rotational structure of the three main isotopes of Zn (⁶⁴Zn, ⁶⁶Zn and ⁶⁸Zn) was resolved in most of the branches.

Address of Fernando, O'Brien and Bernath: Department of Chemistry, University of Arizona, Tucson AZ 85721.

RC6 (9:40)DETERMINATION OF MOLECULAR CONSTANTS OF THE $\tilde{X}^4\Sigma_g^-(v=4-7)$ LEVELS OF C₂⁺ USING STIMULATED EMISSION PUMPING SPECTROSCOPY

F. G. CELII and J. P. MAIER

Using stimulated emission pumping (SEP) spectroscopy, vibrationally excited levels of the $\tilde{X}^4\Sigma_g^-$ ground electronic state of C₂⁺ were characterized. Transitions were detected by decreased total fluorescence from laser-excited $\tilde{B}^4\Sigma_u^-$ levels. To obtain the 2-photon spectra, a modulation scheme which discriminated against one-photon fluorescence signals was successfully employed. Molecular constants determined for the C₂⁺ $\tilde{X}^4\Sigma_g^-$ (v=4-7) levels are presented.

Address of Celii: Code 6174, Naval Research Lab, 4555 Overlook Ave., Washington, D C. 20375-5000.

Address of Maier: Institut für Physikalische Chemie, Universität Basel, CH-4056 Basel, Switzerland

Intermission

RC7 (10:15)

SPECTRA, RADIATIVE LIFETIMES, AND BAND OSCILLATOR STRENGTHS OF THE $A^1\Pi-X^1\Sigma^+$ TRANSITION OF BH

C.H. Douglass, H.H. Nelson and Jane K. Rice

Several vibrational bands of the $A^1\Pi-X^1\Sigma^+$ transition of the BH radical produced by 193 nm photolysis of BH_3CO have been examined. Diagonal ($\Delta v=0$) and off-diagonal ($\Delta v=\pm 1$) bands have been observed using LIF techniques. The new spectroscopic features reported here are excitation spectra of the 0-1 and 1-2 bands.

Relative strengths of the various bands were assessed by collecting dispersed emission spectra. Ratios of Einstein emission coefficients, vibrational transition probabilities, and band absorption oscillator strengths were calculated comparing the 0-0 and 0-1 bands and comparing the 1-0, 1-1, and 1-2 bands. The ratios indicate that transitions occur mainly in the diagonal elements; the off-diagonal elements are two orders of magnitude less intense.

Radiative lifetimes were measured by observing the fluorescence decay over 5-6 lifetimes. The radiative lifetimes of the $v=0,1$, and 2 levels have been measured to be 127 ± 10 ns, 146 ± 12 ns, and 172 ± 14 ns respectively. The Einstein emission coefficient ratios and the lifetime values have been combined to yield Einstein emission coefficients and band oscillator strengths for five bands. The Einstein emission coefficients and lifetime values are compared to previous experimental results and to theoretical calculations of Luh and Stwalley¹ and to the second order polarization propagator results of Diercksen et al.². In some cases, large differences are observed. Our results allow us to assess the accuracy of the transition moments and potential energy curves presently in the literature.

¹ W.T. Luh and W.C. Stwalley, *J. Mol. Spectrosc.* **102**, 212 (1983).

² G.H.L. Diercksen, N.E. Gruner, J.R. Sabin, and J. Oddershede, *Chem. Phys.* **115**, 15 (1987).

Address of Douglass: Applied Research Corporation, 8201 Corporate Drive, Landover, MD 20785.

Address of Nelson and Rice: Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5000

RC8 (10:32)

PERMANENT ELECTRIC DIPOLE MOMENT OF CH

David F. Nachman, Timothy C. Steimle, David A. Fletcher and John M. Brown:

Spectra in the $A^2\Delta-X^2\Pi$ ($\lambda=431$ nm) band system of the CH radical were recorded by the intermodulated fluorescence technique. The Stark effect on the $Q_{2e}(2)$ and $R_1(1)$ branch features was measured, and a determination of the value of the permanent electric dipole moment of the ground state was made. In this determination, a $(2F+1) \times (2F+1)$, $\Delta F = +1$ Hamiltonian matrix, including Stark effect, was set up in a Hund's case (a_2) basis set and diagonalized to produce eigenvectors and eigenvalues. The calculated spectra were optimized to the experimental observations in a least-squares fashion to give the predicted value of $\mu(X^2\Pi)$. The determined value will be given, and compared with the previous determination¹.

¹D.H. Phelps and F.W. Dalby, *Phys. Rev. Lett.* **16**, 3 (1966).

Address of Nachman and Steimle: Department of Chemistry, Arizona State University, Tempe, AZ 85287-1604.

Address of Fletcher and Brown: Physical Chemistry Laboratory, South Parks Road, Oxford University, Oxford OX13QZ, England, UK.

RC9 (10:44)**MICROWAVE OPTICAL DOUBLE RESONANCE STUDIES OF NiH**T.C. Steimle, J. Shirley, D. Fletcher, and J.M. Brown

Magnetic hyperfine constants have long been used as probes of chemical bonding, since they are averages of various functions of the valence electrons near the spinning nucleus. Traditionally, for gas-phase molecules these interactions have been determined from the analysis of splittings in the pure rotational spectra, but the reactive nature of transition metal hydrides (TMH) has precluded them from this experimental approach. Here we report on the first recording, and subsequent analysis, of the microwave spectra of a TMH. Numerous transitions between the Λ -doublet levels in the $X^2\Delta_{3/2}$ state of NiH have been measured using the microwave optical double resonance technique. The data was reduced using an effective hamiltonian approach and magnetic hyperfine parameters were determined. The fine structure parameters were held fixed to those obtained from the recent LMR¹ values.

¹S.P. Beaton, K.M. Evenson, T. Nelis and J.M. Brown, J. Chem. Phys. 89,4446 (1988).

Address of Steimle and Shirley: Department of Chemistry, Arizona State University, Tempe AZ., 85287-1604

Address of Fletcher and Brown: Physical Chemistry Laboratory, South Parks Road, Oxford University, Oxford, England, OX1-3QZ

RC10 (10:56)**The Application of MRS and SOODRZ to the Electronic Spectra of Transition Metal Hydrides**M. C. McCarthy, M. Li, and R. W. Field

Magnetic Rotation Spectroscopy (MRS) and Sideband Optical-Optical Double Resonance Zeeman Spectroscopy (SOODRZ) are diagnostically powerful techniques capable of selectively simplifying spectra, pre-sorting sub-bands and branches, and yielding definitive information about the electronic character and new strategies for absolute rotational assignments of molecular spectra. Consequently, the use of MRS and SOODRZ in the analysis of congested and complicated, non-Hund's-limiting-case diatomic spectra is appealing. We will present progress made in applying these sensitive, absorption-based techniques to the study of the electronic spectra of transition metal hydrides such as NiH, CoH, and PtH, which are currently being analyzed.

Address of McCarthy, Li, and Field: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

RC11 (11:13)**High Resolution Spectroscopy of CoH and CoD**Thomas D. Varberg, Ernest J. Hill and Robert W. Field

Five new bands in the spectrum of gas phase CoH, with band heads near 5650, 5710, 6093, 6446 and 6586 Å, as well as three bands in CoD, have been observed via laser excitation spectroscopy with a cw dye laser. Two of the CoH bands, at 5710 and 6093 Å, have been rotationally analyzed and identified as $\Omega = 4 \leftarrow \Omega = 4$, where the lower state for both transitions is the previously characterized $X \Omega=4$ ($v = 0$) ground state. The two upper states, with approximate molecular constants $T_v = 18360 \text{ cm}^{-1}$, $B_v = 4.7 \text{ cm}^{-1}$ and $T_v = 17260 \text{ cm}^{-1}$, $B_v = 4.9 \text{ cm}^{-1}$, display strong perturbations characteristic of open-shell, transition-metal containing diatomics. A preliminary analysis of these perturbations will be presented.

Address of Varberg, Hill and Field: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

RC12 (11:30)

Rydberg States of CaF Observed by Optical-Optical Double Resonance

J. Murphy, J.M. Berg and R.W. Field

Rydberg states of alkaline earth monohalides are interesting because of the polar closed shell ion core. We have observed Rydberg states of CaF where $n > 5$ using pulsed-pulsed optical-optical double resonance via the intermediate A $^2\Pi_{3/2}$ state. O.O.D.R. transitions are detected by observing a resonant decrease in fluorescence of the intermediate state as the probe laser is scanned.

We will report on the analysis of CaF Rydberg states including an estimate of the ionization potential and quantum defects. An analysis of a perturbation between an n,f and n,d complex could yield a direct measure of the CaF⁺, X $^1\Sigma^+$ dipole moment.

Address of Murphy, Berg and Field: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

RC13 (11:47)

SPIN-ORBIT CI POTENTIAL CURVES FOR CuF

Nora M. Wallace and Russell M. Pitzer

Ab initio potential energy curves for the ground and low-lying excited states of CuF have been calculated using relativistic effective core potentials and including spin-orbit interactions. All potential curves have maxima which have been characterized by height and width. These barriers could allow metastable vibrational states and are caused by the interaction of initially lower-energy bonding ionic potential curves with repulsive, covalent potential curves. Avoided crossings are tabulated by type of interaction with estimates of the energy differences at closest approach. Of the states corresponding to the observed spectra, the Δ states show the greatest effects of spin-orbit interactions. All of the excited states can be characterized by simple descriptions both in the R_e region and at large R. Results for CuCl may also be presented.

Address: Department of Chemistry, The Ohio State University, Columbus, OH 43210

RD1 (8:30)**ROTATIONALLY RESOLVED ONE- AND TWO-PHOTON SPECTROSCOPY OF BENZENE: INVESTIGATION OF INTRAMOLECULAR COUPLINGS**

E. Riedle, Th. Weber, H. J. Neusser

In the last few years we have been able to show, that rotationally resolved electronic spectra of the prototype organic molecule benzene can be obtained by Doppler-free two-photon spectroscopy /1/. The spectra were taken at room temperature and even lines with $J = 100$ have been identified in the meantime. As a result, the rotational constants could be determined with extreme precision and various rotational perturbations were identified. We were able to measure the decay time /2/, linewidth /3/ and emission spectrum of single "quasi-eigenstates". In particular, a strong rotational dependence of the decay behaviour in the regime of high vibrational excess energy ("Channel Three") was found /4/.

The results of the two-photon experiments could, however, not be directly compared to most previous low resolution investigations on benzene, as these were performed by one-photon excitation and therefore led to different vibronic states in S_1 . To obtain sub-Doppler rotationally resolved one-photon spectra, we combined our extremely narrow band pulsed laser ($\Delta\nu = 70$ MHz after frequency doubling) with a collimated molecular beam. This allowed us to measure the resolved spectra of all four e_{2g} fundamentals, some of their progressions and particularly some bands in the "Channel Three" regime. The analysis of the fundamental bands renders for the first time a complete set of Coriolis coupling constants. The couplings found at intermediate excess energy can be compared to the ones found in the two-photon spectrum in the same energy range. The strong rotational dependence of the decay at high excess energy, as seen by the appearance of very few sharp lines in the two-photon spectrum /4/, is also seen in the one-photon spectrum of vibrations at the same excess energy. Hence it is concluded, that the relaxation behaviour of S_1 benzene found from two-photon spectroscopy is not a sole consequence of the symmetry of the observed states, but rather depends mainly on the excess energy.

- /1/ E. Riedle, H.J. Neusser, E. W. Schlag, J.Chem.Phys. **75**, 4231 (1981)
 /2/ U. Schubert, E. Riedle, H.J. Neusser, J.Chem.Phys. **84**, 5326 (1986)
 /3/ E. Riedle, H.J. Neusser, J.Chem.Phys. **80**, 4686 (1984)
 /4/ E. Riedle, H.J. Neusser, E.W. Schlag, J.Phys.Chem. **86**, 4847 (1982)

Address: Institut für Physikalische und Theoretische Chemie, TU München, Lichtenbergstraße 4, D-8046 Garching, West Germany

RD2 (8:47)**ROTATIONAL BANDSHAPES OF JET COOLED BENZYL RADICAL**

P. G. CARRICK AND J. I. SELCO

High resolution rotational emission spectra of the $1^2A_2 \rightarrow 1^2B_2$ electronic, $6b_1^0$ and $6a_1^0$ vibronic transitions of the benzyl radical were observed with the Fourier Transform Spectrometer at Kitt Peak National Observatory. The rotationally cooled, electronically excited benzyl radicals were produced from a mixture of toluene and helium passed through a corona excited supersonic expansion equipped with a slot nozzle.

The resolved $6b_1^0$ bands were modeled using the asymmetric top modeling program developed by Birss et al.¹ The ground state rotational constants obtained from a fit of the resolved features of this band compare favorably well with those obtained from room temperature band contours measured by Cossart-Magos and Leach.² However the excited state constants obtained in this study are significantly different from the room temperature values. A rotational temperature of 20K was deduced by matching the intensities of the resolved branches with the calculated intensities.

The $6a_1^0$ bands were also modeled with this same program and resulted in essentially the same rotational constants. However, the constants derived from this band are less certain due to reduced signal intensities.

¹ F. W. Birss, J. M. Brown, A. R. H. Cole, A. Lofthus, S. L. N. G. Krishnamachari, G. A. Osborne, J. Paldus, D. A. Ramsay, and L. Watmann, Can. J. Phys., **48**, 1230 (1970).

² C. Cossart-Magos and S. Leach, J. Chem. Phys., **56**, 1534 (1972).

Address of Carrick: Air Force Astronautics Laboratory/LSX, Edwards Air Force Base, CA 93523

Address of Selco: Department of Chemistry, University of Redlands, Box 3080, Redlands, CA 92373

RD3 (8:59)

LIF STUDY OF *o,m,p* METHYL BENZYL RADICALS

TAI-YUAN DAVID LIN, CHRISTOPHER C. CARTER, SANG K. LEE, AND TERRY A. MILLER

The methyl derivatives of the benzyl radical are prototypes of substituted aromatic radicals. They also serve as the radical analogs of the corresponding xylenes. Recently several papers have reported on the barriers to methyl rotation in both the ground and first excited state of the xylene molecules. Generally speaking, these papers have concluded that these barriers are dominantly electronic in origin.

Using LIF excitation spectra and laser excited wavelength resolved emission, we have observed transitions among hindered rotor levels of methyl substituted benzyl radicals. We will report upon the methyl barrier heights and positions, based upon analysis of our experimental results. Comparisons to the xylene barriers will be made.

Address of Lin, Carter, Lee, and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

RD4 (9:16)

HIGH RESOLUTION LIF SPECTROSCOPY OF JET-COOLED PHENYL NITRENE

DAVID W. CULLIN, LIAN YU, JAMES M. WILLIAMSON, AND TERRY A. MILLER

A laser induced fluorescence spectrum has been observed from the products of the ArF photolysis of *o*-chloroaniline in a supersonic free jet expansion. The spectrum, with origin at 27143 cm^{-1} , is believed to arise from the T_1-T_0 transition of the phenyl nitrene radical. Although phenyl nitrene is of interest on its own, it should have a similar electronic structure to that of the better known benzyl radical. This talk will concentrate on the verification of the carrier of the spectrum observed as well as a rotational analysis of the spectrum.

Address of Cullin, Yu, Williamson, and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

RD5 (9:33)

ROTATIONAL STRUCTURE IN THE SINGLET-TRIPLET EXCITATION SPECTRA OF POLYATOMIC MOLECULES.¹

L. H. Spangler, K. W. Holtzclaw, and D. W. Pratt

We have observed rotational structure in the beam- and jet-cooled T_1-S_0 phosphorescence excitation spectra of several molecules, including glyoxal, pyrazine and benzaldehyde. Each observed resolved or partially-resolved contour exhibits a significantly different shape, a shape that is also different from the corresponding bands in the S_1-S_0 spectrum. We will discuss the origin of these differences in this talk. Our approach is that of Hougen² which emphasizes the strong connection between the radiative properties of the triplet state in the gas and condensed phase, in a natural way.

¹Work supported by NSF.

²J. T. Hougen, Can. J. Phys. 42, 433 (1964).

Address of Spangler: Department of Chemistry, Montana State University, Bozeman, MT 59717.
 Address of Holtzclaw: Physical Sciences, Inc., Research Park, Andover, MA 01810.
 Address of Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

RD6 (9:50)

HIGH RESOLUTION FLUORESCENCE EXCITATION SPECTRA OF THE 1- AND 2-HYDROXYNAPHTHALENES.

DISTINGUISHING THE CIS AND TRANS ROTAMERS.¹

J. R. Johnson, D. F. Plusquellic, J. L. Tomer, and D. W. Pratt

It has been previously reported that the S_1 - S_0 fluorescence excitation and absorption spectra of the 1- and 2-naphthols can be interpreted by assuming the existence of cis and trans rotamers, each with their own O_0^0 bands and vibrational progressions.^{2,3} However, the evidence for the existence of these rotamers, and the assignment of a particular origin and progression to a specific rotamer, is indirect and inconclusive. We have examined several bands of 1- and 2-naphthol (OH and OD) at high resolution using LIF and a molecular beam. With linewidths on the order of 5 MHz, each band consists of 2000+ resolved rotational lines, and changes in the rotational constants due to the different geometries of the two rotamers can be detected. We have also performed molecular orbital calculations on the S_0 and S_1 states at the single configuration Hartree-Fock level. Taken together, the results give an unambiguous proof of the existence of the different rotamers, an assignment of their spectra, and the key geometry changes that occur in the naphthols upon electronic excitation.

¹Work supported by NSF.

²A. Oikawa, H. Abe, N. Mikami, M. Ito, J. Phys. Chem. **88**, 5180 (1984).

³J. M. Hollas, M. Z. B. Hussein, J. Mol. Spectrosc. **127**, 497 (1988).

Address of Johnson, Plusquellic, Tomer, and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

Intermission

RD7 (10:25)

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 - S_0 fluorescence excitation spectra of the 1- and 2-aminonaphthalenes at a resolution of ~ 15 MHz in the UV. We have determined the rotational constants and inertial defects of both S_0 and S_1 and the orientations of the transition moments for several vibronic bands in the spectrum. We find the O_0^0 band of 1-aminonaphthalene (1AN) to be primarily \underline{b} -axis polarized, contrary to earlier observations 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.

¹Work supported by NSF.

²J. M. Hollas, S. N. Thakur, Mol. Phys. **27**, 1001 (1974).

Address of Plusquellic and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

RD8 (10:42)

TORSIONAL BARRIERS IN LARGE MOLECULES. A HIGH RESOLUTION STUDY OF THE 1- AND 2-METHYLNAPHTHALENES.¹

X.-Q. Tan, W. A. Majewski, D. F. Plusquellic, and D. W. Pratt

The hindered internal rotation of methyl groups continues to be a subject of intense interest. We report here a study of the barriers to such motion in the 1- and 2-methylnaphthalenes, and their dependence on both the vibrational and electronic state of the molecule to which the rotor is attached. New methods for determining absolute barrier heights, based on an analysis of the rotationally resolved S_1-S_0 spectra, will be described. The results of these analyses show, unambiguously, that the magnitudes of the torsional barriers are extraordinarily sensitive to electronic excitation, to the position of the methyl group substitution, and to the presence or absence of vibrational excitation in the naphthalene framework. A rationalization of these results using simple MO theory will be presented.

¹Work supported by NSF.

Address of Tan, Plusquellic, and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

Address of Majewski: Division of Physics, NRC, Canada, Ottawa, Ontario K1A 0R6, CANADA.

RD9 (10:59)

ALL-TRANS-1,4-DIPHENYL-1,3-BUTADIENE. A ROTATIONALLY RESOLVED FLUORESCENCE EXCITATION SPECTRUM OF THE ONE-PHOTON S_1-S_0 OPTICAL TRANSITION.¹

J. F. Pfanstiel, B. B. Champagne, W. A. Majewski, D. F. Plusquellic, and D. W. Pratt

We have obtained rotationally resolved spectra of several bands in the S_1-S_0 one-photon transition of all-trans-1,4-diphenyl-1,3-butadiene² using the new high resolution spectrometer. Band 1 is an a-type transition and can be fit to an asymmetric top rigid rotor Hamiltonian. The changes in rotational constants observed on electronic excitation are consistent with the bond order reversal expected for a HOMO-LUMO excitation in which the orbital exhibits both polyene and phenyl character. The bands to the blue of band 1 exhibit a dependence of the rotational constants upon vibrational mode and, of greater interest, show a marked departure from rigid rotor behavior. K-dependent perturbations are observed as early as band 3; their magnitude appears to increase with K and with vibrational excitation. The perturbation appears to shift entire K subbands which may be individually fit to a rigid rotor Hamiltonian and which yield a dependence of the rotational constants and inertial defects on K. The possibility that these changes are associated with 'motion' along a reaction coordinate associated with isomerization of the excited molecule will be discussed.

¹Work supported by NSF.

²L. A. Heimbrook, B. E. Kohler, and T. A. Spiglanin, Proc. Natl. Acad. Sci. USA 80, 4580 (1983).

Address of Pfanstiel, Champagne, Plusquellic, and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

Address of Majewski: Division of Physics, NRC, Canada, Ottawa, Ontario K1A 0R6, CANADA.

RD10 (11:16)

ROTATIONALLY RESOLVED LIF SPECTRUM OF $\bar{A}^2A_1 \rightarrow \bar{X}^2E$ TRANSITION OF CH_3S AND THE \bar{A}^2A_1 STATE SPIN-ROTATION CONSTANT OF CH_3O

XIANMING LIU, YEN-CHU HSU, STEPHEN C. FOSTER, LIAN YU, JAMES M. WILLIAMSON, AND TERRY A. MILLER

The rotationally resolved laser-induced fluorescence spectrum $\bar{A}^2A_1 \rightarrow \bar{X}^2E$ of the methylthio radical has been obtained in a free-jet supersonic expansion. A detailed rotational analysis of the electronic transition has been carried out. A joint least square fitting of the present electronic transitions and previously observed microwave transitions¹ yields ground and excited state molecular constants. The ground state constants are considerably revised from those previously reported, while the excited state values have been accurately determined for the first time in this experiment.

Particularly interesting are the very large values of the ground state spin-rotation constants in CH_3S and CH_3O . To develop more understanding of the spin-rotation interaction in these radicals, a high resolution LIF spectrum of $\bar{A}^2A_1 \rightarrow \bar{X}^2E$ transition of CH_3O has been taken and the upper state spin-rotation constants have been determined.

¹Y. Endo, S. Saito, and E. Hirota, *J. Chem. Phys.*, 85, 1770 (1986).

Address of Liu, Yu, Williamson, and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

Address of Hsu: Institute of Atomic & Molecular Science, Academia Sinica, P.O. Box 23-166, Taipei, Taiwan, R.O.C.

Address of Foster: Department of Chemistry, Florida State University, Tallahassee, Florida 32306.

RD11 (11:33)

HIGH RESOLUTION ELECTRONIC SPECTROSCOPY OF THE ETHOXY FREE RADICAL

CRISTINO P. DAMO, XIANMING LIU, LIAN YU, STEPHEN C. FOSTER, JAMES M. WILLIAMSON, AND TERRY A. MILLER

Among the chemical intermediates in combustion and atmospheric reactions are the family of alkoxy free radicals. The methoxy radical has been rather well characterized. The next member of the family is the ethoxy radical. Previously, we reported spectra obtained with a YAG-pumped dye laser (fundamental bandwidth ~10 GHz) which partially resolved the rotational structure of the $\bar{A}^2A' \leftarrow \bar{X}^2A''$ 9_0^1 electronic band into about 15 distinct transitions. Recently, we have obtained much higher resolution spectra (>100 rotational lines) with a pulse-amplified argon ion-pumped ring dye laser (fundamental bandwidth ~0.1 GHz). Details of the rotational analysis will be presented.

Address of Damo, Liu, Yu, Williamson, and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

Address of Foster: Department of Chemistry, Florida State University, Tallahassee, Florida 32306-3006.

RD12 (11:50) See page 175 for its Abstract

RE1 (1:30)PRESSURE BROADENING IN THE ROTATIONAL SPECTRUM OF O₂

J. W. C. JOHNS and D. J. KENDALL

Pressure broadening parameters have been measured in the $\Delta N=2$, magnetic dipole, spectrum of O₂ in the region from 10 to 100 cm⁻¹. The measurements have been made at low temperatures as well as at room temperature. Results will be presented for self broadening and nitrogen broadening.

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

Address of Kendall: Space Division, National Research Council of Canada, Ottawa, Ontario, CANADA K1A 0R6.

RE2 (1:47)THE FAR INFRARED SPECTRUM OF C₃O₂

J.W.C. JOHNS AND J. VANDER AUWERA

The spectrum of carbon suboxide has been recorded at a temperature of -60C and at a resolution of 0.003 cm⁻¹ in the region from 15 to 100 cm⁻¹ using a Bomem DA3.002 spectrophotometer. The rotational analysis of the progression of hot bands involving the low frequency bending mode ν_7 ($\nu_7 = 18.3 \text{ cm}^{-1}$)¹ appearing in this region has been undertaken. Preliminary results will be presented.

¹ E.N. Karyakin, A.F. Krupnov and S.M. Shapin, *J. Mol. Spectrosc.* **94**, 283 (1982).

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

RE3 (2:04)

THE VIBRATION-ROTATION SPECTRUM OF THE BISMUTH HYDRIDE AND BISMUTH DEUTERIDE MOLECULES

A.M.R.P. BOPEGEDERA, C.R. BRAZIER AND P.F. BERNATH

The bismuth hydride (BiH) and bismuth deuteride (BiD) molecules were synthesized in a heat pipe oven by the high temperature reaction between the bismuth metal vapor and hydrogen (deuterium).

The vibration-rotation spectra of the 1-0 fundamental band and several hot bands with $\Delta v = 1$ were recorded using a diode laser spectrometer. The analysis of these spectra to obtain the ro-vibrational constants of the BiH and BiD molecules will be presented and discussed.

Address of Bopegedera and Bernath: Department of Chemistry, University of Arizona, Tucson, AZ 85721.

Address of Brazier: Advanced Research in Energy Storage, Air Force Astronautics Lab./LSX, Edwards Air Force Base CA 93523.

RE4 (2:16)

INTERNUCLEAR POTENTIAL AND EQUILIBRIUM STRUCTURE OF N_2O

J.-L. Teffo and A. Chédin

The internuclear potential up to sextic terms and the equilibrium structure of nitrous oxide molecule are reinvestigated using the algebraized contact transformation method previously applied to carbon dioxide. Infrared spectroscopic data for a large number of vibrational levels belonging to six isotopic species of N_2O are included in the refinement. The following R.M.S between calculated and experimental molecular constants are obtained (cm^{-1})

CONSTANTS	NUMBER	R.M.S
G_v	267	0.047
B_v	319	2.16×10^{-5}
D_v	333	5.64×10^{-9}

The equilibrium bond lengths are found to be (A) $r_{NN} = 1.127292(37)$ $r_{NO} = 1.185089(37)$ from which accurate values of equilibrium and ground state rotational constants are calculated for the 12 isotopic species of N_2O .

Address of Teffo : 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 Chédin : Laboratoire de Météorologie Dynamique, CNRS, Ecole Polytechnique, Route Départementale 36, 91128 Palaiseau Cedex, France

RE5 (2:28)

THE ν_6 BAND OF H_2O_2 - $(n,\tau)=(0,1)(0,3)$, $(1,1)(1,3)$ AND $(2,1)$ TORSIONAL STATES.

A. Perrin, J.-M. Flaud, C. Camy-Peyret and A. Goldman

Using high resolution (0.003 cm^{-1}) Fourier transform spectra recorded between 1190 and 1330 cm^{-1} the ν_6 A-type band of H_2O_2 has been revisited. Starting from the work performed by Hillman et al. [1] on the $(n,\tau)=(0,1)$ and $(0,3)$ torsional states of the vibrational $\nu_6=1$ state and using the ground state combination differences from Masset et al. [2] we have obtained 1350 rotational levels of the $(n,\tau)=(0,1), (0,3), (1,1), (1,3)$ and $(2,1)$ torsional states for $\nu_6=1$ with K_a values up to 9. Strong torsion-rotation interactions were observed within the $\nu_6=1$ state involving resonances between the $(0,1) \leftrightarrow (1,1)$, $(1,1) \leftrightarrow (2,1)$, $(0,3) \leftrightarrow (1,3)$ torsional states. Finally using the observed torsional band centers, the torsional potential function for the $\nu_6=1$ state has been derived and the cis- and trans-barriers heights determined.

[1] J.J. Hillman, D.E. Jennings, W.B. Olson and A. Goldman, J. Mol. Spectrosc. **117**, 46 (1986)

[2] F. Masset, L. Lechuga-Fossat, J.-M. Flaud, C. Camy-Peyret, J.W.C. Johns, B. Carli, M. Carlotti, L. Fusina and A. Trombetti, J. Phys. France **49**, 1901 (1988)

Address of Perrin, 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

Address of Goldman : Department of Physics, University of Denver, CO 80208, USA

RE6 (2:45)

THE FAR INFRARED SPECTRUM OF H_2O_2 . FIRST OBSERVATION OF THE STAGGERING OF THE LEVELS

J.-M. Flaud, C. Camy-Peyret, J.W.C. Johns and B. Carli

High resolution spectra of H_2O_2 , recorded by means of Fourier transform spectroscopy between 30 and 460 cm^{-1} have been analysed leading to the determination of the rotational levels of the torsional states (n, τ) for $n=0,1,2,3$. To reproduce these energy levels, Watson type Hamiltonians have been used and it has been possible to observe the staggering of the levels due to the cis-barrier for $n=2$ and 3. The torsional band centers have then been fitted using a torsional Hamiltonian of the form $\{B_{YY}, J_Y^2\} + V(\gamma)$ with the potential energy function $V(\gamma)$ written as $V(\gamma) = V_1 \cos 2\gamma + V_2 \cos 4\gamma + V_3 \cos 6\gamma + V_4 \cos 8\gamma$ where the torsional coordinate 2γ is the dihedral angle defining the relative position of the two O-H bonds. The potential function constants obtained are

$$V_1 = 1036.97 \pm 23.1 \text{ cm}^{-1}, \quad V_2 = 657.53 \pm 5.2 \text{ cm}^{-1},$$

$$V_3 = 50.89 \pm 3.3 \text{ cm}^{-1}, \quad V_4 = 2.524 \pm 0.83 \text{ cm}^{-1}$$

corresponding to the barrier heights

$$V_{\text{trans}} = 387.07 \pm 0.20 \text{ cm}^{-1} \quad V_{\text{cis}} = 2563 \pm 70 \text{ cm}^{-1}$$

and to potential energy minima located at $2\gamma = 111.9^\circ \pm 0.4'$ from the cis-configuration. It is also shown that the rotational constants derived through the fit of the experimental rotational levels cannot be reproduced using a model which does not take into account the vibrational corrections.

Address of 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

Address of Johns : Herzberg Institute of Astrophysics, NRC, Ottawa, Ontario Canada K1A 0R6

Address of Carli : IROE - CNR, Via Panciatichi 64, 50127 Firenze, Italy

Intermission

RE7 (3:20)

ASSIGNMENT OF THE ν_1 AND $2\nu_2$ BANDS OF COF_2 AT 5.2 μM

L. R. BROWN AND E. A. COHEN

Line positions of the ν_1 and $2\nu_2$ bands of COF_2 have been obtained from absorption spectra recorded at 0.0028 cm^{-1} resolution using the 1 meter Fourier transform spectrometer located at Kitt Peak National Observatory/National Solar Observatory. Lines have been assigned up to $J' = 68$ and $J' = 52$ for ν_1 and $2\nu_2$ respectively. The spectra have been fitted using a two band Hamiltonian which treats the Fermi resonance between ν_1 and $2\nu_2$ exactly and includes centrifugal distortion terms through a complete set of sextic constants for the ground state and the diagonal sextic constants for the excited states. The ground state parameters have been redetermined using additional millimeter and submillimeter transitions measured in our laboratory and fixed for the fitting of the infrared spectra. The molecular parameters and evidence of additional perturbations in the infrared spectra will be discussed.

Address of the authors: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

RE8 (3:37)**HOT BANDS IN SYMMETRIC TOP SPECTRA: PROPYNE AS A TEST CASE****G. GRANER**

In the recent years, we have studied at high resolution the spectrum of propyne (or methyl-acetylene) $\text{CH}_3\text{-C}\equiv\text{CH}$ in two spectral regions: the region 9-11 μm which is dominated by the two fundamental bands ν_5 (A_1) and ν_8 (E) and the region of the lowest fundamental band ν_{10} (E) at 30 μm .

Since the $\nu_{10} = 1$ level is so low (Boltzmann factor equal to 0.21), hot bands originating from this level are often seen and, in several cases, their rotational structure can be assigned. Moreover, the fact that it is a E-type level, with the well-known Coriolis splitting and the ℓ -type doubling, produces unusual effects in these hot bands, especially for the subbands with $k''\ell''=1$.

Details will be given on the following hot bands, which belong to five different types: $(\nu_8 + \nu_{10})^2 - \nu_{10}$, $(\nu_8 + \nu_{10})^0 - \nu_{10}$, $(\nu_5 + \nu_{10})^1 - \nu_{10}$, $(2\nu_{10})^2 - \nu_{10}$ and $(2\nu_{10})^0 - \nu_{10}$.

These studies have led to a precise determination of the A_0 rotational constant of propyne.

Address: Laboratoire d'Infrarouge, Bât. 350, Université de Paris-Sud, 91405 ORSAY Cédex, France.

RE9 (3:54)**CYANO-ACETYLENE: SPECTROSCOPY FOR PLANETOLOGICAL PURPOSES****E. ARIE, Ph. ARCAS, DANG NHU M., G. GRANER, H. BÜRGER AND G. PAWELKE**

Cyano-acetylene $\text{HC}\equiv\text{C}-\text{C}\equiv\text{N}$ has been detected in TITAN (a satellite of Saturn) by the IRIS instrument aboard VOYAGER. Two bands have been clearly observed, namely ν_5 at 663 cm^{-1} and ν_6 at 498 cm^{-1} . In order to extract all available information on the spectra of Titan obtained by IRIS and the future CASSINI mission, we are analysing high resolution laboratory spectra of these two bands.

These spectra, recorded at Giessen (FRG) with a 0.002 cm^{-1} resolution, at two different temperatures, show not only the fundamental bands, but also many hot bands since the lowest energy is at 222 cm^{-1} . About 16 different hot bands have been completely assigned at present. Constants obtained for the upper and lower states of these transitions will be compared to each other and to the constants obtained by other authors by microwave spectroscopy. The analysis of $\nu_6 + \nu_7$ will also be reported.

Due to experimental problems, the measurement of intensities of individual lines is not yet very satisfactory. Progress will be reported.

Address of Arié, Arcas, Dang Nhu and Graner: Laboratoire d'Infrarouge, Bât. 350, Université de Paris-Sud, 91405 ORSAY Cédex, France.

Address of Bürger and Pawelke: Anorganische Chemie, FB 9, Universität, 5600 WUPPERTAL 1, West Germany.

RE10 (4:11)**INFRARED SPECTRA OF JET-COOLED 1-BUTYNE AND ETHANOL IN THE METHYL STRETCH REGION****G. A. BETHARDY, J. GO, S. HAMMAD, D. S. PERRY**

Rotationally resolved infrared spectra of jet-cooled 1-butyne and of jet-cooled ethanol were recorded in the methyl C-H stretch region (near 2990 cm^{-1}) by direct absorption. A two-spherical-mirror multiple pass cell was used to enhance absorption of the Burleigh FCL 20 laser beam. To reduce thermal congestion, spectra were recorded at rotational temperatures as low as 0.75 K. For 1-butyne, a c-type band and an a,b-type hybrid band are assigned. For ethanol preliminary spectra show a c-type band.

Address: Department of Chemistry, University of Akron, Akron, Ohio, 44325.

RE11 (4:23)

SLICED-JET SPECTROSCOPY - A NEW TECHNIQUE FOR SUB-DOPPLER INFRARED SPECTROSCOPY OF SUPER-COOLED MOLECULES

SAMEER A. HAMMAD, LOUIS R. MERCORELLI, and DAVID S. PERRY

Direct absorption spectroscopy in a conventional free jet yields Doppler-broadened linewidths comparable to a room temperature gas (300-600 MHz in the 3 micron region). A new sub-Doppler technique called "sliced-jet spectroscopy" is reported here. A razor blade is placed in the jet between the nozzle and the laser crossing to obstruct those molecules with zero Doppler shift and thereby creating a narrow hole in the center of the Doppler profile. The resultant lineshapes resemble those obtained by saturation spectroscopy except that the hole-burning mechanism is mechanical. The best resolution obtained to date is 12 MHz (FWHM of the hole) which is in agreement with the theoretical resolution that determined by the optical properties of the system. The technique has been applied to acetylene, 1-butyne, and 3,3-dideutero-1-butyne.

Address: Department of chemistry, The University of Akron, Akron, Ohio, 44325.

RE12 (4:35)

1 HIGH RESOLUTION SPECTROSCOPY OF THE ν_3 BAND OF NEPTUNIUM HEXAFLUORIDE

R. N. MULFORD, K. C. KIM, BURTON J. KROHN, AND J. P. BAIARDO

The band structure of the ν_3 vibration of NpF_6 between 620 and 630 cm^{-1} has been resolved and analyzed, using a Fourier transform spectrometer at a resolution of 0.005 cm^{-1} and a temperature-controlled long path length cell. The overall band contour allows estimation of the band origin and the Coriolis coupling constant. Fine structure components comprising each J manifold of the ground state are evident in many manifolds at the experimental resolution. The unique pattern of fine structure components within each rotational manifold allows assignment of the J quantum numbers and determination of fine structure scalar and tensor components. Frequencies of J manifold centers can be obtained from the spectrum for the identified rotational states between $J=12$ and $J=40$ in the P and R branches of the molecule. Regression can then be used to obtain spectroscopic constants, including the rotational constant and the exact band origin. The Q branch of NpF_6 shows a regular progression of sub-bandheads similar to that of UF_6 . These sub-bandheads were computer simulated to extract spectroscopic constants. Empirical anharmonicity constants can also be obtained from simulation of vibrational hot band components of the Q branch. Initial data indicate that no unexpected perturbations or interactions are present in the NpF_6 molecule.

Address of authors: Los Alamos National Laboratory, Los Alamos, New Mexico

RE13 (4:52)

TIME-RESOLVED INFRARED SPECTROSCOPY: WHAT IS THE BEST METHOD?

HUGH H. RICHARDSON, VERNON W. PABST, AND JARED A. BUTCHER JR.

A new time-resolved infrared spectrometer has been constructed using a 32 element InSb linear array detector. This spectrometer gives time resolved information in the microsecond range with a noise of 4 parts in a thousand. Recent results will be presented and compared with other infrared techniques. The feasibility of using this spectrometer to obtain time resolved information of surface adsorbates will also be discussed.

Address of Richardson, Pabst, and Butcher: Department of Chemistry, Ohio University, Athens, OH 45701

RE14 (5:09) See page 175 for its abstract

RF1 (1:30)

MICROWAVE SPECTRA OF UNSTABLE SPECIES IN A DISCHARGE OF A MIXTURE OF CS₂ AND N₂.

Takayoshi Amano and Takako Amano

Discharge in a mixture of CS₂ and N₂ is a complex system which produces a variety of nitrogen and sulfur compounds (N_xS_y). In the course of an attempt to detect microwave lines of CS⁺, we found several paramagnetic species including well known NS, CCS (appears stronger without nitrogen), and SO (evidence of a slight leak or impurities).

One of the species detected here is found to contain nitrogen and carbon, and tentatively identified as NCS. NCS has been known by its electronic¹ and EPR² spectra, but no pure rotational lines were detected previously. The microwave spectrum is observed in the range of 250-285 and 330-380 GHz with a microwave system equipped with a tripler-quadrupler. A detailed analysis of this species and an attempt of identification of other species is in progress.

¹ R. N. Dixon and D. A. Ramsay, *Can. J. Phys.* **46**, 2619(1968).

² A. Carrington, A. R. Fabris, and N. J. D. Lucas, *Mol. Phys.* **16**,195(1969).

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

RF2 (1:47)

COLLISIONALLY COOLED SPECTROSCOPY: PRESSURE BROADENING BELOW 5 K

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

The results of experiments on CO, CH₃F, H₂S, NO, DCl, OCS, and HDO pressure broadened by He in the region 1.8 - 4.2 K will be described. It was found that the pressure broadening cross sections varied widely with species, state and temperature. Comparison with room temperature cross sections also showed a large variation with dramatic rises and declines seen among the different species and states. We will compare our results with theoretical expectations and predictions.

Address: Department of Physics, Duke University, Durham, NC 27706

RF3 (2:04)

COLLISIONAL COOLING AT 77 K

T. M. GOYETTE, W. L. EBENSTEIN, and F. C. DE LUCIA

We have recently reported a technique for collisional cooling of gas phase samples to liquid helium temperature.¹ In this paper we report the implementation of this method at liquid nitrogen temperature. This is easier and offers a wider range of straightforward spectroscopic applications than the liquid helium implementation. By use of a heated injector and a variable temperature cell it is possible to separate the vibrational and rotational temperatures of a spectroscopic sample so that they may be varied independently of one another. A comparison of experiment to theory on some transitions of methyl fluoride (¹²CH₃F) is used to illustrate this experimental technique.

¹ Willey, Crownover, Bittner, De Lucia, *J. Chem. Phys.* **89** (1988)

Address of Goyette, Ebenstein, De Lucia: Department of Physics, Duke University, Durham, North Carolina 27706

RF4 (2:21)**THE MICROWAVE SPECTRUM OF THE LiO RADICAL**Chikashi Yamada, Masaharu Fujitake, and Eizi Hirota

The rotational spectra of the ${}^7\text{LiO}$ radical in the $v=0$ and $v=1$ vibrational states were observed in millimeter and sub-millimeter wave region. The LiO radical was generated by the reaction of lithium vapor with N_2O in a heat pipe cell. The rotational and centrifugal distortion constants, Λ -type doubling constants, spin-orbit interaction constant, and hyperfine interaction constants were derived through analysis of the rotational spectra observed in the present study, combined with the radio-frequency spectra of Λ -type transitions reported by S. M. Freund et al.¹ The LiO radical was confirmed to have a ${}^2\Pi_i$ ground electronic state with an exceptionally large Λ -type doubling constant, as in the case of NaO. A pure precession hypothesis applied to the observed "p" constant gives the $\Sigma-\Pi$ energy separation to be 2565 cm^{-1} .

¹S. M. Freund, E. Herbst, R. P. Mariella, Jr., and W. Klemperer, J. Chem. Phys. 56, 1467 (1972)

Address: Institute for Molecular Science, Okazaki 444, Japan.

RF5 (2:33)**THE MICROWAVE SPECTRUM OF AlO**Chikashi Yamada, Masaharu Fujitake, Eizi Hirota, and Edward A. Cohen

The rotational spectrum of the AlO radical was observed in millimeter and sub-millimeter wave region. The AlO radical was generated by the reaction of N_2O and Al vapor in a flow reactor cell. The rotational constant, spin-rotation interaction constant, centrifugal distortion constant, as well as hyperfine interaction constants were determined.

Address of Yamada, Fujitake, and Hirota: Institute for Molecular Science, Okazaki 444, Japan.

Address of Cohen: Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA, 91109

Intermission**RF6 (3:00)****DETECTION OF THE NaO RADICAL BY MICROWAVE SPECTROSCOPY**Chikashi Yamada, Masaharu Fujitake, and Eizi Hirota

The rotational spectra of the NaO radical in the four lowest vibrational states were observed in millimeter and sub-millimeter wave region. The NaO radical was generated by the reaction of sodium vapor with N_2O in a heat pipe cell. Analysis of the observed spectra yielded the rotational and centrifugal distortion constants, Λ -type doubling constants, spin-orbit interaction constant, and hyperfine interaction constants in the four vibrational states. The NaO radical is clearly shown to have a ${}^2\Pi_i$ ground electronic state with an anomalously large Λ -type doubling constant and very small hyperfine interaction constants. The molecular constants derived will be discussed in terms of the ionic character of the bond.

Address: Institute for Molecular Science, Okazaki 444, Japan.

RF7 (3:12)**THE ROTATIONAL SPECTRA OF THE KO RADICAL IN THE $x^2\Pi_1$ and $A^2\Sigma^+$ STATES**

Chikashi Yamada, Masaharu Fujitake, Eizi Hirota,
Shuji Saito, and Satoshi Yamamoto

The rotational spectra of the KO radical in the $x^2\Pi_1$ and $2\Sigma^+$ states were observed in millimeter and sub-millimeter wave region. The KO radical was generated by the reaction of potassium vapor with N_2O in a heat pipe cell. Analysis of the observed spectra, with inclusion of interaction terms between the two electronic states, yielded the rotational and centrifugal distortion constants, Λ -type doubling constants, spin-orbit interaction constant, spin-rotation interaction constants and hyperfine interaction constants in the two electronic states, as well as interaction matrix elements and the energy separation between the two electronic states. We conclude that the ground state is $2\Pi_1$, and the $2\Sigma^+$ states lies 660 cm^{-1} above the ground state.

Address of Yamada, Fujitake, and Hirota: Institute for Molecular Science, Okazaki 444 Japan.

Address of Saito and Yamamoto: Nagoya University, Nagoya 460, Japan

RF8 (3:24)**DETECTION OF THE RbO RADICAL BY MICROWAVE SPECTROSCOPY**

Chikashi Yamada, Masaharu Fujitake, and Eizi Hirota

The rotational spectra of the ^{85}RbO radical in the $v=0$ and $v=1$ vibrational states and of ^{87}RbO radical in the $v=0$ state were observed in sub-millimeter wave region (300-400GHz). The RbO radical was generated by the reaction of rubidium vapor with N_2O in a heat pipe cell. Rubidium vapor was prepared by the reaction of RbCl and lithium at about 500°C . Analysis of the observed spectra yielded the rotational and centrifugal distortion constants, and spin-rotation interaction constants in each vibrational state. Contrary to the LiO, NaO, and KO radicals, RbO is shown to have a $2\Sigma^+$ ground state.

Address: Institute for Molecular Science, Okazaki 444, Japan.

RF9 (3:36)**SUBSTITUTION STRUCTURE OF THE CCH RADICAL FROM THE ANALYSIS OF THE ROTATIONAL SPECTRA OF VARIOUS ISOTOPIC FORMS.**

M. BOGEY, C. DEMUYNCK and J. L. DESTOMBES

The submillimeter wave spectra of ^{13}CCH and C^{13}CH were recently observed inside a R.F. glow discharge in a mixture of ^{13}CO , CH_4 and He. Accurate molecular constants were derived, and the frequencies of the lines of astrophysically interest were predicted.

Using the previously determined rotational constants of CCH and CCD together with those determined in this work, a substitution structure was determined and compared to *ab initio* calculations.

Address : Université de Lille-Flandres-Artois, Laboratoire de Spectroscopie Hertzienne, associé au CNRS. 59655 Villeneuve d'Ascq cedex, France.

RF10 (3:48)

MILLIMETER WAVE SPECTRUM of $\text{MgCl } X^2\Sigma^+$ and ISOTOPOMERS in DIFFERENT VIBRATIONAL STATES. DETERMINATION of MASS INVARIANT PARAMETERS.

M. BOGEY, C. DEMUYNCK and J. L. DESTOMBES

The rotational spectrum of $\text{MgCl } X^2\Sigma^+$, in various isotopic forms and vibrational states was observed in the 130 - 290 GHz frequency range. These measurements led to the determination of an accurate set of mass invariant parameters, including the mass scaling coefficients Δ_{01}^{Mg} and Δ_{01}^{Cl} . The frequencies of the transitions of astrophysical interest were also predicted.

Address : Université de Lille-Flandres-Artois, Laboratoire de Spectroscopie Hertzienne, associé au CNRS. 59655 Villeneuve d'Ascq cedex, France.

RF11 (4:00)

MICROWAVE SPECTRA AND STRUCTURES OF THE $\text{N}_2\text{O-HF}$ AND $\text{N}_2\text{O-DF}$ COMPLEXES.

S. G. KUKOLICH, D. J. PAULEY, AND R. E. BUMGARNER

Rotational spectra for the two-structural isomers of the $\text{N}_2\text{O-HF}$ and $\text{N}_2\text{O-DF}$ complexes were measured using a pulse-beam, Fourier transform microwave spectrometer. Rotational transitions were measured to an accuracy of 10 kHz for ONN-HF and ONN-DF. These data were fit to obtain values for B and D_J . These data are consistent with linear or nearly linear structures with the H of HF bonded to the terminal N of N_2O . A pseudo-diatomic analysis was used to obtain values for the force constant k_s and the stretching frequency ν_s of the weak bond. Thirteen new transitions were measured to an accuracy of 60 kHz for the bent structural isomers, NNO-HF and NNO-DF. These data, combined with previous microwave data were fit to obtain values for $(A + \Delta_K)$, B, and C, and four quartic distortion parameters, Δ_J , Δ_{JK} , δ_J and δ_K . The centrifugal distortion constants were used in an analysis of the stretching and bending force field parameters f_{RR} and f_{∞} . The bending force constant f_{∞} is very small, indicating a large amplitude in-plane bending vibration due to the zero-point energy. The contribution of the H(D) atom to centrifugal distortion parameters is shown to be very small, and this results in a considerable simplification of the analysis.

Address of Kukolich and Pauley: Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Address of Bumgarner: Division of Geology and Planetary Sciences, MS 170-25, California Institute of Technology, Pasadena, CA 91125

RG1 (1:30)**THE DISSOCIATIVE RECOMBINATION OF MOLECULAR HYDROGEN IONS**J.B.A. Mitchell, F.B. Yousif, P. VanderDonk, H. Hus

Rydberg states lying below the ground states of molecular ions play an important role in electron-ion recombination. Their presence is manifest in the form of resonances in the cross section in both theoretical and experimental studies¹.

A review of recent studies on H_2^+ and H_3^+ recombination will be given. In the latter case, studies of the branching ratios for the various recombination channels have revealed that H_3^* can act as an intermediate state in the recombination process.

(Work supported by US AFOSR and Canadian NSERC).

1. Dissociative Recombination: Theory, Experiment and Applications. (eds. J.B.A. Mitchell and S.L. Guberman). World Scientific, Singapore 1989.

Address of Mitchell: Department of Physics, The University of Western Ontario, London, Ontario, Canada. N6A 3K7

Address of Yousif, VanderDonk and Hus: Department of Physics, The University of Western Ontario, London, Ontario, Canada. N6A 3K7

RG2 (2:05)**STATIC AND DYNAMIC STARK EFFECTS IN THE HIGH, RYDBERG LEVELS OF H_2** JAN P. HESSLER AND WALLACE L. GLAB

We have studied the effects of a pulsed electric field on the decay dynamics of high, np ($n > 30$), $J = 1$, singlet, Rydberg levels of H_2 . We have discovered that pulsed fields of magnitudes much less than the classical value required for ionization induce a significant degree of dissociative character into levels which normally do not dissociate. This induced dissociation appears to occur during the slew of the field pulse and can be explained in terms of adiabatic passage through avoided curve crossings between the stable $J = 1$ levels and the $J = 0$ and 2 levels which predissociate.

In addition, we have made simultaneous, high-resolution measurements of the photoionization and photodissociation spectra of molecular hydrogen in the energy region near the first ionization limit in a strong, static, external electric field. Below the classical saddle point energy, $-2|F$, electric field-induced predissociation is the dominant decay mechanism for many of the high Stark components, while above the saddle point energy the rates for field ionization and field-induced predissociation are comparable. We have also observed forced autoionization of the $|7p\sigma, v = 1\rangle$ level through its coupling to the structured continuum of highly excited Stark states, leading to enhanced ionization and dissociation through those Stark states which are nearly degenerate with it.

These effects are explained by the unified treatment of dissociation and ionization developed by Ch. Jungen.¹

¹ Ch Jungen, *Phys. Rev. Lett.* 53, 2394 (1984).

Address of Jan P. Hessler: Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

Current Address of Wallace L. Glab: Department of Chemical Sciences, Pacific Northwest Laboratory, Richland, Washington 99352

RG3 (2:22)

AUTOIONIZATION RATES AND ENERGY LEVELS OF TRIPLET $v=1$ RYDBERG STATES OF PARA- AND ORTHO- H_2 MEASURED BY HIGH-RESOLUTION LASER SPECTROSCOPY.*

MARK D. LINDSAY, A.W. KAM, J.R. LAWALL,⁺ F.M. PIPKIN, and PING ZHAO

We have measured the Lorentzian linewidths and absolute energy levels of 29 triplet Rydberg states of the H_2 molecule with quantum numbers $n=11$ to 22, $v=1$, $R=0$ to 3, $L=3$. This work provides the first measurements of autoionization rates of triplet nf Rydberg states. Measurements of the absolute energy levels of the Rydberg states relative to the metastable $c(2p)^3\Pi_u$ state are seven times more precise than the best previous work.

An 18eV electron beam excites a collimated H_2 beam to the metastable $(2p)^3\Pi_u$ state. Stepwise excitation using two counterpropagating CW single-mode dye laser beams directed perpendicular to the molecular beam path excites the metastable molecule first to an intermediate state, $(3d^3\Sigma$ or $3d^3\Pi)$, then to a triplet nf state. While scanning the IR laser used for the last excitation, we detect H_2^+ ions to measure the lineshape and width. In addition we measure the energy to 0.0015 cm^{-1} of each laser beam (while they are set to the peaks of the transitions) using a travelling-arm interferometer (λ -meter) referenced to a Zeeman-stabilized He-Ne laser.

Calculations based on the long range interaction of the Rydberg electron and the polarizability and quadrupole moment of the H_2^+ core predict the energy levels and autoionization rates.¹ For the $v=1$ Rydberg states we have measured, our data for the widths (rate = 2π (width)) and the energy levels agree well, except for a few well-understood exceptions. Using our measured energy levels we can also derive the ionization potential of the $c(2p)^3\Pi_u$ metastable state. We obtain the preliminary values:

$$\begin{aligned} IP(2p^3\Pi_u, v=1, N=1, J=2): & 27\,137.108(7)\text{ cm}^{-1} \\ IP(2p^3\Pi_u, v=1, N=2, J=3): & 27\,022.078(6)\text{ cm}^{-1} \end{aligned}$$

The model predicts that rates for purely rotationally autoionizing Rydberg states (nf, $v=0$, $R=1$ to 4, $L=3$) will be relatively larger; a study of these transitions is in progress.

* Research supported in part by NSF grant PHY-8704527

+ Bell Fellow

¹ E. E. Eyler, Phys. rev. A, **34**, 2881 (1986)

Address of all authors: Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138

Intermission

RG4 (3:00)

DETERMINATION OF THE (0,1)-(0,3) ROTATIONAL SPLITTING OF H_2^+ FROM MICROWAVE SPECTROSCOPY OF H_2 RYDBERG STATES.*

P.W. ARCUNI, Zhuo-Wu Fu, and S.R. Lundeen

The 1-3 rotational splitting of the ground vibrational state of H_2^+ has been calculated¹ to be $288.861(1)\text{ cm}^{-1}$. As a consequence, the (0,1)28L and (1,3)16L Rydberg states of H_2 are separated in energy by only about 7 GHz. Electric dipole transitions between the two series, which would normally be forbidden, are weakly allowed by virtue of mixing between the two series. This allows a direct determination of the energy difference between states of the two series by microwave spectroscopy, from which the core rotational splitting may be inferred with high precision. Preliminary results of such a determination based on observation of the (0,1)28H₆ - (0,3)16I₇ transition, and other similar transitions will be described.

*Supported by NSF under Grant PHY-87-09707

¹L. Wolniewicz and J.D. Poll, Mol. Phys. **59**, 953 (1986)

Address of Arcuni, Fu, and Lundeen: Dept. of Physics, Univ. of Notre Dame, Notre Dame, IN 46556

RG5 (3:17)

OPTOGALVANIC SPECTRA AND PREDISSOCIATION OF $c^3\Pi_u$ STATE OF H_2 AND D_2

Y. Kawashima

The optogalvanic spectra of the highly excited H_2 and D_2 by dc discharge have been investigated. Five bands of the triplet systems were observed in the 16200-17400 cm^{-1} region; from $c^3\Pi_u$ to $h^3\Sigma_g^+$, $g^3\Sigma_g^+$, $i^3\Pi_g$, and $j^3\Delta_g$ and from $a^3\Sigma_g^+$ to $d^3\Pi_u$ transitions. Comparing the optogalvanic spectra with the ordinary emission spectra of H_2 and D_2 , in the case of H_2 the half of the optogalvanic transitions from $c^3\Pi_u$ state was weak or missing. This fact confirmed that the $c^3\Pi_u^+$ state of H_2 predissociated into the repulsive state $b^3\Sigma_u^+$. However, in the case of D_2 many optogalvanic transitions from $c^3\Pi_u^+$ state were observed. The calculation of Comtet and Bruijn¹ demonstrated that the predissociative lifetime of the $c^3\Pi_u^+$ state in D_2 was much longer than that in H_2 . The observation of many optogalvanic transitions in D_2 is explained as a long predissociative lifetime in D_2 .

¹ G. Comtet and D.P. de Bruijn, Chem. Phys. 94 365 (1985).

Address of Kawashima: Kanagawa Institute of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa 243-02, Japan

RG6 (3:34)

DOUBLY EXCITED STATES OF H_2 .

M. GLASS-MAUJEAN

Neutral double excited states of H_2 lie in the Franck Condon region, at energies beyond 23 eV above the ground state of H_2 , far above the ionization threshold. Dissociation into neutral fragments does complete with autoionization.

The dissociation limit of such doubly excited states is not as simple as it first appears. For instance the states with $(2p\sigma_u, n\ell\lambda_g)$ configuration at short internuclear distance, are correlated to $H(1S) + H^+(n'\ell')$ or to $H^+ + H^-(1s, n'\ell')$; which limit is important? To reach such $H(1S) + H^+(n'\ell')$ limit the corresponding potential curve has to cross all the potential curves of bound states with $n'' > n'$, are these crossings efficient?

We will discuss how a quantitative study of the photodissociation of these states gives some enlightenment on the problem.

Address: Laboratoire de Spectroscopie Hertzienne de l'ENS - Université P. et M. Curie - 4, place Jussieu - 75252 PARIS.

RG7 (3:51)

QUANTUM DEFECT CALCULATIONS OF H_2^+

Hong Gao and Chris H. Greene

Quantum defect techniques are applied to calculate vibrational levels and the photoionization cross section of H_2^+ . Assuming a Born-Oppenheimer approximation at small electron distances, we calculate the body-frame quantum defect function $\mu(\epsilon, R)$ ¹ by exactly solving the fixed-nuclei Schrödinger equation. $\mu(\epsilon, R)$ provides sufficient information to describe electron escape to long range, which is treated by standard QDT procedures. While the energy-dependence of $\mu(\epsilon, R)$ can be neglected in vibrational level calculations, it must be included to obtain the correct ionization cross section.² Although electronic excitations of H_2^+ always result in its dissociation (in this sense H_2^+ cannot be viewed as a Rydberg molecule), the quantum defect calculation nevertheless gives good results. This prototype calculation shows how MQDT can be applied successfully even to a non-Rydberg molecule such as H_2^+ , which is somewhat surprising.

¹Ch. Jungen and O. Atabek, J. Chem. Phys. 66, 5584 (1977).

²D. R. Bates, U. Öpik and G. Poots, Proc. Phys. Soc. A 66, 1113 (1953).

Address of Gao and Greene: JILA and Dept. of Physics, University of Colorado, Boulder, CO 80309

RH1 (1:30)

FLUORESCENCE SPECTROSCOPY AND DYNAMICS OF INELASTIC COLLISIONS BETWEEN RARE GASES AND VIBRATIONALLY EXCITED I_2

K. BUTZ, HONG DU, D. KRAJNOVICH, and C.S. PARMENTER

Crossed beams have been combined with the laser-pump, dispersed fluorescence probe technique to study inelastic collisions. Preliminary results on the $I_2^+ (B\Omega_u^+)$ + He system were reported in this conference last year. The spectroscopy has now provided many state-to-state vibrationally inelastic cross sections for both He and other target gases. The collision energy dependence as well as the initial vibrational state dependence of the cross sections will be presented. Those cross sections give new insights into the collisional dynamics. Landau-Teller modeling and classical trajectory calculations have both been compared with the data. Both replicate aspects of the data, and by some standards, both are fairly successful. The precision of the data are high enough, however, to reveal clearly the inadequacies of the present treatments. The collision dynamics will be discussed in detail based on the classical trajectory calculations.

Address of K. Butz, H. Du and C.S. Parmenter: Department of Chemistry, Indiana University, Bloomington, IN 47405

Address of D. Krajnovich: IBM Almaden Research Center, K07/803, 650 Harry Road, San Jose, CA 95120

RH2 (1:47)

THE DISSOCIATION OF p-DIFLUOROBENZENE-Ar VAN DER WAALS COMPLEXES. THEORY AND SPECTROSCOPY

Hye-Keun O, Charles S. Parmenter and Meng-Chih Su

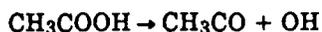
pDFB-Ar is one of about 15 large molecule-atom complexes for which reports describe dissociation following excitation of specific ring levels in the excited S_1 state. Among these, the pDFB fluorescence spectroscopy proves particularly favorable. For each of numerous initial levels, it gives the vibrational predissociation (VP) lifetimes and identifies the vibrationally state-resolved VP channels. New spectroscopy has also revealed several IVR processes that are associated (presumably) with dissociation. Much effort continues on theoretical modeling. The standard models involving direct dissociation of the complex from the pumped state do not work. Even a three dimensional quantal scattering description (Tiller, Peet and Clary) is largely frustrated. In contrast, simple modeling by a sequential dissociation involving, first, IVR into the van der Waals modes followed by an RRKM dissociation does better. Following the techniques of Kelley and Bernstein (JPC 90 (1986) 5164), who worked out such a scheme for s-tetrazine data, we see that IVR is often the rate limiting step. Thus as one learns to model the IVR successfully, a major contributor to the dissociation characteristics receives proper account. Other factors also contribute, however, to the dissociation and to the resulting spectroscopy. An attempt will be made to place these in correct perspective.

Address of H.-K. O and C.S. Parmenter: Department of Chemistry, Indiana University, Bloomington, IN 47405

Address of M.-C. Su: Department of Chemistry, Butler University, 4600 Sunset Ave., Indianapolis, IN 46208

RH3 (2:04)**REACTION PATHWAYS IN THE PHOTOLYSIS OF ACETIC ACID****S. S. HUNNICUTT, L. D. WAITS, AND J. A. GUEST**

Acetic acid has been photolyzed under both room temperature and jet cooled conditions. The nascent OH X²Π (v''=0) photofragment has been probed using laser fluorescence excitation to determine its scalar and vector quantities. Only a few percent of the total available energy is partitioned into rotational energy of OH. Fragment OH is produced in v''=0 only. The F₁(²Π_{3/2}) and F₂(²Π_{1/2}) spin states are statistically populated, and Λ-doublet levels are equally populated. The OH product radical was determined to have no rotational alignment. Doppler spectroscopy shows that a significant fraction, about 49%, of the available energy is imparted to CH₃CO and OH fragment translation. The energy partitioning shows that the dominant path for OH production from 218 nm acetic acid photolysis is



with no subsequent decomposition of the acetyl fragment. An impulsive model predicts the mean fragment translational energies extracted from the experiments. Alternative pathways that lead to methyl radical fragments will be explored.

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

RH4 (2:21)**COLLISION-INDUCED ELECTRONIC QUENCHING OF BH(A¹Π)****C.H. DOUGLASS AND J.K. RICE**

Electronic quenching cross sections of BH (A¹Π) were measured by examining fluorescence decay times in the presence of sixteen collision partners at 298K. The partners exhibit wide variations in mass, electric dipole moment and higher order moments. Except for the extremely low cross sections measured for He and SF₆, values range from 5 to 150 Å². Of the fourteen remaining partners, eleven are represented moderately well by a multipole attractive force model, two (OCS and CH₂F₂) fall well below the expected cross section and one (CHFC1₂) has an experimental cross section larger than predicted by this model. A temperature comparison is made for the quenching of BH (A¹Π) by CO at 298K and 473K. The measured rate constant at 473K exhibits a 10% decrease compared to the 298K value with an uncertainty of ~11%.

Address of Rice: Chemistry Division, Code 6111, Naval Research Laboratory, Washington, DC 20375-5000.
Rice%Chem.decnnet@NRL.ARPA

Address of Douglass: Applied Research Corporation, 8201 Corporate Dr., Landover, MD 20785

RH5 (2:38)**ELECTRONIC QUENCHING OF THE SO A(³Π₁ v'-1) STATE****M. J. McAuliffe, M. Bohn, and E. A. Dorko**

Rates for electronic quenching of SO A³Π v'-1 have been measured for the rare gases, He, Ne, Ar, Kr, Xe and several diatomics and small polyatomics, N₂, O₂, CF₄, and SF₆. The rates are found to be 0.01 to 0.1 times gas kinetic. A good correlation is found between the rare gas quenching efficiencies and the product of the dipole polarizability, α, and the square root of the reduced mass. The molecular species, however fall well off of the correlation line with rates much more efficient than predicted. A correlation with the intermolecular well depth, based on the collision complex model of Lin *et al*¹ was also tried and appears to be of more general value.

1. H.M. Lin, M. Seaver, K.Y.Tang, A.E.W.Knight, and C.S.Parmenter, J. Chem. Phys. 70 (1979), 5442.

Address of Authors: AFWL/ARDI, Air Force Weapons Laboratory, Kirtland AF Base, NM 87117-6008

RH6 (2:50)**SINGLE ROTATIONAL LEVEL PHOTOPHYSICS OF S_1 THIOFORMALDEHYDE**James R. Dunlop, Dennis J. Clouthier, and Richard H. Judge

Measurements of collision-free single rotational level fluorescence lifetimes and relative quantum yields are reported for the 4^1_0 band of the S_1 - S_0 absorption system of thioformaldehyde (H_2CS). These data are compared to spectroscopic evidence¹ for internal conversion and intersystem crossing from the S_1 state.

The radiative lifetime is found to be approximately 170 $\mu s.$, substantially longer than previously reported values, with a number of levels having even longer lifetimes. These anomalously long lifetimes can be explained by the dilution of the oscillator strength due to coupling with dark levels in the ground and first excited triplet states. Quantum yield measurements indicate that some of the long-lived levels have a nonradiative decay component in the coupled state.

The results are interpreted in terms of a qualitative model involving level specific coupling between S_1 and levels in T_1 and S_0 .

1) J. C. Petersen and D. A. Ramsay, Chem. Phys. Lett. 124, 406 (1986) and references therein.

Address of Dunlop and Clouthier: Department of Chemistry, University of Kentucky, Lexington, KY, 40506-0055.

Address of Judge: Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI, 53141-2000.

RH7 (3:07)**Binding Energies of Three Iodine Complexes**T. D. McLean, B.B. Ratcliff, J.Z. Pastalan, and K.K. Innes

The $(I_2)_2$, I_2 -benzene and I_2 -diethyl ether complexes have been studied in a jet expansion. Each complex was photo-dissociated using four blue Ar^+ laser lines. Dispersion of subsequent fluorescence from liberated I_2 molecules has allowed an estimation of the binding energy of each complex.

These values are in qualitative and quantitative agreement with predictions based on atom pair-wise potentials. Calculated potentials have enabled us also to speculate on the most stable geometry of each species.

Department of Chemistry, SUNY at Binghamton, 13901.

RH8 (3:24)**ROTATIONAL ENERGY TRANSFER IN THE $B^3\Pi(0^+)$ STATES OF IF AND ICl: A SYSTEMATIC STUDY OF STATE-TO-STATE RATE COEFFICIENTS***S.J. DAVIS AND K.W. HOLTZCLAW

A CW laser induced fluorescence study has been performed to determine rotational to translational (R-T) energy transfer rate coefficients for selected J' levels in the heteronuclear molecules IF and ICl. Steady state populations of specific rovibronic levels were prepared using either an Ar^+ laser or a ring dye laser. Rate coefficients were determined for state-to-state R-T transfer for a variety of bath gases: He, Ne, Ar, Kr, Xe, N_2 , and CF_4 and for several initially excited rotational levels. Over 1000 rate coefficients for individual ΔJ changing collisions have been measured. Dramatic differences in the abilities of various collision partners to transfer angular momentum to and from IF and ICl are observed. Comparisons are made to theoretical models that predict the scaling of the rate coefficients as a function of ΔJ .

*Supported by Air Force Office of Scientific Research Contract No. F49620-86-C-0061.

Address of Davis and Holtzclaw: Physical Sciences Inc., Research Park, P.O. Box 3100, Andover, MA 01810.

RH9 (3:41)**SECOND HARMONIC GENERATION STUDIES OF COPPER ELECTRODEPOSITION
ON GOLD**

M. Bennahmias, H.S. Lakkaraju, K. Ashley, and B. Stone

Second Harmonic Generation (SHG) was used as a probe to study the electrochemical deposition of Cu from a $\text{CuSO}_4/\text{H}_2\text{SO}_4$ solution onto a Au electrode. The SHG signal was generated by focussing 100 mJoule pulses of p-polarized 1.06 micron radiation from a Nd:YAG laser onto a polished polycrystalline Au electrode surface. Cu electrodeposition onto, and desorption from, the surface was followed using cyclic voltammetry, and the SHG signal was monitored as a function of the applied potential. A significant decrease in SHG intensity was observed as Cu was deposited electrochemically onto the Au electrode surface. This signal was found to reach a constant value during bulk deposition of Cu metal.

Address of Bennahmias and Lakkaraju: Dept. of Physics, San Jose State University, San Jose, CA 95192.

Address of Ashley and Stone: Dept. of Chemistry, San Jose State University, San Jose, CA 95192.

FA1 (8:30)

COLLISIONALLY-EXCITED NAPHTHALENE IN THE GAS PHASE

DANIEL J. GRAHAM AND SCOTT M. HURST

The spectroscopic properties of aromatic hydrocarbons in static gases and molecular beams have been examined to great extent. Laser excitation methods have been employed in these studies more frequently than collisional excitation methods. The latter methods are important as they provide a handle on molecular electronic states with spin multiplicity different from that of the ground state.

Excited triplet nitrogen molecules are present in the afterglow of a corona discharge expansion of nitrogen and helium. Naphthalene can be introduced to this mixture downstream from the discharge. Collisions involving triplet nitrogen lead to electronic excitation of naphthalene. We present high resolution emission spectra which provide insight regarding the state distribution of collisionally excited naphthalene.

Address of Graham and Hurst: Department of Chemistry, Loyola University of Chicago, 6525 North Sheridan Road, Chicago, Illinois 60626

FA2 (8:47)

IDENTIFICATION OF SVL'S OF TWO ISOMERS OF GUAIAZULENE BY POPULATION LABELING SPECTROSCOPY

ANTHONY C. BEVILACQUA and JONATHAN E. KENNY

In a supersonic expansion, 1,4-dimethyl-7-isopropylazulene (guaiazulene) forms two stable conformers upon the cooling of the rotational degree of freedom of the isopropyl group¹. This is reflected in the $S_2 \rightarrow S_0$ fluorescence excitation spectrum which shows two strong origin bands, that of rotamer A being blue-shifted by 106 cm^{-1} from the origin of rotamer B. In order to analyze the vibrational structure of the S_2 state of guaiazulene, a methodology is needed to distinguish the vibrations of each rotamer. Identification by searching the spectrum for pairs of transitions separated by 106 cm^{-1} is not always correct or useful.

Utilizing jet conditions, we have employed an optical-optical double resonance technique. A pulsed (5 nsec) dye laser (ν_1) is resonant with the 0_0^0 band of one rotamer, say rotamer B. This depopulates the $S_0 0_0$ level of rotamer B via electronic excitation. Another pulsed dye laser (ν_2) is tuned to an SVL in the $S_2 \rightarrow S_0$ excitation spectrum, an SVL whose molecular conformation is unknown. The OODR signal from this SVL is reported as the difference of sample (ν_1 off, ν_2 on) and blank (ν_1 on, ν_2 on) fluorescence resulting from the ν_2 excitation. When the unknown SVL is a member of the rotamer A manifold, there is no distinction between sample and blank; the fluorescence intensity of an SVL of A is independent of the concentration (or ground state population) of rotamer B. However, when the SVL belongs to the rotamer B structure, differences of up to 60% are observed. This is due to the depopulation of the 0_0 level of B by ν_1 , resulting in less fluorescence intensity derived from ν_2 . This population labeling experiment unambiguously assigns each SVL and also show that only two conformers exist under our experimental conditions.

1. M.M. Carrabba, T.M. Woudenberg, and J.E. Kenny, *J. Phys. Chem.*, **89**, 4226 (1985).

Address of Bevilacqua and Kenny: Department of Chemistry, Tufts University, Medford, MA 02155

FA3 (9:04)

The $n \rightarrow 3s$ Rydberg Transition of Jet-Cooled Tetrahydropyran, 1,4-Dioxane, and 1,4-Dioxane- d_8 Studied by 2+1 Resonance Enhanced Multiphoton Ionization

Timothy Cornish, Tomas Baer, Lee G. Pedersen

The lowest electronic transitions of tetrahydropyran (THP), 1,4-dioxane, and 1,4-dioxane- d_8 cooled in a free jet expansion have been examined by 2+1 REMPI spectroscopy. The transition in dioxane is not allowed in one photon and in fact has not been reported previously. These ($n \rightarrow 3s$) spectra, which consist primarily of Q-branches, are extremely sharp and intense. The absorption intensity ratio for circularly and linearly polarized light is less than 0.2 which indicates that the transition is between states of the same symmetry, $A' \rightarrow A'$ in the case of THP, and $A \rightarrow A$ for the dioxanes. These assignments were made with the aid of ab initio molecular orbital calculations. Additionally, the Hartree Fock calculations show that the 3s Rydberg orbital is primarily comprised of 3s atomic orbitals from all the carbon atoms in THP and dioxane. Several of the low frequency ring vibrations in the Rydberg spectra of THP and dioxane have been assigned. It is proposed that the relaxation of the C-O-C ether bond is the major consequence of electronic excitation.

Address of Cornish, Baer, and Pedersen: Chemistry Dept, University of North Carolina, Chapel Hill, N.C. 27599-3290

FA4 (9:16)

HIGH RESOLUTION LIF SPECTROSCOPY OF JET-COOLED CYCLOPENTADIENYL RADICALS, C_5H_5 AND C_5D_5 : STRUCTURE AND JAHN-TELLER EFFECT

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

Rotationally resolved LIF spectra of cyclopentadienyl radical associated with the $\bar{A} \ ^2A_2'' \leftarrow \bar{X} \ ^2E_1''$ electronic transition are recorded in a free-jet expansion. C_5H_5 and C_5D_5 are produced in the jet by photolyzing cyclopentadiene ($-h_6$ or $-d_6$) with a KrF excimer laser. The presence of vibrational bands with different rotational structures from that of the origin band indicates the excitation of Jahn-Teller active vibrations. The analysis of the origin bands of both C_5H_5 and C_5D_5 allows for an accurate determination of the radical's structure in both the \bar{X} and the \bar{A} states. Parameters directly related to the Jahn-Teller effect in the $\bar{X} \ ^2E_1''$ state are obtained. Using the isotopic relationships, the implications for the Jahn-Teller distortion and vibronic coupling are discussed.

Address of Yu, Cullin, Williamson and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

Address of Foster: Department of Chemistry, Florida State University, Tallahassee, Florida 32306.

FA5 (9:33)

ROTATIONALLY RESOLVED SPECTRA OF JAHN-TELLER ACTIVE VIBRATIONS IN AN ELECTRONICALLY ALLOWED $A \leftarrow E$ TRANSITION

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

Due to the Jahn-Teller effect, the fundamental band of a Jahn-Teller active vibration becomes allowed in an electronic $A \leftarrow E$ transition. The corresponding rotational selection rules differ from those of the origin band and the intensity gives a good indication of the magnitude of the Jahn-Teller interaction. We have recorded high resolution, rotationally resolved, LIF spectra of a number of different vibronic bands of jet-cooled C_5H_5 ($\bar{A} \ ^2A_2'' \leftarrow \bar{X} \ ^2E_1''$), $C_5F_5H_3^+$ ($\bar{B} \ ^2A_2'' \leftarrow \bar{X} \ ^2E''$) and $C_5F_5^+$ ($\bar{B} \ ^2A_2'' \leftarrow \bar{X} \ ^2E_1''$). Several of these vibronic bands with rotational structures different from those of the corresponding origin bands are assigned to the fundamental transitions of Jahn-Teller active vibrations. Detailed rotational analyses yield, in addition to the normal molecular constants, the values of the angular momenta, ζ , for various Jahn-Teller active vibrations. For $C_5F_5H_3^+$ and $C_5F_5^+$, the previous assignment of the Jahn-Teller active vibrations is confirmed. For C_5F_5 , the first definitive identification of the Jahn-Teller active vibrations is made.

Address of Yu, Williamson and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

Address of Foster: Department of Chemistry, Florida State University, Tallahassee, Florida 32306-3006.

Intermission

FA6 (10:05)

HIGH RESOLUTION LIF SPECTROSCOPY OF JET-COOLED METHYLCYCLOPENTADIENYL RADICAL, $C_5H_5CH_3$

LIAN YU, DAVID W. CULLIN, JAMES M. WILLIAMSON, AND TERRY A. MILLER

Methyl substitution on the cyclopentadienyl radical introduces two interesting effects: the splitting of the originally degenerate \bar{X}^2E_1 state in C_5H_5 due to the symmetry breaking and the coupling between the methyl internal rotation and the overall molecular rotation. We have taken rotationally resolved LIF spectra of methylcyclopentadienyl radical (MeCp) in a free jet expansion. Extremely cold (<1K) MeCp is produced by photolyzing methylcyclopentadiene with a KrF excimer laser in the jet. The band ($29,764\text{ cm}^{-1}$) previously assigned to the electronic origin is resolved into two subbands separated by $\sim 2\text{ cm}^{-1}$, with type a and type b rotational structures, respectively. Based on the preliminary analysis, it seems possible that these two subbands are due to transitions from the split-electronic states. Interestingly, the bands that are assigned to He complexes with MeCp also exhibit similar "two-subband" structures.

Address of Yu, Cullin, Williamson and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

FA7 (10:22)

LIF SPECTROSCOPY OF FREE RADICAL - RARE GAS VAN DER WAALS COMPLEXES

JAMES M. WILLIAMSON, DAVID W. CULLIN, LIAN YU, AND TERRY A. MILLER

The van der Waals complexes between polyatomic open shell molecules and rare gases are of considerable interest. We have recorded vibrationally and rotationally resolved LIF spectra of several free radical - rare gas van der Waals complexes in a free jet expansion. Two examples of the complexes that we have observed are the cyclopentadienyl radical with helium and neon and the methylcyclopentadienyl radical with helium. The LIF spectra and preliminary analysis of the radical - rare gas complexes will be presented.

Address of Williamson, Cullin, Yu, and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

FA8 (10:39)

VIBRATIONAL SHIFTS IN p-DICHLOROBENZENE - RARE GAS VAN DER WAALS COMPLEXES

W. D. SANDS, R. MOORE, AND L. F. JONES

Fluorescence excitation spectra have been obtained for jet-cooled $p\text{-C}_6\text{H}_4\text{Cl}_2$ and $p\text{-C}_6\text{D}_4\text{Cl}_2$ and their van der Waals complexes with Ar and Kr. The van der Waals shifts for the origins of the Ar and Kr complexes are the same for both $p\text{-C}_6\text{H}_4\text{Cl}_2$ and $p\text{-C}_6\text{D}_4\text{Cl}_2$; however, the van der Waals shifts for vibronic transitions in the complexes are isotopically dependent. The vibrationally dependent van der Waals shifts are largest for $16a_0^2$; this appears to be a general property of complexes of rare gases with aromatic systems. The effect of vibrational excitation of ν_{16a} of p-dichlorobenzene on the van der Waals potential is modeled by using the results of ab initio normal mode calculations and atom-atom pair potentials. The model calculations are not in quantitative agreement with experiment, but they correctly predict that for $16a_0^2$ the vibrationally dependent shift is larger for Kr complexes than for Ar complexes, and, for a given rare gas atom, the vibrationally dependent shift is larger for $p\text{-C}_6\text{H}_4\text{Cl}_2$ complexes than for $p\text{-C}_6\text{D}_4\text{Cl}_2$ complexes. In addition, the model calculations lend support to our tentative assignment of $16a_0^2$ in $p\text{-C}_6\text{D}_4\text{Cl}_2 - \text{He}$.

Address of Sands: Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

Address of Moore and Jones: Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia, 23284.

FA9 (10:56)

AB INITIO STUDY OF THE GEOMETRY AND ELECTRONIC STRUCTURE OF SEMICONDUCTOR CLUSTERS. M. SAWAMURA, M. M. MARINO, W. C. ERMILER, AND C. J. SANDROFF

Clusters of the layered semiconductors Pb_xI_{2x} and Bi_xI_{3x} ($x=6,7$) are studied using ab initio Hartree-Fock calculations and relativistic effective core potentials. Total energies, internuclear distances and net atomic charges are calculated for clusters having D_{3d} and D_{3h} point group symmetries. The most stable geometry for Pb_7I_{14} corresponds to 10% expansion horizontally and 20% contraction while increase of the iodine-lead interlayer distance results in a 10% reduction of the in-plane lattice constants relative to the bulk geometry. These results are examined in light of recent structural images obtained using scanning tunneling microscopy.¹ Experimental optical data indicating significant quantum size effects are compared to our theoretical electronic spectra.

¹D. Sarid, T. Hinson, L. Bell, and C. J. Sandroff, J. Vac. Sci. Tech. 6, 424 (1988)

Address of Sawamura: The Department of Physics and Engineering Physics, Stevens Institute of Technology, Hoboken, New Jersey, 07030

Address of Marino and Ermler: The Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030

Address of Sandroff: Bell Communications Research, Red Bank, New Jersey, 07701

FA10 (11:03)

A LIF-TOF STUDY OF IONIC CLUSTERS $C_nF_n^+-R_n$

CHUNG-YI KUNG, ERIC S. ROBLES, AND TERRY A. MILLER

Ionic clusters $C_nF_n^+-R_n$ ($R = He, Ne$ or Ar , $n = 1$ to -10) in a supersonic jet were studied by monitoring their laser-induced fluorescence and time-of-flight (TOF) mass spectra simultaneously. In addition to sharp transitions due to small clusters ($n = 1$ and 2), broad features were observed in the LIF spectra. These features were attributed to the transitions of larger clusters ($n > 2$). The behavior of the cluster transitions under various expansion conditions and the correlation between the LIF and TOF spectra will be discussed. Explanations of the spectral shifts of various cluster sizes, based upon the structure of the clusters, will be offered.

Address of Kung, Robles, and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.

FA11 (11:20)

The Effect of Vibronic Coupling on Methyl Conformation in p-Cresol

Steve Mayer and Lee H. Spangler

Dept. of Chemistry, Montana State University, Bozeman, MT 59717

The jet cooled fluorescence excitation spectrum of S_1 p-cresol shows that the methyl group does not change conformation upon excitation for totally symmetric modes but does for vibronically coupled modes appearing at 709, 1150 and 1529 cm^{-1} above the origin. We speculate that the second electronic state mixed in by the vibronic coupling causes an asymmetry in the electron density with respect to the para axis of the molecule thereby changing the hyperconjugation interaction and affecting the methyl conformation. This result helps confirm the possibility of using methyl groups as a probe of excited state electronic density and character. An assignment of the vibrational structure will be given.

FA12 (11:37)

Spectroscopic Investigation of Polymerization in p-Methyl Styrene

Steve Mayer, Shuxin Yan, and Lee H. Spangler

Dept. of Chemistry, Montana State University, Bozeman, MT 59717

The expansion cooled LIF spectrum of the S_1 state of p-Me-styrene was observed to change markedly with time. The change is inhibited by enclosure of the sample in a glass vessel as opposed to the stainless steel vessel which is normally used, indicating that Ni catalyzed polymerization is occurring in the liquid state before expansion. Spectral features due to polymerization will be discussed as well as the possibility of spectroscopically following the individual polymerization kinetics of the monomer, dimer and trimer.

FB1 (8:30)**DIODE LASER ABSORPTION SPECTROSCOPY OF SUPERSONIC CARBON CLUSTER BEAMS: THE ν_3 Vibration of C_5** J.R. HEATH, A.L. COOKSY, M.H.W. GRUEBELE, C.A. SCHMUTTENMAER, R.J. SAYKALLY

The ν_3 asymmetric stretch rovibrational spectrum of C_5 has been observed by diode laser absorption spectroscopy of laser vaporized graphite in a free jet expansion. The frequencies for the transitions P(40) through R(30) were measured and fit to obtain $\nu_3 = 2169.4404(18) \text{ cm}^{-1}$, $B_0 = 0.085305(31)$, and $B_1 = 0.084900(22)$. These results are consistent with prior *ab initio* calculations² indicating the molecule to be linear with slightly inequivalent C-C bond lengths. The results are also consistent with the vibrational frequency obtained from matrix studies.³ This technique should be generally applicable to the determination of molecular structures and potential energy surfaces for clusters of refractory elements. This, in turn, will permit us to test theoretical studies of these complex systems and elucidate the role of these molecules in interstellar space and other contexts.

1. J.R. Heath, A.L. Cooksy, M.H.W. Gruebele, C.A. Schmuttenmaer, and R.J. Saykally, *Science* (submitted) (1989).
2. K. Raghavachari and J.S. Binkley, *J. Chem. Phys.* **87**, 2191 (1987).
3. M. Vala, T.M. Chandrasekhar, J. Szczepanski, R. Van Zee, and W. Weltner, Jr., *J. Chem. Phys.* **90**, 595 (1989).

Address of Heath, Cooksy, Gruebele, Schmuttenmaer, and Saykally: Department of Chemistry, University of California, Berkeley, CA 94720.

FB2 (8:47)**LABORATORY DETECTION OF C_5 BY DIODE LASER SPECTROSCOPY.**N. Moazzen-Ahmadi, A. R. W. McKellar, and T. Amano

A carbon chain molecule C_5 has been detected by observing the vibration-rotation bands around the 4.6- μm region. C_5 is generated in a hollow cathode discharge in either C_2H_2 or C_2H_4 with He as a buffer gas. The discharge is cooled to -60°C by circulating cooled methanol through copper tubing wound around the cathode, and is amplitude modulated at about 1 kHz. In addition to the fundamental band, hot bands are also observed. The fundamental band is analyzed by using a standard linear molecule vibration-rotation energy expression, and molecular constants thus obtained agree very well with those derived from the analysis of the spectrum observed in the circumstellar shell of IRC+10216 by Bernath¹ *et al.* Our observation extends to higher- J transitions because of our warmer source, and leads to a better determination of the constants. Analyses of the hot bands are in progress.

¹ P. F. Bernath, private communication.

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

FB3 (9:04)**VIBRATIONAL FREQUENCIES OF LINEAR CARBON MOLECULES**D.W. Ewing

A systematic study of the vibrational frequencies of linear C_n , $n=2-5$, molecules is presented. Harmonic frequencies and intensities were calculated at both the Hartree-Fock and second order Moller-Plesset levels of theory, using a variety of basis sets. Based on the accurate calculations for these smaller molecules, predictions of the vibrational spectra for larger carbon molecules are made via Hartree-Fock calculations and small basis sets.

Address of Ewing: Department of Chemistry, John Carroll University, Cleveland, OH 44118.

FB4 (9:16)

MICROWAVE SPECTROSCOPY OF TRANSIENT PYROLYSIS PRODUCTS: 1,1-DIMETHYLSILAETHYLENE*

T. EMILSSON, JANE CHEN, P. J. HAJDUK, AND H. S. GUTOWSKY

Reactive species produced by gas phase pyrolysis have often been studied by microwave spectroscopy. However, the conventional methods are limited to species having lifetimes of the order of seconds or longer. We have extended this range by outfitting a Flygare/Balle, Fourier transform spectrometer with a heated pulsed nozzle. The nozzle heats the sample as high as 1400 K for less than 0.1 msec before cooling the products to a few K by supersonic expansion. The quick quenching of the pyrolysis and the inherent sensitivity of the spectrometer enable us to detect quite readily the rotational transitions of reactive species like chloroketene, difluorocarbene, and 1,1-dimethylsilaethylene (DMSE).

Chloroketene and difluorocarbene have been observed by conventional methods but not DMSE. We have found a number of low-J, b-dipole transitions for DMSE, resolving the fine structure from internal rotation of the methyl groups. The DMSE was produced by pyrolysis of 1,1-dimethylsilacyclobutane at ~1300 K. Preliminary analysis of the data collected thus far gives rigid rotor, rotational constants of 6037.7, 5896.9, and 3093.6 MHz for A, B, and C respectively, and a barrier to internal rotation of 1.0 kcal/mole. The rotational constants agree with the Si-C double-bond length of 1.692 Å predicted theoretically rather than with the electron diffraction result of 1.815 Å.¹ A more detailed analysis will be presented.

*Work supported by NSF and PRF.

¹H. F. Schaefer, *Acc. Chem. Res.* **15**, 283 (1982).

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801.

FB5 (9:33)

ROTATIONAL SPECTRA AND STRUCTURES OF THE HCN-(CO₂)₂ AND HCN-(CO₂)₃ CLUSTERS*

H. S. GUTOWSKY, P. J. HAJDUK, JANE CHEN, AND R. S. RUOFF

Microwave rotational transitions have been studied for several isotopic species of each of these two clusters. The spectra were observed with the Mark II Balle/Flygare Fourier transform spectrometer, as modified. The clusters were formed by supersonic expansion of first-run neon at a backing pressure of ~2 atm with 0.1% HCN and 1 or 2% CO₂. The free CO₂ dimer and trimer were characterized recently by near-infrared laser spectroscopy.¹ Both are planar, the dimer having a slipped parallel structure and the trimer, a cyclic pinwheel with each CO₂ rotated by -43° = β from a C_{3v} structure.

In the clusters we are studying, the HCN lies on the 2- or 3-fold figure axis with the nitrogen end closest to the (CO₂)_n, perturbing its structure significantly. The C-C distance in the HCN-(CO₂)_n is reduced from 3.599 Å in free (CO₂)₂ to 3.506 Å and from 4.038 Å in free (CO₂)₃ to 3.797 Å. The CO₂'s are rotated out of the carbon plane by -17.5° and 36.4° (γ) for n = 2 and 3, respectively, with the rotations preserving the axial symmetry. For HCN-(CO₂)₂ the in-plane angle between CO₂ and the C-C vector is -61.4° versus 58.2° for free (CO₂)₂. The transitions of normal isotopic HCN-(CO₂)₂ are split by ~20 to 200 kHz, probably by inversion of the slipped parallel (CO₂)₂ structure. The splittings for the H¹³CN, HC¹⁵N, (¹³CO₂)₂, and (CO₂¹³CO₂) isotopic species are about 10% less. Experiments are underway with ¹⁸O substituted CO₂ to clarify the origin of the splittings and also to determine the sign of γ in the two clusters and the value of β in HCN-(CO₂)₃.

*Work supported by NSF and PRF.

¹R. E. Miller, *Science* **240**, 447 (1988).

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801.

Intermission

FB6 (10:05)

RELAXATION OF CONFORMERS AND ISOMERS IN SEEDED SUPERSONIC JETS OF RARE GASES*

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

We have studied the relaxation of conformers and the formation/relaxation of isomeric, weakly bonded dimers in pulsed supersonic expansions of seeded rare gases (He, Ne, Ar, Kr). The relaxation was determined from the intensity of a rotational transition for the higher energy species as a function of carrier gas composition, using the Balle/Flygare Fourier transform microwave spectrometer.

Of thirteen molecules with rotational conformers which we examined, those with barriers to internal rotation greater than 400 cm^{-1} did not relax significantly in any of the carriers. The higher energy forms of ethyl formate, ethanol, and isopropanol, with smaller barriers, were not relaxed by He, somewhat relaxed by Ne, and completely relaxed by as little as 5 to 20 mole percent of Ar or Kr in He or Ne.

Similar results have been obtained for the formation/relaxation of the weakly bonded dimer pairs: linear OCO-HCN, T-shaped HCN-CO₂; linear FH-NNO and bent NNO-HF; and bent HF-DF and DF-HF. The case of the HCN/CO₂ dimers is particularly striking.¹ The T-shaped dimer was found first, using Ar as the carrier gas. Five years later the linear form was found with first run neon as carrier, but it could not be detected at all with Ar as the carrier.

*Work supported by NSF and PRF.

¹T. D. Klots, R. S. Ruoff, and H. S. Gutowsky, J. Chem. Phys., in press.

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801.

FB7 (10:22)ROTATIONAL SPECTRA OF EXCITED Σ VIBRATIONAL STATES OF Ar-HCl AND Ar-DCl*

CARL CHUANG AND H. S. GUTOWSKY

The Σ bend and stretching vibration-rotation spectra of Ar-HCl have been characterized recently^{1,2} by far infrared spectroscopy. Using the rotational constants reported for Ar-H³⁵Cl/³⁷Cl we were able to find pure rotational transitions of the Σ states by Fourier transform microwave spectroscopy with supersonic expansion. Analysis of their ³⁵Cl/³⁷Cl isotope effects shows that the H in HCl is pointed predominantly away from the Ar.

Our observation of the rotational transitions was aided by the dependence on carrier gas of the population of excited states in the beam,³ with He giving a better signal than Ne which is better than Ar. About 20,000 FID's are needed to get a spectrum. Using this approach we have observed the Σ bending mode of Ar-D³⁵Cl and Ar-D³⁷Cl, determining B, D, and eQ_{aa} to be 1727.9915 MHz, 39.8 kHz, and -28.247 MHz, respectively, and 1686.4781 MHz, 37.8 kHz, and -2.346 MHz.

The larger centrifugal distortion constants for Ar-DCl compared to the 31.6 and 30.5 kHz for the Ar-HCl species¹ show that deuterium substitution causes the dimer to spend more time in the shallower secondary potential minimum. The B values indicate a more compact structure for the Ar-DCl dimers. Further analysis will be provided along with the results of searches in progress for Ar-DCl in other excited states.

*Work supported by NSF and PRF.

¹K. L. Busarow, G. A. Blake, K. B. Laughlin, R. C. Cohen, Y. T. Lee, and R. J. Saykally, J. Chem. Phys. **89**, 1268 (1988).

²R. L. Robinson, D.-H. Gwo, and R. J. Saykally, J. Chem. Phys. **87**, 5156 (1987).

³R. S. Ruoff, T. D. Klots, T. Emilsson, and H. S. Gutowsky, J. Chem. Phys., in press.

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801.

FB8 (10:39)

A STRUCTURAL STUDY OF THE $\text{H}_2\text{S}\cdot\text{CO}_2$ VAN DER WAALS COMPLEX

J.K. RICE, F.J. LOVAS, R.D. SUENRAM, L.H. COUDERT, K. MATSUMURA,
W. STAHL, D.J. PAULEY, AND S. KUKOLICH

The rotational spectra of $\text{H}_2\text{S}\cdot\text{CO}_2$ and two deuterated forms have been observed using a pulsed beam Fourier transform microwave spectrometer. For each of the three complexes we assign a-type and c-type transitions which are split into a "weak" and a "strong" intensity component.

The analysis based on that previously used for the $(\text{H}_2\text{O})_2$ complex and modified for application to $\text{H}_2\text{S}\cdot\text{CO}_2$ allowed us to assign two internal rotations within the complex. The following rotational constants were determined:

	A (MHz)	B (MHz)	C (MHz)
$\text{H}_2\text{S}\cdot\text{CO}_2$	10783.54 (18)	2147.63 (17)	1806.61 (17)
$\text{HDS}\cdot\text{CO}_2$	10782.94 (4200)	2107.26 (23)	1775.88 (23)
$\text{D}_2\text{S}\cdot\text{CO}_2$	10359.39 (600)	2065.37 (1)	1746.09 (1)

Two structures are possible for the complex. Both have the CO_2 and the S atom of H_2S in a T-shaped configuration. The H_2S plane is situated out of the CO_2 -S plane with the hydrogens pointing either toward ($\Theta=64^\circ$) or away ($\Theta=116^\circ$) from the CO_2 . This is determined by assuming the total dipole moment, μ_T , for $\text{H}_2\text{S}\cdot\text{CO}_2$ the complex ($\mu_T=0.918$ (24) D) is due to the H_2S dipole ($\mu_b=\text{H}_2\text{S}$)=0.9783). For either the $\Theta=64^\circ$ or $\Theta=116^\circ$ structure the R_{cm} bond distance for $\text{H}_2\text{S}\cdot\text{CO}_2$ is 3.494(24)Å.

The importance of the structure of this complex to applications in the area of bimolecular reaction dynamics will be discussed.

Address of Rice: Naval Research Laboratory, Washington, DC 20375-5000.

Rice%chem.decnet@NRL.ARPA

Address of Lovas, Suenram, Coudert and Matsumura: Molecular Spectroscopy, NIST, Gaithersburg, MD 20899.

Address of Stahl: Institute for Physical Chemistry, U. of Kiel, 2300 Kiel 1, FRG.

Address of Pauley and Kukolich, University of Arizona, Tucson, AZ 85721.

FB9 (10:56)

THE STRUCTURE OF $\text{Kr}\cdot\text{PF}_3$ DETERMINED FROM THE NUCLEAR QUADRUPOLE COUPLING CONSTANTS OF $^{83}\text{Kr}\cdot\text{PF}_3$

A. TALEB-BENDIAB, M. S. LABARGE, K. W. HILLIG II, AND R. L. KUCZKOWSKI

The ^{83}Kr nuclear quadrupole coupling constants were measured for the $\text{Kr}\cdot\text{PF}_3$ complex using a FTMW spectrometer. These values were compared with those expected from the Sternheimer equation $q_i = q_i^\circ (1 - \gamma_\infty)$ for four possible structures which are consistent with the rotational constants. The value of q_i° (field gradient arising from PF_3) for each structure was calculated using GAUSSIAN86 for free PF_3 . Information on γ_∞ (Sternheimer shielding factor) necessary for the analysis was obtained by comparison with other ^{83}Kr complexes in the literature. The conclusion was that only one structure is consistent with the quadrupole coupling constants viz the conformation placing the Kr over a PF_2 face. A comparison between *ab initio* calculations and a multipole expansion approximation to estimate the electric field gradient at the rare gas site in van der Waals complexes will be presented.

Address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

FB10 (11:13)THE MICROWAVE SPECTRUM OF THE WATER-PF₃ AND NEON-PF₃ DIMERSK. W. HILLIG II, M. S. LABARGE, AND R. L. KUCZKOWSKI

Studies of the PF₃-Ar system resulted in some six transitions which could not be assigned to that species. Since they appeared with either Ar and Ne carrier gases they were suspected to be a PF₃ dimer and this possibility was mentioned at previous conferences. We have discovered that the transitions are considerably enhanced when water is added to the rare-gas-PF₃ mixture. Twelve transitions have now been assigned and the rotational constants are plausible for a PF₃-water dimer separated by 3.24 Å (R_{cm}). The transitions appear as unequal doublets presumably split by tunneling of the water. The dipole moment of the complex is 2.28 D. This suggests that the water and PF₃ dipoles make an angle of about 110° in the complex (assuming no polarization of either species). A symmetric top spectrum was also found in the PF₃-Ne-H₂O system. Moments of inertia and mixing experiments indicate that this is the PF₃-Ne complex. R_{cm} for this dimer is 3.38 Å. Unlike PF₃-Ar and PF₃-Kr in which the rare-gas atom lies over a PF₂ face, the neon atom lies on the PF₃ symmetry axis. A simple van der Waals radius hard sphere model puts the neon atom over the F₃ face. The dipole moment of the complex is about 1.0 D, similar to free PF₃.

Address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

FC1 (8:30)

ROVIBRONIC SPECTROSCOPY OF H_3^*

L. J. LEMBO, H. HELM, P. C. COSBY, A. PETIT, AND D. L. HUESTIS

Symmetry arguments reveal that the $\tilde{B} 2p \ ^2A_2''$ state of H_3 is metastable with respect to predissociation by the ground $\tilde{X} 2p \ ^2E'$ state for only the rotationless $N = 0$ level, but for any amount and mode of vibrational excitation. We detect the existence of these levels in a fast neutral beam by laser photoabsorption, leading to photodissociation or to reionization. Since we start from only a single N , the resulting spectra are atomic-like in their simplicity.

Vibrationally excited $\tilde{B} 2p \ ^2A_2''$ levels in the beam are detected by "hot bands" in laser photodissociation in the $3s \leftarrow 2p$ and $3d \leftarrow 2p$ transitions and by autoionization in the $ns \leftarrow 2p$ and $nd \leftarrow 2p$ transitions for $n \geq 6$ or 7 for v_1 or v_2 initial vibrational excitation. Vibrationally off-diagonal transitions are observed to $3-7s$ and $3-7d$ electronic states accompanied by one quantum of v_1 symmetric-stretch vibration [by two-photon ionization ($n=3$), ionization-depletion double resonance ($n=3-5$), and autoionization ($n=6,7$)]. Excitation of v_2 asymmetric-stretch or bending vibration changes the electronic selection rules, allowing us to observe transitions to the $3pA_2''$ ($v_1=0, v_2=1$), $3pE'(0,1)$, $3pE'(1,1)$, $3pE'(0,3)$, and $3dE'(0,1)$ states, and tentatively to the $3pE'(0,2)$, $4pE'(0,1)$, and $5pE'(0,1)$ states.

Vibrationless ns ; np ; nd ; and nf Rydberg series have been observed for $n = 3-7, 9-22$; $30-90$; $3-7, 9-100$; and $26-70$; respectively. Excitation of the np and nf field-ionizing Rydberg series is accomplished by two-photon excitation using the $3s$ and $3d$ states as intermediates. In the latter case, the existence of two intermediate states with different amounts of core rotation, $3dE''(N^+=1)$ and $3dA_1'(N^+=3)$, allows us to distinguish the $nf1$ and $nf3$ Rydberg series, converging to the $N^+ = 1$ and $N^+ = 3$ ionization limits.

* Research supported by AFOSR and NSF

Address of Lembo, Helm, Cosby, and Huestis: Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

Permanent address of Petit: Commissariat a L'Energie Atomique, Centre Etude Nucleaires, Saclay France

FC2 (8:47)

ELECTRONIC SPECTROSCOPY OF THE HYDROGEN MOLECULAR ION, D_2^+ .

ALAN CARRINGTON, IAIN R. McNAB, AND CHRISTINE A. MONTGOMERIE

A description of the first measurements of an electronic spectrum of D_2^+ is presented. The lower states involved are the rotational levels of the high-lying vibrational state, $v=21$ of the $1s\sigma_g$ ground state, and the upper states are the vibration-rotation levels of the $2p\sigma_u$ long-range van der Waals state. Transitions between these levels are induced by Doppler tuning an ion beam of D_2^+ into resonance with an infrared laser. Excitation is detected by electric field dissociation of the upper levels, the resulting D^+ fragments being separated from other ions with a magnetic analyser, and detected with an electron multiplier.

Theoretical calculations predict that the $2p\sigma_u$ long-range minimum, arising from the charge/induced-dipole interaction, supports seven vibration-rotation levels. We have detected transitions to all of them, and determined the vibrational and rotational constants which characterise the van der Waals state. A preliminary observation of this spectrum has been reported¹.

¹A. Carrington, I.R. McNab and C.A. Montgomerie, Phys. Rev. Lett. **61**, 1573 (1988).

Address of Carrington, McNab and Montgomerie: Department of Chemistry, Southampton University, Southampton SO9 5NH, United Kingdom.

FC3 (9:04)

TWO-PHOTON SPECTROSCOPY OF THE $F^1\Pi_g$ AND $f^3\Pi_g$ STATES OF F_2^*

G. W. FARIS, M. J. DYER, W. K. BISCHER, AND D. L. HUESTIS

The $F^1\Pi_g$ and $f^3\Pi_g$ states of F_2 are excited from the ground $^1\Sigma_g^+$ by two photons near 207 nm and detected by vuv fluorescence or by ionization by a third photon. The laser source for these measurements is an excimer-pumped dye laser operating with PBBO dye at 415 nm. This light is doubled in a β -BaB₂O₄ crystal and focused into a cell containing a mixture of F_2 in He. The uv wavelengths were calibrated against the $B^2\Pi-X^2\Pi$ (3,0) band in NO, which was calibrated against I_2 in the visible.

Vibrational levels $v' = 0, 1, 2$ were observed in the $F^1\Pi_g$ state and $v' = 3$ in the $f^3\Pi_g$ state, based on the previous electron-impact assignments¹, and partially resolved rotationally (the effective excitation linewidth is 1 cm⁻¹). These assignments are supported by simulations of the two-photon excitation spectra.

Although the fluorescence has not yet been spectrally resolved, we believe that it arises predominantly from the triplet state even when the singlet is initially excited. In the latter case, the fluorescence is temporally delayed, and increases in intensity as the He density is increased.

The two-photon excitation scheme we have developed should be useful in investigating the kinetics of the 158 nm F_2 laser, which is believed to arise from a transition from the outer well of the $f^3\Pi_g$ state to a weakly bound $^3\Pi_u$ state correlating to ground state atoms.²

* Research supported by AFOSR

¹ K. Hoshiba *et al.*, J. Phys. B **18**, L875 (1985).

² T. Sakai *et al.*, J. Phys. B. **21**, 229 (1988).

Address of authors: Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

FC4 (9:21)

A PARTIAL DIFFERENTIAL EQUATION FOR THE RKR INTEGRAL

D. L. HUESTIS

Imposing the requirement that RKR effective potentials derived from different values of J should differ only by the nuclear rotational energy $\hbar^2 J(J+1)/2\mu R^2$, results in a nonlinear partial differential equation relating derivatives of the RKR f and g integrals, from which we can derive restrictions on the permitted forms of rovibrational energy expressions or relations between vibrational and rotational Dunham coefficients.

In the RKR approach to deriving a diatomic potential energy curve from term energies we construct the integral

$$S(U, \xi) = \sqrt{2} \int_0^{\eta(U)} [U - E(\eta, \xi)]^{1/2} d\eta,$$

where $\xi = \hbar^2 J(J+1)/\mu$ and $\eta = \hbar(v+1/2)/\sqrt{\mu}$. The inner and outer turning points are calculated from $R_{\mp} = [f/g + f^2]^{1/2} \mp f$, where $f(U, \xi) = \partial S/\partial U$ and $g(U, \xi) = -2\partial S/\partial \xi$. The Born-Oppenheimer approximation requires that RKR effective potentials, $U_{\xi}(R)$, derived for various values of J (or ξ) should all correspond to the same rotationless potential, $V_0(R) = U_{\xi}(R) - \xi/(2R^2)$. By substituting the turning points into this last relation, and differentiating with respect to U and ξ , we derive a partial differential for the RKR integral,

$$\left(\frac{\partial S}{\partial U}\right)^2 \frac{\partial^2 S}{\partial \xi^2} + \left[-2 \left(\frac{\partial S}{\partial \xi}\right) \left(\frac{\partial S}{\partial U}\right) + 8 \left(\frac{\partial S}{\partial \xi}\right)^2 \left(\frac{\partial S}{\partial U}\right)^2\right] \frac{\partial^2 S}{\partial \xi \partial U} + \left(\frac{\partial S}{\partial \xi}\right)^2 \frac{\partial^2 S}{\partial U^2} = 0.$$

While this equation is formidable to solve directly, we can derive required relations between Dunham coefficients by formal power series manipulation. Furthermore, some simple energy expressions such as $E(v, J) = T(J) + \omega(J)(v+1/2)$ [harmonic oscillator] and $E(n, l) = -1/2(n - \delta_l)^2$ [Rydberg atom] can be manipulated analytically, giving interesting new results.

Address of author: Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

FC5 (9:38)

INTERACTIVE ROTATIONAL ANALYSES OF DIATOMIC MOLECULAR SPECTRA

M. C. ABRAMS, S. P. DAVIS, AND R. PECYNER

The advent of interactive graphics on computers has permitted the development of interactive programs for the rotational analysis of the spectrum of diatomic molecules. The program ANALYSIS was developed specifically for the analysis of the spectra of medium to heavy diatomic molecules and attempts to duplicate the process an experienced spectroscopist uses to decompose a spectrum into bands and branches. Initially lines are identified and trial rotational parameters are computed, extrapolated line positions are suggested and accurate rotational parameters can be determined, even in cases where there are many missing lines or the heads are unresolved.

The advantage of an interactive graphics program, as illustrated in figure 1, is that multiple branches can be displayed and fitted simultaneously and the results displayed in terms of the spectrum on the screen. Fitted lines are indicated by enhancing the linewidth of the display, and the dots below the spectrum indicate the positions of the fitted and extrapolated lines.



Address of Abrams, Davis, and Pecyner: Department of Physics, University of California at Berkeley, Berkeley, Ca. 94720. U.S.A.

FC6 (9:55)

NUCLEAR HYPERFINE STRUCTURE IN THE ELECTRONIC SPECTRUM OF CuCl

Irene Burghardt, Lyndon R. Zink, David A. Fletcher, John M. Brown and Ian R. Beattie.

Laser excitation spectroscopy has been used to record the (0-0) bands of the $D^1\Pi - X^1\Sigma^+$ and $E^1\Sigma^+ - X^1\Sigma^+$ transitions in CuCl. The sample was vapourised in a high temperature nozzle and then cooled by expansion into a vacuum chamber. The observed rotational temperature was 15K and hyperfine structure due to the Cu nucleus was easily resolved in the D-X transition.

The spectra have been analysed and fitted to appropriate effective hamiltonians and several molecular parameters determined. The implication of these values for the structure of CuCl is examined and in particular it is suggested that the D state conforms more closely to a $^1\Pi$ state rather than a $^3\Delta_1$ state, in contradiction to some recent theoretical calculations.

Address of Burghardt, Zink, Fletcher and Brown: Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, England.

Address of Beattie: Department of Chemistry, The University, Southampton, SO9 5NH, England.

FC7 (10:07)**SPECTROSCOPY OF HIGHLY ROTATIONALLY EXCITED BaI C²Π - X²Σ⁺****D. ZHAO, P. H. VACCARO, A. A. TSEKOURAS, and R. N. ZARE**

A supersonic beam of HI crosses an effusive beam of Ba and the resulting BaI X²Σ⁺ product is probed using a single-mode CW ring dye laser at ~ 550nm via laser induced fluorescence of the BaI C²Π - X²Σ⁺ band system. Under these experimental conditions, BaI v=0 product is formed with rotational quantum numbers in excess of 500. For the isolated P₂ and P₁₂ branches of the C - X(0,0) band, single rovibronic transitions with J ranging from ~ 350 to ~ 500 are readily resolved. Previous studies¹ employing a thermal oven source provided definitive assignments of the BaI C - X(0,0) band for low J values (J < 200). These data were combined with the line positions obtained in the present study to perform a nonlinear least squares fit to the energy differences calculated from the upper and lower state model Hamiltonians. This permits rotational assignment of the high J transitions. The resulting spectroscopic constants enable a detailed explanation of the observed high-J bandhead features in the BaI C- X Δv = 0 sequence that characterize the BaI product.

¹ M. A. Johnson, C. Noda, J. S. McKillop, and R. N. Zare, Can. J. Phys. **62**,1467 (1984).

Address: Department of Chemistry, Stanford University, Stanford, CA 94305

Intermission**FC8 (10:35)****A REINVESTIGATION OF THE GOODMAN BANDS OF IODINE****T.D. McLEAN AND G.W. KING**

The Goodman bands¹ form the strongest evidence for the existence of bound states in the 28000 < T_e < 40000 cm⁻¹ region of I₂.

We have recorded the Goodman system in fluorescence following one and two-color excitation. Spectra have been obtained for both ¹²⁷I₂ and ¹²⁹I₂ using dye laser frequencies covering 16500 - 18500 cm⁻¹. At high resolution each band is resolved to reveal a cluster of 4-15 rotational lines. Our analysis has shown that the upper state is accessed via a resonance enhanced three-photon absorption process. A vibrational and rotational analysis has positively identified the upper terminus as the FO_v⁺ state (T_e = 47218 cm⁻¹), a member of the second tier of ion-pair states.

¹K.K. Lehmann, J. Smolarek, and L. Goodman, J. Chem Phys. **69**, 1569, 1978.

Address of McLean: Department of Chemistry, S.U.N.Y. Binghamton, Binghamton N.Y. 13901

Address of King: Department of Chemistry, McMaster University, Hamilton Ontario, Canada L8S-4M1

FC9 (10:47)

MICROWAVE-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF $A^3\Pi(1)$ ICl NEAR THE DISSOCIATION LIMIT.¹

J. R. Johnson, T. J. Slotterback, K. C. Janda, and D. W. Pratt

Vibrational bands near the dissociation limit of the ICl $A^3\Pi(1)$ state have been examined using microwave-optical double resonance techniques. By using a single mode ring laser and a skimmed molecular beam, hyperfine structure of the rotational lines is resolved at the MHz level. With Doppler linewidths of < 5 MHz, splittings in the optical transitions due to the chlorine nuclear quadrupole coupling are partially resolved. Analysis of these spectra results in values for the electric quadrupole and magnetic hyperfine constants which reveal changes in the electronic distribution of the molecule as it approaches dissociation. Applications of the method to the electronically excited states of polyatomic molecules will be discussed.

¹Work supported by NSF.

Address of Johnson, Slotterback, Janda, and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

FC10 (11:04)

HIGH RESOLUTION MOLECULAR-BEAM LASER SPECTROSCOPY OF STRONTIUM MONOFLUORIDE (SrF)⁺

Yoshiro Azuma and William J. Childs

The laser induced fluorescence spectrum of the red $A^2\Pi - X^2\Sigma$ system of SrF has been recorded. Typical line widths of 20MHz are obtained with the laser beam crossing the molecular beam orthogonally.

Each rotational line of the ^{88}SrF main isotope and ^{86}SrF lesser isotope is split into two components by the magnetic hyperfine interaction between the unpaired electron and the ^{19}F nuclear spin of 1/2. The rotational line assignment of this band was confirmed by the rf labelling method (1), using previously measured ground state splittings (2).

In addition, with our excellent S/N ratio, it was possible to record many lines from the much less abundant isotope ^{87}SrF , clearly showing hyperfine structure due to the ^{87}Sr nuclear spin of 9/2 as well as the hfs due to the ^{19}F with its spin of 1/2. Efforts to measure the ground state hyperfine splitting of ^{87}SrF by the rf-laser double resonance method are currently underway.

*This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract W-31-109-ENG-38.

- (1) W.J. Childs, Z. Phys. D 7, 107-112 (1987)
- (2) W.J. Childs, L.S. Goodman, and I. Renhorn, J. Mol. Spectrosc. 87, 522-533 (1981)

Address of Azuma and Childs: Physics Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, Illinois 60439

FC11 (11:21)

VIBRATIONAL ANALYSIS OF THREE NEW STATES OF CrF

T. C. DeVore, M. McQuaid, J. L. Gole

Three new electronic states of CrF and two electronic transitions tentatively assigned as Cr_2F were observed in the chemiluminescent flame resulting from the oxidation of chromium vapor under multiple collision conditions. The CrF transitions have been vibrationally analyzed and term symbols have been assigned for each. These new transitions correlated well with previously observed transitions in the "pseudo-isoelectronic" molecules MnO, CrH, and CrCl. This correlation provided the basis for determining the electronic configurations of these CrF states.

Address of DeVore: Department of Chemistry, James Madison University, Harrisonburg, VA 22807.

Address of McQuaid and Gole: School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332.

FC12 (11:38)SINGLE-LASER OODR SPECTROSCOPY OF THE $2^1\Sigma_g^+$ STATE OF Li_2 R. A. BERNHEIM, L. P. GOLD, AND CHUN HE

The Raman-shifted output of a single YAG-pumped dye laser has been used to produce two-photon transitions from the ground $X^1\Sigma_g^+$ state to the $2^1\Sigma_g^+$ state of $^7\text{Li}_2$. The lower vibrational levels of this excited state have been studied by Barakat et al.¹; our work extends the measurements to the dissociation limit at $v = 24$. The molecular constants and potential curve will be presented.

1. B. Barakat, et al., J. Mol. Spectrosc. 116, 271 (1986).

Address of Bernheim, Gold, and He: Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802

FC13 (11:50)

THE EXCITED ELECTRONIC STATE STRUCTURE OF THE LITHIUM DIMER

R. A. BERNHEIM

A detailed, comprehensive investigation of the excited electronic state structure of Li_2 has been carried out using a number of different multiphoton techniques. The results are of considerable interest, especially when compared with the corresponding states of H_2 . The core electrons are responsible for many of the major differences.

The spectroscopic studies include values for the molecular ionization potential and molecular constants for the ground state of Li_2^+ as well as for excited states of the neutral molecule. In addition, the Rydberg state structure, compound states of the neutral molecule. In addition, the Zeeman splitting and fine-structure of the triplet states will be discussed.

Address of Bernheim: 152 Davey laboratory, The Pennsylvania State University, University Park, PA 16802

RD12 (11:50)

THE DISTRIBUTION OF EXCESS CHARGE IN WATER CLUSTERS BY NEGATIVE ION PHOTOELECTRON SPECTROSCOPY

J.V. COE, G.H. LEE, J.G. EATON, S.T. ARNOLD, C. LUDEWIGT, H. HABERLAND, AND K.H. BOWEN

Trends in the vertical detachment energies of negatively charged water clusters are interpreted in terms of different structures for accommodation of the excess charge. Interpretation of the data has been aided by some elegant molecular simulations¹ as well as intuition gained from calculations on the binding of excess electrons to dielectric spheres^{1,2}. A plot of the vertical detachment energies vs. cluster size indicates three different regions which are interpreted as a progression from surface states for small cluster sizes, to internal states without cavities for intermediate cluster sizes, and internal states with cavities for the largest cluster sizes.

¹R.N. Barnett, U. Landman, C.L. Cleveland, and J. Jortner, *J. Chem. Phys.* **88**, 4429 (1988).

²P.R. Antoniewicz, G.T. Bennett, and J.C. Thompson, *J. Chem. Phys.* **77**, 4573 (1982).

Address of Arnold, Eaton, Lee, and Bowen: Department of Chemistry, The Johns Hopkins University, Baltimore MD 21218

Address of Coe: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus OH 43210

Address of Ludewigt and Haberland: Fakultat fur Physik, Universitat Freiburg, Freiburg West Germany

RE14 (5:09)

HIGH RESOLUTION INFRARED SPECTRA OF THE ν_5 , ν_6 AND ν_7 BANDS OF CYANOACETYLENE

A. V. PETERS, S. J. DAUNT AND W. E. BLASS

The three bending fundamentals of cyanoacetylene (HC₃N) have been recorded on the BOMEM FTS at the HIA/NRC in Ottawa with resolutions of 0.0025 cm⁻¹ for ν_5 (663 cm⁻¹) and ν_6 (499 cm⁻¹) and 0.010 cm⁻¹ for ν_7 (222.5 cm⁻¹). The ν_5 and ν_6 bands have been observed in the Voyager/IRIS data¹ and were the motivation for this study. None of these bands had been recorded with high resolution methods previously although excellent excited state MW have been reported.² The lowest fundamental had been seen only once before at low resolution (0.6 cm⁻¹).

The rotational structure for the fundamentals has been assigned and analyzed. Ground state constants in excellent agreement with the MW have been obtained confirming the assignments. Upper state constants have also been obtained for the fundamentals and will be reported.

Assignment of the many hot and hot-hot bands is in progress along with diode laser measurements of individual line strengths. These will be utilized to complete the modelling effort needed for both simulating the infrared spectrum of the Titanian atmosphere and for the interpretation of ground based laser heterodyne experiments.

¹ V. G. Kunde, *et al.* *Nature* **292**, 686-688 (1981).

² K. M. T. Yamada and R. A. Creswell, *J. Mol. Spectrosc.* **116**, 384-405 (1986).

Address of Peters and Daunt: Department of Chemistry, Concordia University, H-1139, 1455 de Maisonneuve Blvd. W., Montréal, Québec H3G 1M8, Canada.

Address of Daunt and Blass: Department of Physics & Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200.

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 KNIGHT, R. D.--CHAIRING
 SESSION RB
 KOFRANEK, M.--WF9, WF10,
 WF11
 KOZIN, I. N.--WF12
 KRAJNOVICH, D.--RH1
 KROHN, B. J.--MF8, RE12
 KRUPNOV, A. F.--WF12
 KUBULAT, K.--TE2
 KUCZKOWSKI, R. L.--TF5,
 TF6, FB9, FB10, CHAIRING
 SESSION TF
 KUKOLICH, S.--FB8, RF11
 KUNG, C.-Y.--FA10
 KUNZE, KATHRYN L.--MH9

L

LABARGE, M. S.--TF5, TF6,
 FB9, FB10
 LACOSSE, J. P.--ME1, ME2
 LAFFERTY, W. J.--WF12
 LAKKARAJU, H. S.--RH9
 LAO, K. Q.--MH1
 LAPIERRE, L.--TF9, TF10
 LAWALL, J. R.--RG3
 LEE, G. H.--RD12
 LEE, M. J.--TC9
 LEE, S.-i.--TG6
 LEE, SANG K.--RD3
 LEE, S. Y.--TG6
 LEE, SZETSEN--TG3
 LEE, Y. T.--ME5
 LEHMANN, K. K.--MH2
 LEMBO, L. J.--FC1
 LENG, J. M.--WE7
 LEROI, G. E.--WG'3, WG'4,
 WG'5
 LE ROY, ROBERT J.--TD12,
 TG8
 LESZCZYNSKI, J. R.--TE2
 LEUNG, H. O.--ME8
 LI, M.--RC10
 LIN, TAI-YUAN DAVID--RD3
 LINDSAY, MARK D.--RG3
 LINDSAY, N. E.--TC10

LINTON, C.--TD6, TD7
 LISCHKA, H.--WF9, WF10,
 WF11
 LIST, R. S.--WE3
 LISY, J. M.--ME1, ME2, ME3
 LITTLE, T. S.--TC11, TC12
 LIU, J. Z.--WE3
 LIU, MUJIAN--TC6
 LIU, R.--WE3
 LIU, WEN-LONG--ME3
 LIU, X.--RD10, RD11
 LOVAS, F. J.--ME4, ME10,
 TA5, TA8, TA9, TA10,
 TF3, TF4, FB8
 LUDEWIGT, C.--RD12
 LUNDBERG, J. K.--TH2, TH3
 LUNDEEN, S. R.--RB3, RG4
 LYMAN, J. L.--MF8
 LYNCH, D. L.--RB5

M

MACLER, M.A.P.--MG3
 MACPHAIL, R. A.--TB10, TB11
 MAIER, J. P.--RC6
 MAJEWSKI, W. A.--RA2, RD8,
 RD9
 MALATHY DEVI, V.--TB8, TE7,
 TE8, TE9, TE10, TE11,
 CHAIRING SESSION RF
 MANDIN, J.-Y.--TE13
 MANTZ, A. W.--TB3
 MANZKE, R.--WE6
 MARINO, M. M.--FA9
 MARSHALL, M. D.--ME8, WF9,
 WF10, WF11
 MARTIN, F.--TD6
 MARTIN, RICHARD L.--WE2
 MARTIN, R. M.--WE5
 MATHEWS, C. W.--TH10
 MATOS, J.--TF6
 MATSUMURA, K.--TA9, TF3,
 ME4, ME10, FB8
 MATSUO, Y.--MF4, MF5, MF10
 MAY, R. D.--TE14
 MAYER, STEVE--FA11, FA12
 MAYHUGH, J. E.--RC4
 McAULIFFE, M. J.--RH5
 McCALL, R. P.--WE7
 McCARRON, E. M.--WE7
 MCCARTHY, M. C.--RC10
 McCORMACK, E.--RB1
 McDOWELL, R. S.--MF8
 MCKELLAR, A.R.W.--MF1, MF2,
 TB7, RA11, FB2, CHAIRING
 SESSION WA
 MCKOY, V.--RB5
 McLEAN, T. D.--RH7, FC9
 McMAHAN, A. K.--WE5
 McNAB, I. R.--RA4, FC2
 McQUAID, M.--FC11
 MEERTS, W. L.--TA1
 MERCORELLI, L. R.--RE11
 MERRY, WAL"ER--MH5

MERZBACHER, C. I.--WE4
 MILLER, ROGER E.--MA1, TA3,
 TE1, TF7, WF13
 MILLER, S.--RA2
 MILLER, TERRY A.--TD3, TD4,
 RD3, RD4, RD10, RD11,
 FA4, FA5, FA6, FA7, FA10
 MITCHELL, J.B.A.--RG1
 MITCHELL, S. A.--TD1, TD10
 MOAZZEN-AHMADI, N.--MF1,
 MF2, RA11, FB2
 MONTGOMERIE, C. A.--RA4,
 FC2
 MOORE, R.--FAB
 MOULE, D. C.--MH10
 MUEENTER, J. S.--TH8
 MUKHOPADHYAY, I.--MF2, TC2
 MULFORD, R. N.--RE12
 MURPHY, J.--RC12
 MURPHY, W. F.--WG1

N

NACHMAN, D. F.--TD5, RC8
 NAKAI, S.--WE6
 NELSON, H. H.--RC7
 NEUSSER, H. J.--RD1
 NEWBURGH, A.--TE3
 NICOLAS, C.--TB3
 NISHIWAKI, N.--WF6, WF7
 NOCERA, DANIEL G.--WG'4,
 WG'5
 NODA, C.--MG11, MG12
 NOH, T. W.--TG6
 NORTHRUP, F. J.--WF4
 NOVICK, S. E.--TA8
 NUCKER, N.--WE6

O

O'BRIEN, L. C.--RC5
 OH, J.-J.--TF6
 O'HALLORAN, M. A.--RB4
 OKA, T.--TG1, TG2, TG3,
 TG4, RA3, RA5, RA6,
 RA9, RA10
 OKUMURA, M.--TG1, TG4
 OLIPHANT, N. H.--MH8
 OLSON, C. G.--WE3
 OWRUTSKY, J. C.--RA1
 OZIEP I.--MF1, MF2, TA1

P

PABST, VERNON W.--RE13
 PAK, K.--TD2
 PARKINSON, W. H.--RC1, RC2,
 RC3
 PARMENTER, C. S.--RH1, RH2
 PASTALAN, J. Z.--RH7
 PAULEY, D. J.--FB8, RF11
 PAULIKAS, A. P.--WE3
 PAWELKE, G.--RE9
 PECYNER, R.--FC5

PEDERSEN, L. G.--FA3
 PERRIN, A.--RE5
 PERRIN, M. Y.--TE5
 PERRY, D. S.--RE10, RE11,
 CHAIRING SESSION WF
 PERSON, M. D.--MH1
 PERSON, WILLIS B.--TE2
 PETERS, ANTONI--RE14
 PETERSON, K. I.--TA10, TA11
 PETIT, A.--FC1
 PFANSTIEL, J. F.--RD9
 PICKETT, H. M.--TF2
 PINE, A. S.--ME7, TB7, TF1
 PIPKIN, F. M.--RG3
 PIQUE, J. P.--TH2, TH3
 PITZER, R. M.--WE4, RC13
 CHAIRING SESSION WE
 PLIVA, J.--MF12
 PLUSQUELLIC, D. F.--RD6,
 RD7, RD8, RD9
 POLL, J. D.--TG5, TG6
 POLYANSKY, O. L.--WF12
 PRATT, D. W.--RD5, RD6,
 RD7, RD8, RD9, FC9
 PRATT, S. T.--RB4
 PURSELL, C. J.--RA9, RA10

Q

QIAN, X.--WG'6, WG'7
 QUADE, C. RICHARD--TC6

R

RANASINGHE, Y.--WG5
 RATCLIFF, B. B.--RH7
 REHFUSS, B. D.--TG1, RA3,
 RA5, RA6
 REUTER, D. C.--MF3
 RICE, JANE K.--RC7, RH4,
 FB8, CHAIRING SESSION TD
 RICHARDSON, HUGH--MG12,
 RE13
 RICHMOND, GERALDINE L.--MA4
 RIEDLE, E.--RD1, CHAIRING
 SESSION TH
 RINSLAND, C. P.--TB8, TE7,
 TB8, TE9, TE10, TE11
 RITTER, A.--MH5
 ROBERTS, J. A.--TC5,
 CHAIRING SESSION TC
 ROBLES, E. S.--FA10
 ROMBERG, H.--WE6
 ROSENMANN, L.--TE5
 ROTHMAN, L. S.--TE3
 RUDOLPH, H.--RB5
 RUOFF, R. S.--FB5, FB6

S

SAITO, S.--RF7
 SANDER, S. P.--TF2
 SANDROFF, C. J.--FA9

SANDS, W. D.--FA8
 SARKAR, MUNNA--WG'8
 SARKER, J. C.--TC2
 SATPATHY, S.--WE5
 SAWAMURA, T. M.--FA9
 SAYKALLY, R. J.--ME5, RA1,
 FB1
 SCHMUTTENMAER, C. A.--FB1
 SCHIRBER, J. E.--WE3
 SCHWENDEMAN, R. H.--MF4,
 MF5, MF10, MF11
 SEARS, T. J.--MF8, WF4, WF5
 SELCO, J. I.--RD2
 SENGUPTA, P. K.--WG'8
 SHAH, S. I.--WE7
 SHEEHAN, T. G.--TC10
 SHINN, N. D.--WE3
 SHIRLEY, J. E.--TE5, RC9
 SHOSTAK, S. L.--TC4
 SIMARD, B.--TD8, TD9
 SINGER, SHERWIN J.--TF11
 SLOTTERBACK, T. J.--FC9
 SMITH, M.A.H.--TB8, TE7,
 TE8, TE9, TE10, TE11
 SMITH, P. L.--RC2
 SNAVELY, D. L.--WG5,
 CHAIRING SESSION MG
 SOHL, JOHN E.--CHAIRING
 SESSION RG
 SPANGLER, LEE H.--RD5,
 FA11, FA12
 STAHL, W.--TF4, FB8
 STARK, G.--RC2
 STEIMLE, T. C.--TD5, RC8,
 RC9
 STEPHENS, J. A.--RB5
 STONE, B.--RH9
 STROH, F.--MF7
 SU, C. F.--TC7
 SU, MENG-CHIH--RH2
 SUBRAMANIAN, S.--TC7
 SUDHAKARAN, G. R.--TC2
 SUENRAM, R. D.--ME10, TA4,
 TA5, TA8, TA9, TA10,
 TF3, TF4, WF12, FB8
 SULLIVAN, J. F.--TC8
 SUSSKIND, J.--MF3
 SUZUKI, T.--WF1
 SWEETING, BARBARA R.--TH10,
 CHAIRING SESSION MH
 SZCZEPANIAK, K.--TE2
 SZTAINBUCH, I.--WG'3

T

TALEB-BENDIAB, A.--TF5, FB9
 TAM, H. S.--TC5
 TAN, X.-Q.--RD8
 TANK, VOLKER--TE15
 TANNER, S.--TH9
 TAYLOR, C. D.--MH3
 TEFFO, J.-L.--RE4
 TEMPLE, D. K.--WE4

TENNYSON, J.--RA2
 THOMPSON, J. D.--WE3
 THOMPSON, R. I.--MF2
 THOMPSON, WARREN E.--MG8,
 MG9
 THORNE, A. P.--RC3
 TIPPING, R. H.--TG5, TG6
 TOMER, J. L.--RD6
 TOMKINS, F. S.--RB4
 TOTH, R. A.--TE12
 TRETYAKOV, M. YU.--WF12
 TRUDEL, M.--MG13
 TSAY, S.-J.--TD2, TD4
 TSEKOURAS, A. A.--FC7
 TSOO, CHIACHIN--TF11
 TUCKER, T. R.--WG3

U

URBAN, WOLFGANG--TB4,
 CHAIRING SESSION TB

V

VACCARO, P. H.--FC7
 VALENTIN, A.--MF12
 VANDER AUWERA, J.--RE2
 VANDERDONK, P.--RG1
 VANDERVOORT, K.--WE3
 VAN ZEE, R. J.--MG1, MG2
 VARANASI, P.--TB9
 VARBERG, T. D.--RC11
 VARIYAR, E. J.--TB10, TB11
 VEAL, B. W.--WE3
 VIOLET, C. F.--WE4

W

WAGNER, G.--MF6
 WAITS, L. D.--RH3
 WALLACE, N. M.--RC13
 WANG, A. Y.--TC11
 WARNER, H. E.--RA8, RA11
 WATSON, J.K.G.--RA2
 WATSON, R. B.--TE3
 WEBER, M.--MF13
 WEBER, TH.--RD1
 WEBSTER, C. R.--TE14
 WELTNER, W., JR.--MG1, MG2
 WILLEY, D. R.--RF2
 WESTRE, S. G.--MH13
 WILLIAMSON, J. M.--RD4,
 RD10, RD11, FA4, FA5,
 FA6, FA7
 WINNEWISSER, B. P.--MF6,
 CHAIRING SESSION TG
 WINNEWISSER, M.--MF6, MF7
 WINTER, NICHOLAS W.--WE4

X

XAYARIBOUN, P.--MH1
 XIE, W.--TH1

XU, LI WEI--RA3, RA5, RA6

Y

YAMADA, CHIKASHI--WF3, WF6,
WF7, RF4, RF5, RF6, RF7,
RF8, CHAIRING SESSION RA
YAMAMOTO, S.--RF7
YAN, SHUXIN--FA12
YAN, WEN-BIN--MH2
YANG, A.-B.--WE3
YARON, D.--ME9, TA10, TA11
YE, H. J.--WE7
YEO, G. A.--WG2
YOSHINO, K.--RC1, RC2, RC3
YOUSIF, F. B.--RG1
YU, JEONG-A--WG'4, WG'5
YU, L.--RD4, RD10, RD11,
FA4, FA5, FA6, FA7

Z

ZARE, R. N.--FC7
ZHAO, D.--FC7
ZHAO, P.--RG3
ZHU, F.--WG5
ZINK, L. R.--FC6
ZOBOV, N. F.--WF12
ZOLANDZ, D.--TA10
ZUCKER, D.--RC2