

25th INTERNATIONAL SYMPOSIUM ON FREE RADICALS

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Symposium Address:
Department of Chemistry
The Ohio State University
120 W. 18th Avenue
Columbus, Ohio 43210, USA
email: frs@frs.mps.ohio-state.edu
<http://frs.mps.ohio-state.edu/frs>

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Contents

TALKS

Monday morning (MA)	1
Monday evening (MB)	2
Tuesday morning (TA)	7
Tuesday evening (TB)	8
Wednesday morning (WA)	13
Wednesday evening (WB)	14
Thursday morning (RA)	19
Friday morning (FA)	20

ABSTRACTS

Monday morning (MA)	21
Monday evening (MB)	24
Tuesday morning (TA)	39
Tuesday evening (TB)	41
Wednesday morning (WA)	55
Wednesday evening (WB)	57
Thursday morning (RA)	72
Friday morning (FA)	74

AUTHOR INDEX	76
PARTICIPANT LIST	79

MA. MONDAY MORNING SESSION**AUGUST 16, 1999 – 8:15 AM****Room: BALLROOM, LITTLE AMERICA HOTEL****Chair: BRIAN THRUSH, Cambridge University, Cambridge, United Kingdom****Opening Remarks****15 min 8:15****MA01****40 min 8:30**STIMULATED EMISSION PUMPING STUDIES OF HIGHLY VIBRATIONALLY EXCITED DCO (\tilde{X}^2A'): FROM SPECTRA TO UNIMOLECULAR DYNAMICSF. TEMPS, *Institut für Physikalische Chemie, Universität Kiel, Olshausenstr., 24098 Kiel, Germany.***MA02****40 min 9:15**

TURNING REACTIONS OFF AND ON WITH VIBRATIONAL EXCITATION

F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin - Madison, Madison, Wisconsin 53706.***Intermission****MA03****40 min 10:20**

TERAHERTZ SPECTROSCOPY OF FREE RADICALS

G. WINNEWISSER, *I. Physikalisches Institut, Universität zu Köln, D-50913 Cologne.***MA04****40 min 11:05**

CARBON CHAINS, CARBON RING-CHAINS, AND CARBON CLUSTERS

MICHAEL C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA, mccarthy@cfa.harvard.edu.*

MB. MONDAY POSTER PRESENTATIONS**AUGUST 16, 1999 – 7:30 PM****Room: BALLROOM, LITTLE AMERICA HOTEL****Chair: ANTHONY MERER, University of British Columbia, Vancouver, BC, Canada****MB01****1 min 7:30**

MICROWAVE SPECTROSCOPY OF TWO ISOELECTRONIC RADICALS:

2,4,6-HEPTATRIYNYL, $\text{H}_2\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$, AND 2,4-HEXADIYNYLNITRILE, $\text{H}_2\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$

WEI CHEN, *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138; and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138; and Department of Chemistry, Wesleyan University, Middletown, CT 06459; STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06459; M. C. McCARTHY, P. THADDEUS, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138; and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138.*

MB02**1 min 7:31**INFRARED SPECTRA OF MOLECULAR IONS PRODUCED FROM OCS AND CS_2 AND TRAPPED IN SOLID NEON

CATHERINE L. LUGEZ, WARREN E. THOMPSON, and MARILYN E. JACOX, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.*

MB03**1 min 7:32**

FTIR OBSERVATION OF NOVEL SILICON-CARBON AND GERMANIUM-CARBON CLUSTERS FORMED BY LASER ABLATION AND TRAPPED IN SOLID Ar

W. R. M. GRAHAM, X. D. DING, D. L. ROBBINS, S. L. WANG, and C. M. L. RITBY, *Department of Physics and Astronomy, Texas Christian University, Fort Worth, TX 76129.*

MB04**1 min 7:33**

THE ELECTRONIC STRUCTURE AND SPECTRUM OF RHODIUM MONOCARBIDE

WALTER J. BALFOUR, SCOTT G. FOUGERE, ROMNEY F. HEUFF, CHARLES X. W. QIAN, and CHI ZHOU, *Department of Chemistry, University of Victoria, B.C. Canada V8W 3V6.*

MB05**1 min 7:34**

ELECTRONIC STATES AND SPECTRA OF BiOH, BiSH AND RELATED RADICALS

EWALD H. FINK, RALF GIELEN, and OLEG SHESTAKOV, *Fachbereich Chemie, Bergische Universität-GH Wuppertal, Gaußstraße 20, D-42097 Wuppertal, Germany.*

MB06**1 min 7:35** CF_3OBr FORMATION FROM REACTION OF $\text{O}(^1\text{D})$ WITH CF_3Br IN AN ARGON MATRIX

Q. Z. QIN, L. N. ZHANG, X. F. WANG, M. H. CHEN and Q. K. ZHENG, *Laser Chemistry Institute, Fudan University, Shanghai 200433, China.*

MB07 **1 min 7:36**

ELECTRONIC AND VIBRATIONAL SPECTROSCOPY OF THE D₂-METHOXY RADICAL, CHD₂O

W.Y.FAN, I.KALINOVSKI, A.M.MANN and C.BRADLEY MOORE, *Chemical Sciences Division of the Lawrence Berkeley National Laboratory and Department of Chemistry, UC Berkeley, Berkeley 94720-1460, California, USA.*

MB08 **1 min 7:37**

$\nu_1 + \nu_5$ OF HCCN: DETERMINATION OF THE ν_5 VIBRATION ENERGY AND BARRIER TO LINEARITY

P. Y. HUNG, JIAXIANG HAN, JOHN DESAIN, W. E. JONES and R. F. CURL, *Chemistry Department and Rice Quantum Institute, Houston, Texas 77251.*

MB09 **1 min 7:38**

CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY - NITROGEN CATION

M. ALDENER, B. LINDGREN, A. PETTERSSON and U. SASSENBERG, *Department of Physics, Stockholm University, Box 6730, S-113 85 Stockholm, Sweden.*

MB10 **1 min 7:39**

INTEGRATED ABSORPTION INTENSITY AND EINSTEIN COEFFICIENTS FOR THE O₂ a¹Δ_g - X³Σ_g⁻ (0,0) TRANSITION DETERMINED BY CAVITY RING-DOWN AND HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY

IAN C. LANE, STUART M. NEWMAN, and ANDREW J. ORR-EWING, *School of Chemistry, University of Bristol, Bristol, United Kingdom BS8 1TS*; DAVID A. NEWNHAM, and JOHN BALLARD, *Atmospheric Science Division, Space Science Department, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, United Kingdom OX11 0QX.*

MB11 **1 min 7:40**

PREDISSOCIATION DYNAMICS OF THE ClO A²Π STATE STUDIED BY CAVITY RING-DOWN SPECTROSCOPY AND *AB INITIO* CALCULATIONS

WENDY H. HOWIE, IAN C. LANE, STUART M. NEWMAN, and ANDREW J. ORR-EWING, *School of Chemistry, University of Bristol, Bristol, United Kingdom BS8 1TS.*

MB12 **1 min 7:41**

THE ELECTRIC DIPOLE MOMENT OF THE B¹Π STATE OF ZrO

A. PETTERSSON, B. LINDGREN, C. LUNDEVALL, W. SHI, AND U. SASSENBERG, *Department of Physics, Stockholm University, P.O. Box 6730, 11385 Stockholm, Sweden.*

MB13 **1 min 7:42**

MICROWAVE SPECTROSCOPY OF Na₃ CLUSTERS

WOLFGANG E. ERNST, *Departments of Physics and Chemistry, The Pennsylvania State University, 104 Davey Laboratory, University Park, PA 16802*; OLEG GOLONZKA, *Frances Bitter Laboratory, MIT, Bldg. NW 14, Rm. 1215, 170 Albany Street, Cambridge, MA 02139.*

MB14 **1 min 7:43**

THE $A'^3\Sigma^+ - X^1\Sigma^+$ TRANSITION OF SILVER CHLORIDE

L.C. O'BRIEN and T.L. KELLERMAN, *Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652.*

MB15 **1 min 7:44**

INVESTIGATION OF $\text{HO}_2 + \text{RO}_2$ GAS PHASE REACTIONS USING SIMULTANEOUS UV AND NEAR-IR PROBES

S. SANDER, *The Jet Propulsion Laboratory, Pasadena, CA 91109*; L. CHRISTENSEN, M. OKUMURA, *Department of Chemistry, The California Institute of Technology, Pasadena, CA 91125.*

MB16 **1 min 7:45**

THE $\text{MgH } B'^2\Sigma^+ - X^2\Sigma^+$ TRANSITION: A NEW TOOL FOR STUDYING MAGNESIUM ISOTOPE ABUNDANCES

P. BERNATH, G. LI, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*; L. WALLACE, K. HINKLE, *Kitt Peak National Observatory, National Optical Astronomy Observatories, Tucson, AZ 85726*; R. S. RAM, *Dept. of Chemistry, University of Arizona, Tucson, AZ 85721.*

MB17 **1 min 7:46**

LABORATORY DETECTION OF FOUR NEW CUMULENE CARBENES: H_2C_7 , H_2C_8 , H_2C_9 and D_2C_{10}

ALDO J. APPONI, MICHAEL C. MCCARTHY, CARL A. GOTTLIEB AND PATRICK THADDEUS, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street MS 72, Cambridge, MA 02138.*

MB18 **1 min 7:47**

LABORATORY DETECTION OF FIVE NEW SILICON-CARBON MOLECULES: SiC_n ($n = 3, 5-8$)

ALDO J. APPONI, MICHAEL C. MCCARTHY, CARL A. GOTTLIEB AND PATRICK THADDEUS, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street MS 72, Cambridge, MA 02138.*

MB19 **1 min 7:48**

ACCURATE EQUILIBRIUM STRUCTURES AND PREDICTIONS OF SPECTROSCOPIC PROPERTIES FOR LINEAR CARBON-SILICON CLUSTERS.

PETER BOTSCHWINA, *Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße. 6, D-37077 Göttingen.*

MB20 **1 min 7:49**

DIRECT DETERMINATION OF ATMOSPHERIC ORGANIC PEROXY RADICALS USING CW-CRD (CAVITY RING-DOWN) SPECTROSCOPY

D. B. ATKINSON, *Department of Chemistry, Portland State University, Portland, OR 97207-0751.*

MB21 **1 min 7:50**

AB INITIO CALCULATION OF JAHN-TELLER COUPLING CONSTANTS

BRIAN E. APPLGATE, TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210*; and TIMOTHY A. BARCKHOLTZ, *JILA, National Institute of Standards and Technology and The Department of Chemistry and Biochemistry, University of Colorado Boulder, CO 80309 - 0440.*

MB22**1 min 7:51**

AB INITIO CALCULATIONS ON THE SPIN-ORBIT SPLITTING IN THE \tilde{C} STATE OF CF_4^+ INCLUDING DYNAMICAL JAHN-TELLER EFFECT.

H.T SOMMERDIJK and M.C. VAN HEMERT, *Leiden University, Leiden Institute of Chemistry, P.O. Box 9502, 2300RA Leiden, Netherlands.*

MB23**1 min 7:52**

OPTICAL-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF THE $1_g(^3P_2) - A^3\Pi(1_u) - X^1\Sigma_g^+$ TRANSITION OF I_2

ERIKO KAGI, HISASHI FUJIWARA, MASARU FUKUSHIMA, and TAKASHI ISHIWATA, *Hiroshima City University, Faculty of Information Sciences, Asa-Minami, Hiroshima 731-3149, JAPAN.*

MB24**1 min 7:53**

$1+1'$ PFI-ZEKE PHOTOELECTRON SPECTROSCOPY OF ACETYLENE-THE RENNER-TELLER EFFECT OF ACETYLENE CATION

SHUENN-JIUN TANG, JIM JR-MIN LIN, AND YEN-CHU HSU, *Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box23-166, Taipei, Taiwan, R.O.C. and Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C..*

MB25**1 min 7:54**

PHOTOIONIZATION SPECTROSCOPY OF ZINC MONOETHYL RADICAL AND ITS CATION

MICHAEL B. PUSHKARSKY, VADIM L. STAKHURSKY, AND TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210.*

MB26**1 min 7:55**

PHOTOCHEMISTRY, THERMOCHEMISTRY AND SPECTROSCOPY OF CARBENES

JOSEPH GUSS, PAMELA KNEPP, TIMOTHY SCHMIDT and SCOTT H. KABLE, *School of Chemistry, University of Sydney Sydney, NSW, 2006, Australia.*

MB27**1 min 7:56**

KrF EXCIMER-LASER INDUCED OZONE FORMATION AND HYDROCARBON OXIDATION IN SUPERCRITICAL CARBON DIOXIDE

JUNICHIRO OTOMO, AKINORI TAKAMI, YOSHITO OSHIMA and SEIICHIRO KODA, *Department of Chemical System Engineering, School of Engineering, The University of Tokyo Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan.*

MB28**1 min 7:57**

INFRARED DIODE LASER VELOCITY MODULATION SPECTROSCOPY OF BORON CONTAINING MOLECULAR IONS

N. T. HUNT, W. Y. FAN, Z. LIU and P. B. DAVIES, *Department of Chemistry, University of Cambridge, Cambridge, UK.*

MB29 **1 min 7:58**

KINETIC SPECTROSCOPY OF THE NCI $b^1\Sigma^+ - X^3\Sigma^-$

ANATOLY V. KOMISSAROV, MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322*; STEVE J. DAVIS, *Physical Science Inc. 20 New England Business Center, Andover, MA 01810*; GERRY C. MANKE II, *Air Force Research Laboratory, Kirtland AFB, NM 87117*.

MB30 **1 min 7:59**

NEAR THRESHOLD PHOTODISSOCIATION OF STORED OH⁺ IONS

U. HECHTFISCHER, J. LEVIN, L. KNOLL, M. LANGE, G. SAATHOF, R. WESTER, A. WOLF, D. SCHWALM, *Max-Planck-Institut für Kernphysik, D-69029 Heidelberg, Germany*; D. ZAJFMAN, *Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel*.

MB31 **1 min 8:00**

A CROSSED BEAM STUDY OF THE REACTIONS C(¹D)+ H₂ AND C(¹D)+ CH₄

A. BERGEAT, L. CARTECHINI, P. CASAVECCHIA, and G. G. VOLPI, *Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy*.

MB32 **1 min 8:01**

DISSOCIATIVE RECOMBINATION OF O₂⁺ AND THE GREEN AIRGLOW

M. LARSSON, A. AL-KHALILI, S. ROSN, L. VIKOR, J. SEMANIAK, A. LE PADELLEC, H. DANARED, M. AF UGGLAS, *Department of Physics, Box 6730, Stockholm University, S-113 53 Stockholm, Sweden*; R. PEVERALL, W. VAN DER ZANDE, *FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*; R. BOBBENKAMP, *Faculty of Physics, University of Bielefeld, 33615 Bielefeld*; J.R. PETERSON, *Molecular Physics Laboratory, SRI International, Menlo Park, California 94025*.

MB33 **1 min 8:02**

PREREACTIVE EVOLUTION OF SUBSTITUTED ETHYLENES EXCITED IN THE 6eV REGION

M.ELHANINE, B.SOEP, *Laboratoire de Photophysique Molculaire Bat 210 Universit Paris Sud 91405 Orsay France*; J.M.MESTDAGH, J.P.VISTICOT, *DRECAM, SPAM CE Saclay BP Gif sur Yvette France*.

TA. TUESDAY MORNING CARRINGTON SESSION**AUGUST 17, 1999 – 8:15 AM****Room: BALLROOM, LITTLE AMERICA HOTEL****Chair: ROBERT CURL, Rice University, Houston, TX****Alan Carrington Tribute****15 min 8:15****TA01****40 min 8:30**

MICROWAVE SPECTROSCOPY AT THE DISSOCIATION LIMIT

ALAN CARRINGTON, *Department of Chemistry, University of Southampton, UK.***TA02****40 min 9:15**SPECTROSCOPY AND DYNAMICS OF H₂OHDAVID C. CLARY, *Department of Chemistry, University College London, London WC1H 0J, UK.***Intermission****TA03****40 min 10:20**

FREE RADICAL SPECTROSCOPY AND DYNAMICS BY LASER ABSORPTION TECHNIQUES

TREVOR J. SEARS, *CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY, UPTON, NY 11973-5000.***TA04****40 min 11:05**

FAR-INFRARED LASER MAGNETIC RESONANCE

KENNETH M. EVENSON, *Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO 80303-3328.*

TB. TUESDAY POSTER PRESENTATIONS

AUGUST 17, 1999 – 7:30 PM

Room: BALLROOM, LITTLE AMERICA HOTEL

Chair: PETER BOTSCHWINA, Universitat Gottingen, Gottingen, Germany

TB01

1 min 7:30

LASER-INDUCED FLUORESCENCE DETECTION OF ATMOSPHERIC NO₂ AT PARTS PER TRILLION MIXING RATIOS: IMPLICATIONS FOR NITROGEN OXIDE PHOTOCHEMISTRY IN THE STRATOSPHERE AND TROPOSPHERE

PROFESSOR RONALD C. COHEN, B64A HILDEBRAND, DEPARTMENT OF CHEMISTRY, AND DEPARTMENT OF GEOLOGY AND GEOPHYSICS, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720-1460.

TB02

1 min 7:31

EFFECT OF WATER ON PARTICLE FORMATION IN DILUTE AROMATIC GAS MIXTURES

REGINA J. CODY, Astrochemistry Branch, NASA's Goddard Space Flight Center, Greenbelt, MD 20771; MARK A. IANNONE, Department of Chemistry, Millersville University, Millersville, PA 17551; and FRED L. NESBITT, Department of Natural Sciences, Coppin State College, Baltimore, MD 21216.

TB03

1 min 7:32

HIGH-RESOLUTION INFRARED SPECTROSCOPY OF Ar-OH

MARTYN D. WHEELER, R. TIMOTHY BONN, and MARSHA I. LESTER, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

TB04

1 min 7:33

CROSSED BEAM REACTIVE SCATTERING OF CONTINUOUS SUPERSONIC BEAMS OF C(³P, ¹D) ATOMS AND CN(²Σ⁺) RADICALS

A BERGEAT, L. CARTECHINI, P. CASAVECCHIA, and G. G. VOLPI, Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy.

TB05

1 min 7:34

FLASH PYROLYSIS INFRARED LASER JET SPECTROSCOPY OF FREE RADICALS AND TRANSIENT MOLECULES

RAY J. LIVINGSTONE, ZHUAN LIU and PAUL B. DAVIES, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

TB06

1 min 7:35

ALL ELECTRON AB INITIO INVESTIGATIONS OF DIATOMIC TRANSITION METAL CARBIDES

I. SHIM, Technical University of Denmark, Department of Applied Chemistry, DTU 375 DK2800 Lyngby, Denmark; K. A. GINGERICH, Texas A&M University, Chemistry Department, PO Box 300012, College Station, TX 77843-3012, U.S.A.

- TB07** **1 min 7:36**
 EPR AND MO CALCULATION STUDIES ON AMINOANTHRAQUINONE ANION RADICALS
 VIRPI VATANEN, JUSSI ELORANTA, MIKKO VUOLLE, *Dpartment of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40351 Jyväskylä, Finland.*
- TB08** **1 min 7:37**
 OBSERVATION AND ANALYSIS OF THE ELECTRONIC EMISSION OF $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi_i$ OF THE FREE RADICAL $HC\dot{S}i$.
 R. CIREASA, D. COSSART, and M. VERVLOET, *Laboratoire de Photophysique Moléculaire du CNRS, Bât. 213, Université Paris-Sud, 91405 Orsay Cedex, France.*
- TB09** **1 min 7:38**
 FEMTOSECOND LASER SPECTROSCOPY ON THE VIBRATIONAL WAVE PACKET DYNAMICS OF THE $D^1\Pi_u$ STATE OF Rb_2
 BO ZHANG, TONY HANSSON, LARS-ERIK BERG and RENÉE ANDERSSON, *Physics Department I, The Royal Institute of Technology, S-100 44 Stockholm, Sweden.*
- TB10** **1 min 7:39**
 PRODUCTION OF HO_2 FROM ETHYL RADICAL + O_2 MEASURED FROM 298-700 K
E. CLIFFORD, J. FARRELL, J. DESAIN, C. TAATJES, *Combustion Research Facility, MS 9055, Sandia National Laboratories, 7011 East Avenue, Livermore, CA 94550.*
- TB11** **1 min 7:40**
 ON MAPPING COMETARY MAGNETIC FIELDS BY HANLE-EFFECT MEASUREMENTS
J. E. ALLEN, JR., *Astrochemistry Branch, NASA Goddard Space Flight Center, Greenbelt, MD 20771.*
- TB12** **1 min 7:41**
 THE NEAR INFRARED TRANSITION OF COPPER CHLORIDE BY INTRACAVITY LASER SPECTROSCOPY
J.J. O'BRIEN, *Department of Chemistry, University of Missouri, St. Louis, MO 63121-4499*; L.C. O'BRIEN, *Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652.*
- TB13** **1 min 7:42**
 HIGH RESOLUTION SPECTROSCOPIC STUDIES OF BENDING VIBRATIONS OF CARBON CHAIN FREE-RADICALS
MICHAEL D. ALLEN, KENNETH M. EVENSON, *Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO 80303-3328*; FUGE SUN, ROBERT F. CURL, *Department of Chemistry MS60, Rice University, 6100 South Main, Houston, TX 77005*; and JOHN M. BROWN, *The Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom.*
- TB14** **1 min 7:43**
 DISCRIMINATION OF PRODUCT ISOMERS IN THE PHOTODISSOCIATION OF HYDROCARBON MOLECULES (PROPYLENE, ALLENE, AND 1,3-BUTADIENE) AT 1933 Å
WEIZHONG SUN, KIICHI YOKOYAMA, JASON C. ROBINSON, AND DANIEL M. NEUMARK, *Department of Chemistry, University of California, Berkeley, CA 94720, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720.*

TB15 **1 min 7:44**

CALCULATION OF STATE-TO-STATE RATE COEFFICIENTS FOR $H_2(v,j) + H_2(v',j')$

M. E. MANDY, *Program in Chemistry, University of Northern British Columbia, 3333 University Way, Prince George, BC V2N 4Z9.*

TB16 **1 min 7:45**

STEREODYNAMICS OF THE $H + CO_2 \rightarrow OH + CO$ REACTION

M. BROUARD, W. DENZER, D. W. HUGHES, K. S. KALOGERAKIS, V. G. STAVROS, and J.P. SIMONS, *Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom.*

TB17 **1 min 7:46**

UV-LASER PHOTOLYSIS OF BROMOFORM: KINETIC ROTATIONAL SPECTROSCOPY OF CBr AND HCB_r

MARCEL BOGEY, CLAIRE DEMUYNCK, MELINDA HASSOUNA and ADAM WALTERS, *Laboratoire PhLAM, CERLA, University of Lille 1, F-59655 Villeneuve d'Ascq, France.*

TB18 **1 min 7:47**

EMPIRICAL POTENTIAL ENERGY SURFACES FOR THE R·XH/D (R=Ne, Ar, Kr; X=O, S) FAMILY OF COMPLEXES

CHRISTOPHER C. CARTER, HEE-SEUNG LEE, ANNE B. MCCOY, EDWARD F. HAYES, AND TERRY A. MILLER, *Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.*

TB19 **1 min 7:48**

HIGH RESOLUTION STUDIES OF THE PHOTOCHEMISTRY OF THE \tilde{A}^2A_1 STATE OF THE CH₃S RADICAL

BRIAN E. APPELEGATE, MICHAEL B. PUSHKARSKY, AND TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210.*

TB20 **1 min 7:49**

CAVITY RINGDOWN SPECTROSCOPY OF HC₇H AND HC₉H

C. D. BALL, M. C. MCCARTHY, and P. THADDEUS, *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138 and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138.*

TB21 **1 min 7:50**

THE ROTATIONAL SPECTRUM OF IODINE DIOXIDE, OIO

CHARLES E. MILLER, *Department of Chemistry, Haverford College, Haverford, PA 19041-1392;* and EDWARD A. COHEN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099.*

TB22 **1 min 7:51**

THE ROTATIONAL SPECTRA OF IO AND BrO

CHARLES E. MILLER, *Department of Chemistry, Haverford College, Haverford, PA 19041-1392;* EDWARD A. COHEN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099* ; and HOLGER S. P. MÜLLER, *I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, D-50937 Köln, Germany.*

TB23 **1 min 7:52**

FOURIER TRANSFORM EMISSION SPECTROSCOPY AND AB INITIO CALCULATIONS ON OsN

P. BERNATH, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*;
R. S. RAM, *Dept. of Chemistry, University of Arizona, Tucson, AZ 85721*; J. LIEVIN, *Universite Libre de Bruxelles, Laboratoire de Chimie Physique Moleculaire, CP 160/09 Av. F. D. Roosevelt 50, Bruxelles, Belgium.*

TB24 **1 min 7:53**

ROTATIONALLY RESOLVED SPECTRA OF ISOVALENT NbCr AND VCr

SHANE M. SICKAFOOSE, JON D. LANGENBERG, AND MICHAEL D. MORSE, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112.*

TB25 **1 min 7:54**

LIFETIME MEASUREMENT OF THE $C^3\Delta$ STATE OF TiS AND THE $E^3\Pi$ STATE OF TiO

CECILIA LUNDEVALL, *Department of Physics, Stockholm University, Box 6730, 11385 Stockholm, Sweden*;

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TB26 **1 min 7:55**

REMPE SPECTROSCOPY OF TRANSITION METAL CONTAINING MOLECULES

JOHN A. DICKINSON, and TIMOTHY C. STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe, Az, 85287-1604.*

TB27 **1 min 7:56**

SPECTROSCOPIC INVESTIGATION OF NiSi: IDENTIFICATION OF THE GROUND AND EXCITED ELECTRONIC STATES.

NED F. LINDHOLM, GRETCHEN K. ROTHSCOPF, DALE J. BRUGH, AND MICHAEL D. MORSE, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112.*

TB28 **1 min 7:57**

LASER SPECTROSCOPY OF SILVER-AMMONIA COMPLEXES

JUN MIYAWAKI, KO-ICHI SUGAWARA and HARUTOSHI TAKEO, *National Institute of Materials and Chemical Research, National Institute for Advanced Interdisciplinary Research, Higashi 1-1-4, Tsukuba, Ibaraki 305, Japan.*

TB29 **1 min 7:58**

INFRARED LINESHAPES IN FINITE CLUSTERS AND MATRIX ISOLATION

JOHN S. WINN and PING HU, *Department of Chemistry, Dartmouth College, Hanover, NH 03755.*

TB30 **1 min 7:59**

IR SPECTRUM OF HNNO IN SOLID XE MATRIX

SANDRA L. LAURSEN, *NOAA Aeronomy Lab, R/E/AL2, 325 Broadway, Boulder, CO 80303*; ALICE E. DELIA, KWASI MITCHELL, *Kalamazoo College, Kalamazoo, MI 49006.*

TB31**1 min 8:00**

ULTRAFAST REACTIVITY OF INFRARED EXCITED ELECTRON AND EARLY FORMATION OF A SULFUR-CENTERED RADICAL ANION IN SOLUTION

Y. GAUDUEL, H. GELABERT and F. GUILLOUD, *Laboratoire d'Optique Appliquée, CNRS UMR 7639 - INSERM U 451, Ecole Polytechnique-ENSTA, 91761 Palaiseau cedex, FRANCE.*

TB32**1 min 8:01**

PHOTODISSOCIATION OF VINYL RADICAL (C_2H_3) VIA THE FIRST EXCITED STATE: THE $C_2H_2(\tilde{X}^1\Sigma_g^+) + H$ CHANNEL

KESHENG XU and JINGSONG ZHANG, *Department of Chemistry and Air Pollution Research Center, University of California, Riverside, CA 92521-0403.*

TB33**1 min 8:02**

ABNORMAL BEHAVIOR OF THE DEPOLARIZATION FACTOR OF BENZENE

O. ELOUTASSI, A. HAJJARI, and M. HAMEDOUN, *Faculty of Sciences Dhar Mahraz Fes, BP. 1796, Fes-Atlas, Morocco*; L. LETAMENDIA, *Bordeaux I Sciences University, CPMOH, Dept. de Recherche Physique, 33405 Talence Cedex, France.*

WA. WEDNESDAY MORNING SESSION**AUGUST 18, 1999 – 8:15 AM****Room: BALLROOM, LITTLE AMERICA HOTEL**

Chair: JOHN S. WINN, Dartmouth College, Hanover, NH
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WA01 **40 min 8:15**

PHOTODISSOCIATION DYNAMICS OF HYDROCARBON RADICALS

PETER CHEN, *Laboratorium für Org. Chemie, ETH Zürich, Zürich, Switzerland.*

WA02 **40 min 9:00**

MICROWAVE AND LASER SPECTROSCOPIC STUDIES OF CARBON-CHAIN FREE RADICALS

YASUKI ENDO, *Department of Basic Sciences, The University of Tokyo, 153-8902 Tokyo, Japan.*

Intermission**WA03** **40 min 10:15**

ELECTRONIC SPECTROSCOPY OF ATMOSPHERIC RADICALS

PROFESSOR VERONICA VAIDA, *University of Colorado at Boulder, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215.*

WA04 **40 min 11:00**

STUDY OF HIGHLY-PREDISSOCIATIVE STATES OF FREE RADICALS USING TWO-COLOR RESONANT FOUR-WAVE MIXING TECHNIQUE

YUAN-PERN LEE, *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043.*

WB. WEDNESDAY POSTER PRESENTATIONS

AUGUST 18, 1999 – 7:30 PM

Room: BALLROOM, LITTLE AMERICA HOTEL

Chair: MATS LARSSON, Stockholm University, Stockholm, Sweden

WB01 **1 min 7:30**

REMPI STUDIES OF CF AND CF₃ FREE RADICALS

Q. LI, Q. ZHANG, J. SHU, X. ZHOU, S. YU, C. CHEN, AND X. MA, *Department of Chemical Physics, Open Laboratory of Bond-Selective Chemistry of CAS, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.*

WB02 **1 min 7:31**

OBSERVATION OF MOLECULAR HYPERFINE QUANTUM BEATS USING NANOSECOND TRANSIENT GRATING SPECTROSCOPY

S.A. REID, J.P. SCHMIDT, Y. TANG, and B. LIANG, *Department of Chemistry, Marquette University, Milwaukee, WI 53201-1881.*

WB03 **1 min 7:32**

VIBRATIONAL SPECTROSCOPY OF ENTRANCE CHANNEL COMPLEXES

MARTYN D. WHEELER, MICHAEL W. TODD, DAVID T. ANDERSON, MARIA TSIOURIS, and MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

WB04 **1 min 7:33**

THE VISIBLE SPECTRUM OF THE VINYL RADICAL MEASURED WITH CAVITY RING-DOWN LASER ABSORPTION SPECTROSCOPY.

J.B. HALPERN, K. PATRICK, S. ALFRED, *Department of Chemistry, Howard University, Washington, DC 20059*; C. D. PIBEL, *Department of Chemistry, American University, 4400 Massachusetts Ave. NW, Washington, D.C. 20016-8014*; A. MCILROY AND C. A. TAATJES, *Combustion Research Facility, Sandia National Laboratory, Livermore, CA 94551-0969.*

WB05 **1 min 7:34**

ELECTRONIC SPECTRA OF YOH AND YOD IN THE VISIBLE REGION; STRONG VIBRONIC COUPLING BETWEEN THE $\tilde{B}^1\Pi$ AND $\tilde{C}^1\Sigma^+$ STATES

A. G. ADAM, *Department of Chemistry, University of New Brunswick, Bag Service 45222, Fredericton, N.B. E3B 6E2, Canada*; K. ATHANASSENAS, C. T. KINGSTON, A. J. MERER, J. R. D. PEERS, S. J. RIXON, *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada*; and D.A. GILLET, *Lambda-Physik, Inc., 3201 West Commercial Blvd., Fort Lauderdale, FL 33309.*

WB06 **1 min 7:35**

DISPERSED FLUORESCENCE SPECTROSCOPY OF MoC, RuC, and PdC: AN EXAMINATION OF LOW-LYING ELECTRONIC STATES

RYAN S. DaBELL, RAYMOND G. MEYER, and MICHAEL D. MORSE, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112.*

WB07 **1 min 7:36**
SPECTROSCOPY OF THE SO RADICAL

JOHN M. F. ELKS and COLIN M. WESTERN, *School of Chemistry, University of Bristol, Cantock's Close, Bristol. BS8 1TS. UK. (e-mail: John.Elks@bristol.ac.uk, C.M.Western@bristol.ac.uk).*

WB08 **1 min 7:37**
UV AND VISIBLE ABSORPTION CROSS-SECTIONS OF O₂

R.COLIN, S.FALLY, M.CARLEER, *UNIVERSITE LIBRE DE BRUXELLES, LABORATOIRE DE CHIMIE PHYSIQUE MOLECULAIRE, CP160/09, 50, AV.F.D. ROOSEVELT, 1050 BRUSSELS, BELGIUM*; B.COQUART, A.JENOUVRIER, M.-F.MERIENNE, *GROUPE DE SPECTROMETRIE MOLECULAIRE ET ATMOSPHERIQUE, URAD1434, UFR SCIENCES, MOULIN DE LA HOUSSE, 51687 REIMS CEDEX 2, FRANCE*; and A.C.VANDAELE, *INSTITUT D'AERONOMIE SPATIALE DE BELGIQUE, 3 AV.CIRCULAIRE, 1180 BRUSSELS, BELGIUM.*

WB09 **1 min 7:38**
TRAPPING AND SPECTROSCOPY OF MOLECULES IN COLD HELIUM DROPLETS

FRANK RUEDIGER BRUEHL, M. KENT BALLARD, AND WOLFGANG E. ERNST, *Departments of Physics and Chemistry, The Pennsylvania State University, 104 Davey Laboratory, University Park, PA 16802.*

WB10 **1 min 7:39**
PREDISSOCIATION DYNAMICS AND DYNAMICS OF HCP: DIRECT DETECTION OF CP RADICAL

HARUKI ISHIKAWA, TOSHIYUKI SASAKI, and NAHIKO MIKAMI, *Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan.*

WB11 **1 min 7:40**
STUDY OF VINYLIDENE-ACETYLENE ISOMERIZATION BY COULOMB EXPLOSION IMAGING

J. LEVIN, *Max-Planck-Institut für Kernphysik, D-69029 Heidelberg, Germany*; H. FELDMAN, A. BAER, D. BEN HAMU, D. ZAJFMAN, Z. VAGER, *Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel.*

WB12 **1 min 7:41**
INVESTIGATION OF THE FORMYL AND ISOFORMYL STRUCTURAL ISOMERS BY COULOMB EXPLOSION IMAGING

R. WESTER, U. HECHTFISCHER, L. KNOLL, M. LANGE, J. LEVIN, M. SCHEFFEL, D. SCHWALM, A. WOLF, *Max-Planck-Institut für Kernphysik, D-69029 Heidelberg, Germany*; A. BAER, Z. VAGER, D. ZAJFMAN, *Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel.*

WB13 **1 min 7:42**
EXPERIMENTAL DETERMINATION OF BOND ANGLE DISTRIBUTION IN QUASILINEAR MOLECULES

ADAM BAER, Z. VAGER, D. ZAJFMAN, *Particle Physics, Weizmann Institute of Science, Rehovot 76100, Israel*; J. LEVIN, L. KNOLL, A. WOLF, R. WESTER, D. SCHWALM, *Max-Planck-Institut für Kernphysik, 69029 Heidelberg, Germany.*

WB14**1 min 7:43**

COLLISIONAL PROCESSES NEAR THE CH B $^2\Sigma^-v' = 0, 1$ PREDISSOCIATION LIMIT AND THEIR APPLICATION TO LASER-INDUCED FLUORESCENCE FLAME DIAGNOSTICS

ROBERT J.H. KLEIN-DOUWEL, JORGE LUQUE, JAY B. JEFFRIES, GREG P. SMITH, and DAVID R. CROSLY, *Molecular Physics Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025.*

WB15**1 min 7:44**

INVESTIGATION OF THE ROTATIONAL SPECTRUM OF BiO IN THE $X^2\Pi$ ELECTRONIC STATE

EDWARD A. COHEN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109-8099*; DAMIAN M. GOODRIDGE and KENTAROU KAWAGUCHI, *Nobeyama Radio Observatory, Minamimaki, Minamisaku, Nagano 384-1305, Japan.*

WB16**1 min 7:45**

SOLVATION OF MAGNESIUM AND SINGLY IONISED MAGNESIUM ATOMS IN NH₃ CLUSTERS , THEORY AND EXPERIMENT

M.ELHANINE, B.SOEP, *Laboratoire de Photophysique Molculaire Bat 210 Universit Paris Sud 91405 Orsay France*; L. DUKAN, P. MAITRE, *Laboratoire de Chimie Thorique, Universite Paris-Sud, Bt. 490*; W.H.BRECKENRIDGE, S. MASSICK, *Department of Chemistry University of Utah Salt Lake city.*

WB17**1 min 7:46**

ISOTOPE EFFECTS ON STRUCTURE AND DYNAMICS OF SOME RADICAL CATIONS STUDIED BY AB INITIO AND DFT CALCULATIONS AND ESR SPECTROSCOPY

S. LUNELL and T. FÄ NGSTRÖ M, *Department of Quantum Chemistry, Uppsala University, Box 518, S-751 20 Uppsala, Sweden*; P. WANG, and M. SHIOTANI, *Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739, Japan.*

WB18**1 min 7:47**

A THEORETICAL STUDY OF THE ACETYLIDE ANION, HCC⁻

MIRJANA MLADENOVIĆ, PETER BOTSCHWINA, *Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße 6, D-37077 Göttingen*; PETER SEBALD, *Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany*; STUART CARTER, *Department of Chemistry, University of Reading, Reading RG6 2AD, United Kingdom.*

WB19**1 min 7:48**

THE ELECTRONIC STATES OF THE FeH RADICAL : A PROGRESS REPORT

JOHN M BROWN, RICHARD F. BARROW, DANIEL F. HULLAH and CATHERINE WILSON, *The Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ, United Kingdom.*

WB20**1 min 7:49**

PURE ROTATIONAL AND FINE-STRUCTURE TRANSITIONS OF NITRIC OXIDE (NO) IN ITS GROUND VIBRATIONAL STATE

THOMAS D. VARBERG, *Department of Chemistry, Macalester College, St. Paul, MN 55105*; FRED STROH, *Institute for Stratospheric Chemistry, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*; KENNETH M. EVENSON, *Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO 80303.*

WB21**1 min 7:50**

IDENTIFICATION OF NEW LOW-LYING ELECTRONIC STATES OF THE TiCl^+ AND TiF^+ MOLECULAR IONS BY DISPERSED LASER INDUCED FLUORESCENCE

C. FOCSA ^a, B. PINCHEMEL, and M. BOGEY, *Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523, Centre d'Etudes et de Recherches Lasers et Applications, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France.*

^aPresent address: Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

WB22**1 min 7:51**

MILLIMETER-WAVE SPECTROSCOPY OF ALKALI AND ALKALINE-EARTH AMIDE SPECIES

M. A. BREWSTER, P. M. SHERIDAN, J. M. THOMPSEN, J. XIN, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and the Steward Observatory, University of Arizona, Tucson, AZ 85719.*

WB23**1 min 7:52**

LIF STUDIES ON THE UNIMOLECULAR DECOMPOSITION OF CHEMICALLY ACTIVATED SILANOL

ATSUKO TAKAHARA, RYUTA ARAKI, ATSUMU TEZAKI, and HIROYUKI MATSUI, *The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656 Japan.*

WB24**1 min 7:53**

FAST-SCAN, PULSED-JET SUBMILLIMETER WAVE ABSORPTION SPECTROSCOPY OF TRANSIENT SPECIES

DMITRY G. MELNIK, SANDHYA GOPALAKRISHNAN, TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210*; and FRANK C. DE LUCIA, *The Ohio State University, Dept. of Physics, Microwave Laboratory, 174 W. 18th Avenue, Columbus OH 43210.*

WB25**1 min 7:54**

OPTICAL STARK MEASUREMENT OF THE $\text{C}^3\Delta - \text{X}^3\Delta$ BAND OF TiS AND THE $\text{C}^1\Sigma^+ - \text{X}^1\Sigma^+$ BAND OF ZrS

ROBERT R. BOUSQUET, KEI-ICHI C. NAMIKI and TIMOTHY C. STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe, Az, 85287-1604.*

WB26**1 min 7:55**

THE PERMANENT ELECTRIC DIPOLE MOMENTS OF THE $\text{A}''^1\Sigma^+$ AND $\text{A}^1\Pi$ STATES OF P^1C

SARA BEATON, ROBERT BOUSQUET AND TIMOTHY STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604.*

WB27**1 min 7:56**

LIF JET SPECTROSCOPY OF METAL-BEARING FREE RADICALS

MASARU FUKUSHIMA and TAKASHI ISHIWATA, *Department of Information Sciences, Hiroshima City University, Asa-Minami, Hiroshima 731-3194, Japan.*

WB28**1 min 7:57**

EFFECTS DETERMINING THE 1+1' PFI-ZEKE PHOTOELECTRON SPECTRUM OF ACETYLENE

SHUENN-JIUN TANG, JIM JR-MIN LIN, AND YEN-CHU HSU, *Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 107, Taiwan, R. O. C. and Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O. C.*

WB29**1 min 7:58**TRANSITION STATE DYNAMICS OF THE OH + OH > O (³P) + H₂O REACTION

HANS-JUERGEN DEYERL and R. E. CONTINETTI, *Department of Chemistry and Biochemistry, University of California San Diego (UCSD), 9500 Gilman Drive, La Jolla CA 92093.*

WB30**1 min 7:59**THE CONSERVATION OF ANGULAR MOMENTUM IN POLYATOMIC PHOTOCHEMICAL REACTIONS: H₂CO AND D₂CO

SIOBHAN E. WAUGH, ONDREJ VOTAVA and SCOTT H. KABLE, *School of Chemistry, University of Sydney Sydney, NSW, 2006, Australia.*

WB31**1 min 8:00**CROSSED BEAM STUDIES OF THE REACTION DYNAMICS OF NITROGEN ATOMS WITH SATURATED AND UNSATURATED HYDROCARBONS: N(²D)+CH₄, C₂H₂, AND C₂H₄

M. ALAGIA, N. BALUCANI, A. BERGEAT, L. CARTECHINI, P. CASAVECCHIA, and G. G. VOLPI, *Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy.*

WB32**1 min 8:01**ELECTRONIC SPECTROSCOPY OF THE CN-H₂/D₂ VAN DER WAALS COMPLEX

YALING CHEN, ALEXEY L. KALEDIN, and MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

WB33**1 min 8:02**DETERMINATION OF MOLECULAR CONSTANTS OF C_S⁺ BY VELOCITY MODULATION LASER SPECTROSCOPY

YUYAN LIU, HONGPING LIU, HUI GAO, CHUANXI DUAN, *Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, PRC*; P. A. HAMILTON, *Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London, UK E1 4NS*; P. B. DAVIES, *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW.*

RA. THURSDAY MORNING SESSION**AUGUST 19, 1999 – 8:15 AM****Room: BALLROOM, LITTLE AMERICA HOTEL****Chair: MICHAEL MORSE, University of Utah, Salt Lake City, UT****RA01****40 min 8:15**

RAPID EVAPORATIVE COOLING SUPPRESSES FRAGMENTATION IN MASS SPECTROMETRY: SYNTHESIS OF “UNPROTONATED” WATER CLUSTER IONS

RIENK T. JONGMA, YUHUI HUANG, SHIMING SHI, and ALEC WODTKE, *Department of Chemistry, University of California, Santa Barbara, CA 93106.*

RA02**40 min 9:00**

ON THE PHOTOIONIZATION OF STATE-SELECTED ACYL RADICALS: CATION STRUCTURE AND VIBRATIONAL RELAXATION DYNAMICS

R. J. FOLTYNOWICZ, E. ZUCKERMAN, J. D. ROBINSON, H. G. HEDDERICH, and E. R. GRANT, *Department of Chemistry, Purdue University, West Lafayette, IN 47907.*

Intermission**RA03****40 min 10:05**

METAL-LIGANDS AND METAL-METAL INTERACTIONS: SPECTROSCOPY AND KINETICS

BENOIT SIMARD, *Molecular Spectroscopy Program, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6.*

FA. FRIDAY MORNING SESSION**AUGUST 20, 1999 – 8:15 AM****Room: BALLROOM, LITTLE AMERICA HOTEL**

Chair: PETER BERNATH, University of Waterloo, Waterloo, Ontario, Canada
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FA01 **40 min 8:15**PHOTOELECTRON STUDIES OF METHYLNITRENE, CH₃N

BARNEY ELLISON, *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215.*

FA02 **40 min 9:00**THE INFRARED SPECTRUM OF CH₅⁺

TAKESHI OKA, *Department of Chemistry, Department of Astronomy and Astrophysics, and the Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637.*

Intermission**FA03** **40 min 10:05**

SPECTROSCOPY OF CARBON CHAINS AND THEIR IONS

J. P. MAIER, *Institute for Physical Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.*

FA04 **40 min 10:50**

FREE RADICAL REACTION DYNAMICS WITH CROSSED BEAMS

PIERGIORGIO CASAVECCHIA, *Departimento di Chimica, Università di Perugia, 06123 Perugia, Italy.*

Closing Remarks **15 min 11:35**

MA. MONDAY MORNING SESSION

AUGUST 16, 1999 – 8:15 AM

Room: BALLROOM, LITTLE AMERICA HOTEL

Chair: BRIAN THRUSH, Cambridge University, Cambridge, United Kingdom

Opening Remarks

15 min 8:15

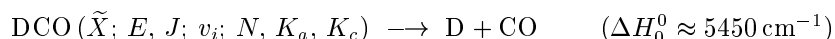
MA01

40 min 8:30

STIMULATED EMISSION PUMPING STUDIES OF HIGHLY VIBRATIONALLY EXCITED DCO (\tilde{X}^2A'): FROM SPECTRA TO UNIMOLECULAR DYNAMICS

F. TEMPS, *Institut für Physikalische Chemie, Universität Kiel, Olshausenstr., 24098 Kiel, Germany.*

The deuterated formyl radical, DCO (\tilde{X}^2A'), and its unimolecular dissociation reaction according to



provide a nearly ideal model system for investigating the unimolecular dissociation dynamics of highly vibrationally excited molecules at a fully quantum state resolved level. Stimulated Emission Pumping (SEP) experiments yield precise energies and widths, *i.e.* state-specific unimolecular decay rates, of ≥ 100 short-lived “resonance states” of the radical up to excitation energies of $18\,200 \text{ cm}^{-1}$, *i.e.* very far above the asymptotic dissociation limit. Great importance arises from an almost perfect 1 : 1 : 2 degeneracy between the radical’s three vibrational modes. Recent analyses of the measured spectra provide extraordinarily rich insight into the unimolecular dynamics. Focusing on these new results, observed spectra of DCO (\tilde{X}) are analyzed and assigned using an effective Hamiltonian based on a local mode, anharmonic oscillator, vibrational polyad model. The model calculations are in excellent agreement with the available experimental data *and* with the available quantum dynamics calculations. A one-to-one correspondence between the different data is established. The fitted parameters of the effective Hamiltonian reflect fundamental features of the PES and reveal the coupling between the conserved and disappearing oscillators during the dissociation. The calculated vibrational eigenfunctions are examined regarding their compositions in terms of chemically meaningful basis functions and regarding the fractionation of the bright state character (the CO stretching mode) among the other modes. The eigenfunctions are used furthermore to explore intramolecular energy redistribution rates and pathways. The state-specific unimolecular decay rates exhibit fluctuations over 4-5 orders of magnitude. Using the calculated wavefunctions from the polyad model, attempts are made to rationalize these fluctuations. Furthermore, the model in principle predicts *all* existing resonance states, giving direct access to the density of states in the continuum region of the PES above the D-CO dissociation limit. Results are compared with calculations employing classical phase space integration. Last but not least, the measured decay rates are compared with predictions by statistical unimolecular rate theory.

TURNING REACTIONS OFF AND ON WITH VIBRATIONAL EXCITATION

F. FLEMING CRIM, *Department of Chemistry, University of Wisconsin - Madison, Madison, Wisconsin 53706.*

Vibrational excitation can control the course of a bimolecular H-atom abstraction reaction. The bond-selected reaction of HOD with H, Cl, or O atoms is a prototypical example in which excitation of a stretching overtone vibration of either the O-H or the O-D bond leads to preferential cleavage of that bond. The energy available in the reaction preferentially appears in the new bond with the bond that breaks being essentially a spectator to the reaction. The ability to drive these direct reactions by exciting vibrational eigenstates that closely resemble bond stretching vibrations and involve motion along the reaction coordinate raises the question of the role of vibrations that are "perpendicular" to the reaction coordinate.

Preparation of well-characterized vibrational states in the region of three quanta of N-H stretching excitation ($3\nu_1$) in isocyanic acid (HNCO) permits experimental investigation of the extent to which vibrations perpendicular to the reaction coordinate can direct the bimolecular reaction of Cl atoms with HNCO to form HCl and NCO. Angular momentum states corresponding to different amounts of a-axis rotation in HNCO are well separated in energy, and perturbations by background states make each of the eigenstates a different mixture of zero-order states. Molecules in the essentially unperturbed $K = 1$ and 4 states, which are nearly pure N-H stretching excitation, react efficiently, but those in the perturbed states, $K = 0, 2,$ and 3 , which are a mixture of N-H stretching and bending excitation, react only half as fast. Detailed analysis of resolved, perturbed eigenstates for $J = 6$ and 7 of $K = 3$ reveals the reactivity of the two interacting zero-order states separately. The less reactive zero-order state, which most likely contains only two quanta of N-H stretch and several quanta of bending excitation, reacts only 10% as well as the pure N-H stretch zero-order state. Ab initio calculations suggest that bending excitation inhibits the reaction by changing the interaction potential between HNCO and the approaching Cl atom.

Intermission

MA03**40 min 10:20**

TERAHERTZ SPECTROSCOPY OF FREE RADICALS

G. WINNEWISSER, *I. Physikalisches Institut, Universität zu Köln, D-50913 Cologne.*

The first molecular species detected in space were the radicals CH, CH⁺, and CN. Free radicals and ions constitute a sizeable fraction of the detected interstellar and circumstellar molecules. Recent detailed mapping of the interstellar distribution of CN reveal the different interstellar distribution between open shell and closed shell molecules.

High resolution, broadband scanning spectroscopy with microwave accuracy has been extended into the terahertz region by frequency and phase stabilization of continuously tunable Backward Wave Oscillators (BWOs) at frequencies up to 2 THz. In combination with frequency multiplication techniques and alternatively laser side band techniques, this BWO based method allows broadband scanning spectroscopy to be extended to 3 THz. In case the FIR-laser is frequency and phase stabilized to an atomic clock, microwave accuracy is achieved. With this Cologne terahertz spectrometer the rotational spectra of a large number of closed- and open-shell molecules have been measured in a variety of different discharges cooled to liquid nitrogen temperature. Amongst these are many astrophysically important light hydrides and the fine structure transitions ³P₂ – ³P₁ of atomic carbon, ¹²C and ¹³C, at 809 341.970(50) MHz and 809 493.7(2) MHz respectively. The latter frequency refers to the F=2.5←1.5 hyperfine transitions. Larger carbon chain radicals e.g. C₄, C₉, C₁₁ have been detected by tunable diode laser spectroscopy using laser ablation techniques.

We have observed many astrophysically relevant molecular free radicals in the frequency region up to 1.3 THz. Amongst these are the important light hydride radicals CH, CD; NH, ND; PH, PD; SH, SD; NHH, NHD, NDD; CCH, CCD. In addition, many heavier free radicals have been measured such as CF, CN, CP, NO, OO, PS; SSH and SSD together with their heavier isotopic variants. The detailed study of the higher rotational transitions of the heavier radicals did reveal the gradual change from one Hund's coupling scheme to the other. Details will be discussed. Some of these new laboratory data have led to interstellar detections, others are pending. Some of the stable species such as CO, NH₃, HCl, HCN, and others have been investigated by saturation spectroscopy, resulting in line widths of < 40 kHz, well below the Doppler line widths, and in favourable cases with line center determinations of < 1 kHz at frequencies near 1 THz. With an intracavity millimeter wave spectrometer, the Orotron spectrometer, we have detected in the laboratory the astrophysically relevant molecular van der Waals complexes CO-HH, CO-He, and CO-CO.

MA04**40 min 11:05**

CARBON CHAINS, CARBON RING-CHAINS, AND CARBON CLUSTERS

MICHAEL C. McCARTHY, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA, mccarthy@cfa.harvard.edu.*

Some of the most exciting, current problems in science, including the discovery of the soccer ball molecule C₆₀, have come directly from laboratory studies of molecules known or thought to occur in space. With the radio discovery of OH some 30 years ago and the subsequent identification of more than 120 astronomical molecules, we now know that the interstellar medium is a fascinatingly rich source for many familiar and exotic species; many more can probably be found if rest frequencies can be measured in the laboratory. Laboratory detection has proved challenging, but recently good progress has been achieved by applying Fourier transform microwave spectroscopy to supersonic molecular beams of reactive species. During the past three years we have detected the rotational spectra of many new carbon chains, carbon rings, and silicon-carbon clusters. Almost all are highly polar, and several possess either unusual carbon ring-chain or bicyclic structures. The largest molecule so far detected is a polyynene chain (HC₁₇N) with 19 atoms and a molecular weight of 219 amu. On the basis of the laboratory data, five chains and one ring have already been detected in space, including the largest interstellar molecule HC₁₁N and ring, rhomboidal SiC₃.

The detection sensitivity of the present microwave spectrometer is still very far from fundamental limits set by modern technology, and an increase of an order of magnitude or more may be possible with liquid helium cooling, cryogenically cooled ultra-low-noise amplifiers, and other refinements. Such improvements may enable laboratory detection of new carbon molecules, including large molecular ions, planar and polycyclic rings, and other molecules which by symmetry are generally nonpolar. Many of our carbon molecules almost certainly have low-lying isomers that can be detected with the present techniques, and most chains are produced in sufficient abundance in our molecular beam that detection of their electronic spectra should be possible with standard laser fluorescence and absorption spectroscopies.

MB. MONDAY POSTER PRESENTATIONS

AUGUST 16, 1999 – 7:30 PM

Room: BALLROOM, LITTLE AMERICA HOTEL

Chair: ANTHONY MERER, University of British Columbia, Vancouver, BC, Canada

MB01

1 min 7:30

MICROWAVE SPECTROSCOPY OF TWO ISOELECTRONIC RADICALS:

2,4,6-HEPTATRIYNYL, $\text{H}_2\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$, AND 2,4-HEXADIYNYLNITRILE, $\text{H}_2\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$

WEI CHEN, *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138; and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138; and Department of Chemistry, Wesleyan University, Middletown, CT 06459*; STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, Middletown, CT 06459*; M. C. McCARTHY, P. THADDEUS, *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138; and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138.*

The isoelectronic pair of radicals 2,4,6-heptatriynyl, $\text{H}_2\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{H}$, and 2,4-hexadiynynitrile, $\text{H}_2\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{N}$, were produced in a pulsed discharge supersonic jet and detected by Fourier transform microwave spectroscopy. Seven rotational transitions of the heptatriynyl radical from $N' = 4$ to 10 and six rotational transitions of the hexadiynynitrile radical from $N' = 4$ to 9 in the $K_a = 0$ ladder were observed between 6 and 17 GHz. For each species, over 50 hyperfine components were measured and assigned with an uncertainty of 5 kHz. Precise rotational, centrifugal distortion, spin-rotation, and various hyperfine coupling constants were determined for both $\text{H}_2\text{C}_7\text{H}$ and $\text{H}_2\text{C}_6\text{N}$. The trends in the spectroscopic constants for these radicals and the shorter members of the series $\text{H}_2\text{C}_3\text{H}$, $\text{H}_2\text{C}_5\text{H}$, and $\text{H}_2\text{C}_2\text{N}$, $\text{H}_2\text{C}_4\text{N}$ will be presented. In addition, the results from density functional calculations which reproduce the measured hyperfine constants, will be displayed.

MB02

1 min 7:31

INFRARED SPECTRA OF MOLECULAR IONS PRODUCED FROM OCS AND CS_2 AND TRAPPED IN SOLID NEON

CATHERINE L. LUGEZ, WARREN E. THOMPSON, and MARILYN E. JACOX, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441.*

When a mixture of OCS or CS_2 in a large excess of neon is subjected to photoionization and/or Penning ionization by a beam of excited neon atoms and then rapidly frozen at approximately 5 K, the resulting solid deposit shows infrared absorptions of both molecular cations and molecular anions. The two stretching fundamental absorptions of OCS^+ appear close to the gas-phase band centers, and the two stretching fundamental absorptions of OCS^- are identified for the first time. Detailed isotopic substitution studies support these identifications. In the experiments on CS_2 , the ν_3 fundamental of CS_2^+ appears close to the gas-phase band center, and the ν_3 absorption of CS_2^- lies close to the position recently reported by another laboratory. The infrared absorption of CS^+ is also present in the spectra of Ne: CS_2 samples. In each of the two systems, infrared absorptions also appear which may be contributed by small concentrations of dimer ions.

MB03**1 min 7:32****FTIR OBSERVATION OF NOVEL SILICON-CARBON AND GERMANIUM-CARBON CLUSTERS FORMED BY LASER ABLATION AND TRAPPED IN SOLID Ar**

W. R. M. GRAHAM, X. D. DING, D. L. ROBBINS, S. L. WANG, and C. M. L. RITTBY, *Department of Physics and Astronomy, Texas Christian University, Fort Worth, TX 76129.*

Well resolved vibrational spectra of new silicon-carbon and germanium-carbon clusters have been produced by trapping the products from the pulsed laser evaporation of pure Si, Ge, and C rods in solid Ar at 10 K. This method has permitted the investigation of long carbon chains with a single terminal silicon, such as SiC₇ and SiC₉, molecules of potential astrophysical interest. Results for germanium-carbon clusters are compared with those for previous investigations of the spectra and structures of Si_mC_n clusters. Comparison of the results of extensive measurements of isotopic shifts obtained from the naturally occurring isotopes of Si and Ge and by carbon-13 enrichment with the predictions of density functional theory calculations enables the identification of vibrational modes and the determination of structures.

MB04**1 min 7:33****THE ELECTRONIC STRUCTURE AND SPECTRUM OF RHODIUM MONOCARBIDE**

WALTER J. BALFOUR, SCOTT G. FOUGERE, ROMÉY F. HEUFF, CHARLES X. W. QIAN, and CHI ZHOU, *Department of Chemistry, University of Victoria, B.C. Canada V8W 3V6.*

Rhodium monocarbide (RhC) molecules have been generated using a laser ablation/supersonic molecular beam source. Laser-induced and dispersed fluorescence (DF) techniques have been used to study the visible spectrum between 400 and 530 nm. Rh¹²C/Rh¹³C isotope shifts, DF and excited level lifetime measurements have assisted in classifying the observed bands into three series: the known C²Σ⁺-X²Σ⁺ system (short excited state lifetimes) and the two spin subsystems of a ²Π_i - X²Σ⁺ transition (long excited state lifetimes). A time-filtering technique has been employed to separate effectively emission from close-lying ²Π and C²Σ levels. The C - X system is inherently strong, the ²Π_i - ²Σ⁺ system very weak. The ²Π_{1/2} - ²Σ⁺ component is identified with the B - X system, previously taken to be of ²Σ⁺ - ²Σ⁺ symmetry. The ²Π_{3/2} component gives rise to local perturbations in the C state. Many new bands in the ²Π_i - X²Σ⁺ transition have been recorded and analyzed and the interactions/ perturbations amongst the ²Σ⁺ and the newly established ²Π_i states have been examined in detail.

MB05**1 min 7:34****ELECTRONIC STATES AND SPECTRA OF BiOH, BiSH AND RELATED RADICALS**

EWALD H. FINK, RALF GIELEN, and OLEG SHESTAKOV, *Fachbereich Chemie, Bergische Universität-GH Wuppertal, Gaußstraße 20, D-42097 Wuppertal, Germany.*

Visible and NIR spectra of BiOH, BiSH, BiSeH, BiTeH, and the corresponding deuterides have been studied by FTS and LIF. The molecules are isoelectronic with the diatomic bismuth halides and have a number of stable A' and A'' states arising from the fine structure and Λ-doubling components of the ³Σ⁻, ¹Δ, and ¹Σ⁺ states in the linear configuration. For BiOH and BiOD, five electronic transitions have been observed including fine structure transitions between the three A' and A'' components of the ³A'' ground states.

MB06**1 min 7:35****CF₃OBr FORMATION FROM REACTION OF O(¹D) WITH CF₃Br IN AN ARGON MATRIX**

Q. Z. QIN, L. N. ZHANG, X. F. WANG, M. H. CHEN and Q. K. ZHENG, *Laser Chemistry Institute, Fudan University, Shanghai 200433, China.*

266nm laser photolysis of argon matrices containing dilute O₃ and CF₃Br gives rise to three chief IR bands at 1249.4, 1204.2 and 1201.9 cm⁻¹. The primary possible intermediates CF₃BrO and CF₃OBr, which might generate from reactions between mobile O(¹D) atoms and isolated CF₃Br, are characterized by DFT calculations for the first time. Geometries, energies, vibrational frequencies and the IR intensities of these two intermediates are obtained. Theoretical studies support the assignments of the observed IR bands to C-F stretching modes of the hypobromite compound CF₃OBr. Mechanism is proposed as reaction between O(¹D) and CF₃Br to generate excited CF₃BrO initially, which readily undergoes fragmentation to CF₃ and BrO due to the weak bonding of C-Br in CF₃BrO, and fast recombination of CF₃ and BrO in the matrix cage produces the final product CF₃OBr.

MB07**1 min 7:36****ELECTRONIC AND VIBRATIONAL SPECTROSCOPY OF THE D₂-METHOXY RADICAL, CHD₂O**

W.Y.FAN, I.KALINOVSKI, A.M.MANN and C.BRADLEY MOORE, *Chemical Sciences Division of the Lawrence Berkeley National Laboratory and Department of Chemistry, UC Berkeley, Berkeley 94720-1460, California, USA.*

The CHD₂O radicals were produced by 355 nm photolysis of CHD₂ONO seeded in argon. Supersonic jet expansion cooled the radicals rotationally and the fluorescence-excitation spectrum was probed by a frequency-doubled dye laser 2.5 cm downstream. The band origin of the spectrum was detected around 31610 cm⁻¹ and many vibrational progressions were observed up to 36000 cm⁻¹. Unfortunately, the C-H stretch is weakly Franck-Condon active and hence its energy levels are difficult to access via SEP. Instead, infrared excitation detected by fluorescence depletion spectroscopy is used to populate the C-H rovibrational energy levels in the ground electronic state. Individual rovibronic fluorescence-excitation transitions of the 3¹ band were chosen for detection of ground-state depletion by an IR laser. In this double resonance spectroscopy, first an IR laser (Optical Parametric Oscillator (OPO)) pulse passes through the jet and then a uv excitation laser is focussed along the same path. Depletion in the fluorescence signal occurs whenever there are transitions or population transfers to the C-H stretching mode. Hence by scanning the OPO laser, an IR spectrum is obtained for each pumped rovibronic transition. A vibrational band around 2770 cm⁻¹ has been observed using this technique. Currently, work is in progress to record and analyze states throughout the fundamental and overtone regions for CH stretching.

This work was supported by the Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

MB08

1 min 7:37

 $\nu_1 + \nu_5$ OF HCCN: DETERMINATION OF THE ν_5 VIBRATION ENERGY AND BARRIER TO LINEARITY

P. Y. HUNG, JIAXIANG HAN, JOHN DESAIN, W. E. JONES and R. F. CURL, *Chemistry Department and Rice Quantum Institute, Houston, Texas 77251.*

The $\nu_1 + \nu_5$ combination band of the quasilinear HCCN radical has been observed in high resolution as a transient infrared absorption spectrum. The radical was produced through 193 nm ArF laser photolysis of CHBr_2CN and the transient spectrum observed using a cw color center laser (Burleigh Instruments, FCL-20, Li:RbCl crystal) pumped by a krypton ion laser. The spectrum obtained in the region of 3323 cm^{-1} to 3382 cm^{-1} is assigned as the combination band of $\nu_1 + \nu_5$ with the band origin at $3355.504(2)\text{ cm}^{-1}$. When this band is combined with the information from the $\nu_1 + \nu_5 - \nu_5$ spectrum,^a the energy of the lowest excited state with angular momentum about the a-axis, ν_5 , is determined to be $128.9072(6)\text{ cm}^{-1}$. This value is lower than the result obtained by relative intensity measurements on the millimeter-wave spectra^b [$145(15)\text{ cm}^{-1}$] or that obtained from similar relative intensity measurements on the IR spectra^a [$187 \pm 20\text{ cm}^{-1}$]. The barrier to linearity based on this ν_5 value is in good agreement with that obtained from the corresponding band of DCCN^c and is higher than either result obtained by relative intensity measurements.^{a, b}

^aC. L. Morter, S. K. Farhat and R. F. Curl *Chem. Phys. Lett.* **207**, 153 (1993).

^bM. C. McCarthy, C. A. Gottlieb, A. L. Cooksy and R. Thaddeus *J. Chem. Phys.* **103**, 7779 (1995).

^cFuge Sun, A. Kosterev, G. Scott, V. Litosh and R. F. Curl *J. Chem. Phys.* **109**, 8851 (1998).

MB09

1 min 7:38

CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY - NITROGEN CATION

M. ALDENER, B. LINDGREN, A. PETERSSON and U. SASSENBERG, *Department of Physics, Stockholm University, Box 6730, S-113 85 Stockholm, Sweden.*

Two hitherto unanalysed bands (5,1) and (10,5) of the $A^2\Pi_u - X^2\Sigma_g^+$ system of the N_2^+ molecule have been studied using the Cavity Ringdown Laser Absorption Spectroscopy (CRLAS) technique. A method for distinguishing between ionic lines and neutral ones is reported as is a rotational analysis of the observed bands. Lines in the (15,8) band has also been observed which provides a sensitivity comparison with velocity modulation spectroscopy technique. The ion was generated in a pulsed hollow cathode source, similar to the one described in [1], containing a mixture of nitrogen and helium (1:3). By comparing the spectra at different times, relative to the discharge pulse, the ion and the neutral lines can be separated. This is because of the large difference in intrinsic lifetimes.

References:

[1] M. Kotterer, J. Conceicao, J.P. Maier, *Chem. Phys. Letters* 259,233 (1996).

MB10**1 min 7:39****INTEGRATED ABSORPTION INTENSITY AND EINSTEIN COEFFICIENTS FOR THE O_2 $a^1\Delta_g - X^3\Sigma_g^-$ (0,0) TRANSITION DETERMINED BY CAVITY RING-DOWN AND HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY**

IAN C. LANE, STUART M. NEWMAN, and ANDREW J. ORR-EWING, *School of Chemistry, University of Bristol, Bristol, United Kingdom BS8 1TS*; DAVID A. NEWNHAM, and JOHN BALLARD, *Atmospheric Science Division, Space Science Department, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, United Kingdom OX11 0QX*.

The two experimental techniques of cavity ring-down spectroscopy and high-resolution, long-path Fourier transform spectroscopy have been used to measure quantitative absorption spectra and determine the integrated absorption intensity ($S_{int,B}$) for the O_2 (0,0) band. Einstein A-factors and radiative lifetimes for the O_2 $a^1\Delta_g$ $v = 0$ state have been derived from the $S_{int,B}$ values. The two methods give values for the integrated absorption intensity that agree to within 2%. The value recommended from the results of this study is $S_{int,B} = 3.10 \pm 0.10 \times 10^{-24}$ cm molecule $^{-1}$, corresponding to an Einstein-A coefficient of $A = 2.19 \pm 0.07 \times 10^{-4}$ s $^{-1}$ and a radiative lifetime of $t_{rad} = 76$ min. The measurements are in excellent agreement with the recent absorption study of Lafferty *et al.*^a and greatly reduce the uncertainty in these parameters, for which accurate values are required for determination of upper stratospheric and mesospheric ozone concentrations.

^aW. J. Lafferty, A. M. Solodov, C. L. Lugez and G. T. Fraser *Appl. Opt.* **37**, 2264 1998.

MB11**1 min 7:40****PREDISSOCIATION DYNAMICS OF THE ClO $A^2\Pi$ STATE STUDIED BY CAVITY RING-DOWN SPECTROSCOPY AND $AB - INITIO$ CALCULATIONS**

WENDY H. HOWIE, IAN C. LANE, STUART M. NEWMAN, and ANDREW J. ORR-EWING, *School of Chemistry, University of Bristol, Bristol, United Kingdom BS8 1TS*.

The (0,0) to (7,0) bands of the $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ and $A^2\Pi_{1/2} - X^2\Pi_{1/2}$ transitions in ClO have been investigated using cavity-ring down spectroscopy between 285 and 320 nm. The previously unobserved $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ (0,0) and (1,0) absorption bands have been recorded with rotational resolution, and spectra of the (1,0), (5,0) and (6,0) bands of the $A^2\Pi_{1/2} - X^2\Pi_{1/2}$ transition are shown for the first time. Analysis of the spectra gives refined band origins and rotational constants for the $A^2\Pi_{\Omega}$ ($\Omega = 1/2$ or $3/2$) v' levels and reveals a strong v' dependence in the linewidths of rotational features. The predissociation rates for the two spin-orbit components of the $A^2\Pi_{\Omega}$ state are markedly different. No evidence of J' -dependence in the predissociation is found, in contrast to the IO radical. *Ab - initio* calculations at the MRCI level have been performed on the valence doublet and quartet electronic states in order to explore the predissociation dynamics of the $A^2\Pi_{\Omega}$ state. The *ab - initio* calculations neglect spin-orbit coupling. In total, the potential energies of fifteen valence states were computed. The $X^2\Pi$, $A^2\Pi$ and $a^4\Sigma^-$ potentials are bound; all the other states are repulsive. Using arguments based on electronic configurations and simulations of the predissociation performed by Fermi golden rule calculations for each vibrational level, the principal players in the predissociation are revealed to be the $1^4\Sigma^+$, $2^4\Sigma^-$ and $3^2\Pi$ states, with good agreement between the calculated and the experimental predissociation rates.

MB12**1 min 7:41**THE ELECTRIC DIPOLE MOMENT OF THE $B^1\Pi$ STATE OF ZrO

A. PETTERSSON, B. LINDGREN, C. LUNDEVALL, W. SHI, AND U. SASSENBERG, *Department of Physics, Stockholm University, P.O. Box 6730, 11385 Stockholm, Sweden.*

A laser ablation source combined with a time of flight mass spectrometer has been constructed. The static electric field in the mass spectrometer gives rise to a first order Stark effect splitting from which the permanent electric dipole moment can be determined. By using a pulsed amplified ring-dye-laser this splitting can be resolved.

The permanent electric dipole moment for the $X^1\Sigma^+$ - ground state of ZrO is known to be 2.55 D[1]. In this work we have measured the first order Stark splitting of the $B^1\Pi$ state ($v=0$) of ^{90}ZrO and from that determined the dipole moment to be 3.43 ± 0.07 D. The $X^1\Sigma^+$ and $B^1\Pi$ states are further investigated and compared with the results of *ab initio* calculations.

References

1. R. D. Suenram et al. J. Chem. Phys. **92** (8). 4724

MB13**1 min 7:42**MICROWAVE SPECTROSCOPY OF Na_3 CLUSTERS

WOLFGANG E. ERNST, *Departments of Physics and Chemistry, The Pennsylvania State University, 104 Davey Laboratory, University Park, PA 16802*; OLEG GOLONZKA, *Frances Bitter Laboratory, MIT, Bldg. NW 14, Rm. 1215, 170 Albany Street, Cambridge, MA 02139.*

The direct measurement of hyperfine and fine structure as well as tunneling splittings in small clusters can provide information on the localization of electrons and an electron-nuclear coupling mechanism. The ground state of the sodium trimer is split by Jahn-Teller interaction. Energy minima of the potential surface for the nuclei are found corresponding to an isosceles triangle geometry with 80 degree apex angle. The Jahn-Teller distortion gives rise to a small electric dipole moment. Using our new resonant two-photon ionization detection scheme for the absorption of microwaves, we measured rotational transitions in the 12 to 17 GHz region. From intensity measurements, an extremely small electric dipole moment on the order of 0.01 D can be concluded. The detection scheme involves as intermediate steps the optical excitation into various excited electronic states for which the symmetries of rotational levels had previously been assigned. Through careful studies of several rotational states, we found that in some ground state levels, the tunneling splitting is so small that hyperfine mixing forbids any clear assignment of A and E symmetries. Assuming the classical linear and quadratic Jahn-Teller coupling formation, a lower limit of 200 cm^{-1} for the barrier to free pseudorotation is derived. The measured hyperfine structure indicates a Fermi contact term of about equal size on all three nuclei. The absolute magnitude is only about 1 the hyperfine structure of free Na 3s.

MB14**1 min 7:43**THE $A'^3\Sigma^+ - X^1\Sigma^+$ TRANSITION OF SILVER CHLORIDE

L.C. O'BRIEN and T.L. KELLERMAN, *Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652.*

The visible electronic transition of AgCl has been observed for the first time. The spectrum of the $A'^3\Sigma^+ - X^1\Sigma^+$ transition, labeled by analogy with the AgF visible electronic transition, was recorded with the Fourier transform spectrometer associated with the McMath-Pierce Solar Telescope, Kitt Peak, AZ. The AgCl molecules were produced in a King-type carbon tube furnace operating at 1900 C and at a total pressure of approximately 200 torr. The electronic transition energy and rotational constants for the $A'^3\Sigma^+$ state will be presented.

MB15**1 min 7:44****INVESTIGATION OF HO₂ + RO₂ GAS PHASE REACTIONS USING SIMULTANEOUS UV AND NEAR-IR PROBES**

S. SANDER, *The Jet Propulsion Laboratory, Pasadena, CA 91109*; L. CHRISTENSEN, M. OKUMURA, *Department of Chemistry, The California Institute of Technology, Pasadena, CA 91125*.

The reaction kinetics of HO₂ and organic peroxy radicals are being studied using pulsed photolysis with simultaneous long-path absorption UV and near-IR probes. The near-IR probe is a 1.43 micron DFB diode laser which is used to probe the $1^2A' - X^2A'$ transition of HO₂. The diode laser current is modulated in the MHz regime and the resultant signal is demodulated at the second harmonic (2f detection). RO₂ radicals are detected in the UV region by probing the $2^2A'' - X^2A''$ transition. Results will be presented on the kinetics of the CH₃O₂ + HO₂ and C₂H₅O₂ + HO₂ reactions using this technique.

MB16**1 min 7:45****THE MgH B'²Σ⁺ – X²Σ⁺ TRANSITION: A NEW TOOL FOR STUDYING MAGNESIUM ISOTOPE ABUNDANCES**

P. BERNATH, G. LI, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*; L. WALLACE, K. HINKLE, *Kitt Peak National Observatory, National Optical Astronomy Observatories, Tucson, AZ 85726*; R. S. RAM, *Dept. of Chemistry, University of Arizona, Tucson, AZ 85721*.

We have identified lines from the 0-3, 0-4, 0-5, 0-6, 0-7, 1-3, 1-4, 1-7 and 1-8 bands of the $^{24}\text{MgH } B'^2\Sigma^+ - X^2\Sigma^+$ transition in sunspot umbral spectra. Lines of the 0-7 and 1-8 bands in the uncluttered 750 nm region are the most obvious but $B'^2\Sigma^+ - X^2\Sigma^+$ lines have been tracked as far to the blue as 530 nm. In combination with weak lines of the 0-7 bands of the ^{25}MgH and ^{26}MgH isotopes, the solar isotope ratio $^{24}\text{Mg}:^{25}\text{Mg}:^{26}\text{Mg}$ has been measured as 76:12:12, in agreement with the much better determined terrestrial ratio 79:10:11. The intensity distribution of bands with v'' from 4 to 8 has been measured and found to show no anomalies; the excitation temperature of 3100K agrees well with a value of 3200K determined from SiO in a sunspot spectrum.

We have also analysed an archival hollow cathode emission spectrum and combined these new data with the existing millimeter wave and solar measurements to obtain improved spectroscopic constants.

The lines of the MgH $B'^2\Sigma^+ - X^2\Sigma^+$ transition are much more cleanly separated and much less blended than lines from the stronger $A^2\Pi - X^2\Sigma^+$ transition. The $B'^2\Sigma^+ - X^2\Sigma^+$ lines should prove useful in isotopic abundance analyses for stars where the $A^2\Pi - X^2\Sigma^+$ transition is too strong to yield useful results.

MB17**1 min 7:46****LABORATORY DETECTION OF FOUR NEW CUMULENE CARBENES: H₂C₇, H₂C₈, H₂C₉ and D₂C₁₀**

ALDO J. APPONI, MICHAEL C. MCCARTHY, CARL A. GOTTLIEB AND PATRICK THADDEUS, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street MS 72, Cambridge, MA 02138*.

Four new cumulene carbenes, H₂C₇, H₂C₈, H₂C₉ and D₂C₁₀, were detected by Fourier transform microwave spectroscopy. Like the shorter cumulenes, all four new chains were found to have singlet electronic ground states and linear carbon chain backbones. Rotational and centrifugal distortion constants were determined to high accuracy for all the H₂ species such that the entire radio spectrum can be calculated to better than 0.3 km s⁻¹ equivalent radio velocity up to 100 GHz. Upper limits of the H₂C₇, H₂C₈ and H₂C₉ column density have been estimated for the circumstellar shell of IRC+10216.

MB18**1 min 7:47**LABORATORY DETECTION OF FIVE NEW SILICON-CARBON MOLECULES: SiC_n (n = 3, 5-8)

ALDO J. APPONI, MICHAEL C. MCCARTHY, CARL A. GOTTLIEB AND PATRICK THADDEUS,
Harvard-Smithsonian Center for Astrophysics, 60 Garden Street MS 72, Cambridge, MA 02138.

The rotational spectra of five new linear SiC_n chains (n = 3, 5-8) have been observed in the laboratory using Fourier transform microwave spectroscopy. The molecules were generated in a pulsed discharge source through the reaction of silane and diacetylene heavily diluted in Ne in the throat of a supersonic nozzle. The ground state of each SiC_n chain was found to be X¹Σ for even n and X³Σ for odd n. Spectroscopic constants including the spin-spin and spin-rotation coupling constants for SiC₃, SiC₅ and SiC₇ were determined to high accuracy for each member. The spin-spin constant rapidly increases with chain length which is similar to the that observed in the C_nO series (Ohshima, Endo and Ogata, J. Chem. Phys. 1995, 102, 1493). Astrophysical searches for these species are currently being conducted.

MB19**1 min 7:48**

ACCURATE EQUILIBRIUM STRUCTURES AND PREDICTIONS OF SPECTROSCOPIC PROPERTIES FOR LINEAR CARBON-SILICON CLUSTERS.

PETER BOTSCHWINA, *Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße. 6, D-37077 Göttingen.*

On the basis of large-scale coupled cluster calculations including connected triple substitutions and experimental ground-state rotational constants for seven different isotopomers of C₄Si, accurate equilibrium geometries have been established for linear C₄Si, C₃Si₂, C₆Si, C₅Si₂, C₈Si and C₇Si₂ in their electronic ground-states. The calculated harmonic vibrational wavenumbers for C₄Si and C₃Si₂ should be accurate to a few cm⁻¹ and a full set of vibration-rotation coupling constants has been calculated for both species which appear to be rather well-behaved semi-rigid molecules.

MB20**1 min 7:49**

DIRECT DETERMINATION OF ATMOSPHERIC ORGANIC PEROXY RADICALS USING CW-CRD (CAVITY RING-DOWN) SPECTROSCOPY

D. B. ATKINSON, *Department of Chemistry, Portland State University, Portland, OR 97207-0751.*

A direct spectroscopic technique is used to measure the concentration of organic peroxy radicals in the nascent air via their structured near-infrared (NIR) absorptions. Peroxy radicals are the secondary oxidation products of hydrocarbons in the atmosphere (following attack by hydroxyl radicals) and are implicated in tropospheric ozone production. A continuous-wave cavity ring-down (CW-CRD) absorption spectrometer with wavelength coverage near 1310 nm has been constructed and tested and offers part per billion absorption sensitivity (cm⁻¹) with 1 MHz spectral resolution. The design is similar to that recently reported and used to measure the overtone spectra of N₂O and CHCl₃.^a Controlled generation of the ethylperoxy radical (C₂H₅O₂) has been accomplished under laboratory conditions, allowing a rovibrationally resolved spectrum to be recorded. Spectra of continuously sampled atmospheric air at a variety of total pressures will be presented, illustrating the viability of this direct analytical approach.

^aY. He, M. Hippler, and M. Quack, Chem. Phys. Lett. 289, 527 (1998).

MB21**1 min 7:50****AB INITIO CALCULATION OF JAHN-TELLER COUPLING CONSTANTS**

BRIAN E. APPLGATE, TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210*; and TIMOTHY A. BARCKHOLTZ, *JILA, National Institute of Standards and Technology and The Department of Chemistry and Biochemistry, University of Colorado Boulder, CO 80309 - 0440*.

A recently developed *ab initio* method^a for calculating Jahn-Teller constants has been employed to investigate the Jahn-Teller effect in the methoxy family of radicals (CH₃O, CF₃O, CH₃S, and CF₃S) as well as the cyclopentadienyl radical (C₅H₅). This method combines the complete active space self-consistent field (CASSCF) wavefunction available in the Gaussian94/98 program and the generalized restricted Hartree-Fock (GRHF) wavefunction available in the CADPAC program. The energy of the symmetric configuration of the nuclei is calculated, using a CASSCF wavefunction, as a conical intersection between the two components of the degenerate electronic state, whose degeneracy is lifted by the Jahn-Teller effect. The energy of the distorted configuration is calculated with a CASSCF wavefunction that has the same occupancies and active space as the conical intersection calculation. The difference in the energy of these two calculations corresponds to the linear Jahn-Teller stabilization energy. In addition to determining the energy of the symmetric configuration, the conical intersection calculation also determines the vector along which the molecule will distort. By projecting this vector onto the normal modes of the molecule, obtained from a GRHF calculation, the experimentally observable linear Jahn-Teller coupling constants are estimated. Details of the computational approach along with results on systems presently investigated will be presented.

^aBarckholtz T. A.; and Miller T. A., *J. Phys. Chem.*, **1999**, 103, 2321.

MB22**1 min 7:51****AB INITIO CALCULATIONS ON THE SPIN-ORBIT SPLITTING IN THE \tilde{C} STATE OF CF₄⁺ INCLUDING DYNAMICAL JAHN-TELLER EFFECT.**

H.T SOMMERDIJK and M.C. VAN HEMERT, *Leiden University, Leiden Institute of Chemistry, P.O. Box 9502, 2300RA Leiden, Netherlands*.

Previous semi-empirical calculations^a on 2T_2 states of XY₄⁺ cations resulted in spin-orbit splittings an order of magnitude larger than the experimental splittings. Our large mrci calculations on the purely electronic spin-orbit interaction in the $\tilde{C} {}^2T_2$ state of CF₄⁺, using the full Breit-Pauli approximation for the spin-orbit interaction, give the same result as Dixon and Tuckett, almost independent of the geometry. We calculated the coupled 9-dimensional potential surface for the components of the $\tilde{C} {}^2T_2$ state of CF₄⁺ and the vibronic wave functions. The spin-orbit splitting between the vibronic wave functions is much smaller than between the purely electronic wave functions and much closer to the experimental value. The vibronic reduction of the spin-orbit interaction is caused by the Jahn-Teller distortions in the potential surface (Dynamical Jahn-Teller effect). This reduction is also known as the Ham effect. All asymmetric vibrational modes contribute significantly. The Jahn-Teller-effect can not be measured directly. Comparing experimental and calculated spin-orbit splitting is therefore a useful test on the accuracy of calculated Jahn-Teller distortions.

^aR.N. Dixon and R.P. Tuckett, *Chem. Phys. Lett.* **140**, 553 (1987).

MB23

1 min 7:52

OPTICAL-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF THE $1_g(^3P_2) - A^3\Pi(1_u) - X^1\Sigma_g^+$ TRANSITION OF I_2

ERIKO KAGI, HISASHI FUJIWARA, MASARU FUKUSHIMA, and TAKASHI ISHIWATA, *Hiroshima City University, Faculty of Information Sciences, Asa-Minami, Hiroshima 731-3149, JAPAN.*

The optical-optical double resonance spectroscopy was applied to study the $1_g(^3P_2)$ ion-pair state of I_2 correlating $I^-(^1S) + I^+(^3P_2)$. The excitation of I_2 to the ion-pair state was performed by using a tunable dye laser and a OPO radiation pumped by a Nd^{3+} :YAG laser. The pump laser operated in the near-IR region excited the $A^3\Pi(1_u) - X^1\Sigma_g^+$ transition at a fixed frequency for the state selection while the probe laser frequency was scanned to observe the $1_g(^3P_2) - A^3\Pi(1_u)$ resonance. The ultraviolet emission from the I_2 ionic state was monitored through a monochromator, and the photomultiplier signals were averaged by a boxcar integrator. Since the accurate molecular constants of the $A^3\Pi(1_u)$ state were reported, we could easily make an assignment of the observed transitions according to the selection rule $\Delta J = \pm 1$. A rotational analysis on the $1_g(^3P_2) - A^3\Pi(1_u)$ system was carried out on 25 vibrational bands ($\nu' < 15$), leading to the following improved constants (cm^{-1} unit) for the $1_g(^3P_2)$ state with 1σ in parentheses:

$$T_e = 47558.6449(21), \omega_e = 106.6564(11), \quad \omega_e x_e = 0.22334(18), \quad \omega_e y_e = 2.541(80) \times 10^{-4}, \\ B_e = 0.0219273(46), \alpha_e = 6.0320(35) \times 10^{-5}, \quad D_e = 3.017(23) \times 10^{-9}, \quad p_e = 3.92(23) \times 10^{-6}.$$

The equilibrium internuclear distance of the $1_g(^3P_2)$ state was derived to be 3.549 Å. Using these constants, the potential energy curve for the $1_g(^3P_2)$ state was also determined to obtain Franck-Condon factor.

MB24

1 min 7:53

1+1' PFI-ZEKE PHOTOELECTRON SPECTROSCOPY OF ACETYLENE-THE RENNER-TELLER EFFECT OF ACETYLENE CATION

SHUENN-JIUN TANG, JIM JR-MIN LIN, AND YEN-CHU HSU, *Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box23-166, Taipei, Taiwan, R.O.C. and Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C..*

This paper presents the 1+1' pulsed-field induced zero-kinetic energy (PFI-ZEKE) photoelectron spectrum of C_2H_2 and C_2D_2 recorded in the range of 91900-95600 cm^{-1} via a single rovibrational level of \tilde{A}^1A_u as the intermediate. The prominent spectral features were assigned as the trans-bending vibration progression ($V_4^+ = 0-6, K^+ = 0-3$)/($V_4^+ = 0-5, K^+ = 0-3$) of the $\tilde{X}^2\Pi_u$ state of $C_2H_2^+/C_2D_2^+$. Although transitions to levels of the cis-bending vibration and levels with combination of ν_2^+, ν_4^+ and ν_5^+ vibrational excitation were generally much weaker, the combination levels of (0,0,0,1,1) of $C_2H_2^+$ were fairly easily detected. From the parities and symmetries of the nuclear spin of the observed rovibrational levels of the cations and the intermediate, we deduced that both odd and even partial waves were given off in the pulsed-field photoionization of the \tilde{A} state of acetylene. The spectroscopic parameters of acetylene and its deuterated isotopomer such as the trans-bending/cis-bending vibrational frequencies, anharmonicity constants, the g_K corrections, and Renner-Teller parameters obtained from the best fit to the observed vibronic levels with a model of including two bending vibrational modes to the Renner-Teller effect of the tetra-atomic molecule with two bending vibrational modes will be presented.

MB25**1 min 7:54**

PHOTOIONIZATION SPECTROSCOPY OF ZINC MONOETHYL RADICAL AND ITS CATION

MICHAEL B. PUSHKARSKY, VADIM L. STAKHURSKY, AND TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210.*

Closed-shell ions constitute an important class of highly reactive species responsible for many chemical processes. ZEKE spectroscopy applied to open-shell radicals produced *in situ* in free jets enables one to probe the ground electronic state of the corresponding closed-shell ions. In the recent past we have investigated^{a,b} the spectroscopy of three Group IIa and IIb organometallic radicals, MCH₃, (M=Mg, Zn, Cd) and their cations. Here we present the spectroscopic study of the zinc monoethyl radical, and its positive ion. The vibrational structure of the \tilde{A} electronic state of the zinc monoethyl radical and the \tilde{X} state of its cation have been probed by (1+1') REMPI and ZEKE, respectively. The zinc monoethyl ionization potential has been found to be 56380(5) cm⁻¹. The ZEKE study has revealed complex vibrational structure in the ground electronic state of the ion, dominated by progressions involving ν_9 , ($\omega_9 = 210(3)$ cm⁻¹), the low frequency in-plane Zn-C-C bending mode. The analysis of the data on the four members of the family provides the insight into the the carbon-metal bonding in the metal alkyl radical molecular systems.

^aS. E. Panov, D. E. Powers, and T. A. Miller, *J. Phys. Chem.*, **108**, 1335 (1998).

^bT. A. Barckholtz, D. E. Powers, T. A. Miller, and B. E. Bursten, *J. Am. Chem. Soc.*, **121**, 2576 (1999).

MB26**1 min 7:55**

PHOTOCHEMISTRY, THERMOCHEMISTRY AND SPECTROSCOPY OF CARBENES

JOSEPH GUSS, PAMELA KNEPP, TIMOTHY SCHMIDT and SCOTT H. KABLE, *School of Chemistry, University of Sydney Sydney, NSW, 2006, Australia.*

We have been investigating the spectroscopy and photochemistry of small carbenes for a number of years. Four triatomic fluorocarbenes, namely CF₂, CHF, CFCl and CFBr, have been the focus of our attention to date. In these experiments, we create free jet expansions of carbenes by either pyrolysis or photolysis at the nozzle orifice of appropriate halomethane precursors. Several spectroscopic techniques have been employed to probe their electronic and vibrational structure, including laser induced fluorescence, dispersed fluorescence, and photofragment excitation spectroscopy. Excited state dynamics have been probed by measuring their fluorescence lifetimes and by measuring the internal energy distribution of the nascent CF photofragment. *Abinitio* theoretical calculations of the X and A-state potential energy surfaces support the experimental investigation. Although members of a closely related family, the spectroscopy, photophysics and photochemistry of the first excited singlet states of each carbene is quite different. The reason for this lies in the variation in the heights of two barriers on the A-state surface: the barrier to XCF bond cleavage, and the "barrier" to linearity. The A and X-states are Renner-Teller pairs and are degenerate at linearity. Efficient crossing back to the ground state in the region of this "barrier" ensues. In CFBr, the barrier to bond cleavage is below the Renner-Teller intersection and it hence undergoes direct C-Br bond cleavage for A-state vibrational energies in excess of 3360 cm⁻¹. In HCF, on the other hand, the Renner-Teller intersection, which lies 6400 cm⁻¹ above the zero-point level in the A-state, is below the barrier for bond cleavage and hence no reaction takes place. CF₂, is remarkably stable, because the increased symmetry and strong electronegativity of the fluorine ensures that neither barrier is reached within the Franck-Condon region of the A-state. The bond cleavage barrier and linearity region have been calculated to be nearer to each other in energy for CFCl. We are currently undertaking experiments on this molecule to determine which barrier is higher, and whether any unusual dynamics might result if they turn out to be very close in energy. In this seminar, the data and calculations to support these statements will be presented, along with any new data and conclusions on CFCl.

MB27

1 min 7:56

KrF EXCIMER-LASER INDUCED OZONE FORMATION AND HYDROCARBON OXIDATION IN SUPERCRITICAL CARBON DIOXIDE

JUNICHIRO OTOMO, AKINORI TAKAMI, YOSHITO OSHIMA and SEIICHIRO KODA, *Department of Chemical System Engineering, School of Engineering, The University of Tokyo Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan.*

Pulsed KrF excimer laser irradiation to O₂/CO₂ and hydrocarbon/O₂/CO₂ mixtures up to 15 MPa was studied at 308 K. Ozone was produced under the irradiation to O₂/CO₂ mixtures in spite of the fact that the KrF excimer laser light at 248 nm can not energetically dissociate isolated O₂ molecules. The ozone formation was a one-photon process, and the O₃ yield increased with the irradiation time and then saturated due to the subsequent O₃ photolysis. The excited state O₂ molecule in the Herzberg systems is considered to be produced via the laser light absorption to react with ground state O₂ to yield O₃ and O(³P). The quantum yield of O₃ production decreased with the increase of the CO₂ density, which suggests a contribution of quenching by CO₂ during the above reaction progress. No special CO₂ pressure effect near the critical point was observed. In the simultaneous presence of saturated hydrocarbons such as ethane, partial oxidation products were produced with moderate quantum yields, which suggests a certain direct reaction of O₂ in the Herzberg states with saturated hydrocarbons.

MB28

1 min 7:57

INFRARED DIODE LASER VELOCITY MODULATION SPECTROSCOPY OF BORON CONTAINING MOLECULAR IONS

N. T. HUNT, W. Y. FAN, Z. LIU and P. B. DAVIES, *Department of Chemistry, University of Cambridge, Cambridge, UK.*

The infrared spectra of the ν_3 (B-X stretching) mode of HBCl⁺ and HBrBr⁺ have been observed using a tunable diode laser and velocity modulation spectroscopy. The ions were produced in ac glow discharges containing a flowing mixture of H₂ and BX₃ (X = Cl and Br respectively).

Thirty-two transitions of the fundamental band of the most naturally abundant H¹¹B³⁵Cl⁺ isotopomer, between 1105 and 1170 cm⁻¹ have been assigned. The ν_3 band origin and rotational constants have been determined to be $\nu_0 = 1121.5677(20)$ cm⁻¹, $B_0 = 0.63089(23)$ cm⁻¹ and $B_1 = 0.62699(21)$ cm⁻¹. A second series of lines have been attributed to the H¹¹B³⁷Cl⁺ isotopomer, although it has not yet been possible to make an unambiguous J assignment of these lines.

Thirty-three transitions of H¹¹B⁷⁹Br⁺ and the same number of lines of the H¹¹B⁸¹Br⁺ isotopomer have been assigned. The band origins and rotational constants are H¹¹B⁷⁹Br⁺: $\nu_0 = 937.5696(13)$ cm⁻¹, $B_0 = 0.461822(42)$ cm⁻¹ and $B_1 = 0.459254(41)$ cm⁻¹. H¹¹B⁸¹Br⁺: $\nu_0 = 936.0554(11)$ cm⁻¹, $B_0 = 0.460330(45)$ cm⁻¹ and $B_1 = 0.457778(43)$ cm⁻¹. *Ab initio* calculations of the band origins and the internuclear distances have been performed using the GAUSSIAN 94 package. The calculated values are in highly satisfactory agreement with the experimental results.

MB29

1 min 7:58

KINETIC SPECTROSCOPY OF THE NCl $b^1\Sigma^+ - X^3\Sigma^-$

ANATOLY V. KOMISSAROV, MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322*; STEVE J. DAVIS, *Physical Science Inc. 20 New England Business Center, Andover, MA 01810*; GERRY C. MANKE II, *Air Force Research Laboratory, Kirtland AFB, NM 87117*.

Renewed interest in the low-lying metastable electronic states of NCl has been generated by the realization that NCl($a^1\Delta$) may be used as energy carrier in chemical laser devices^a. In order to characterize the conditions within a device (local temperature, pressure and concentration) we are currently developing spectroscopic diagnostics based on direct absorption measurements of NCl $b^1\Sigma^+ - X^3\Sigma^-$ transition.

We report studies of the $b^1\Sigma^+ - X^3\Sigma^-$ system using photolytic generation of NCl, combined with long-path absorption measurements. A CW ring dye laser was used to obtain high resolution (Doppler limited) spectra. Branching ratios for $N_3Cl + h\nu \rightarrow NCl(X^3\Sigma^-/a^1\Delta) + N_2$ were determined for 193 and 248 nm photolysis. Time-resolved measurements provided information about NCl energy transfer and reaction kinetics. The relevance of the results to NCl($a^1\Delta$)/I transfer lasers will be discussed.

^aThomas *et al* Chem. Phys. Lett. **299**, 583(1999).

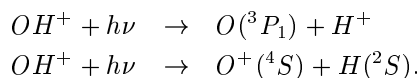
MB30

1 min 7:59

NEAR THRESHOLD PHOTODISSOCIATION OF STORED OH⁺ IONS

U. HECHTFISCHER, J. LEVIN, L. KNOLL, M. LANGE, G. SAATHOF, R. WESTER, A. WOLF, D. SCHWALM, *Max-Planck-Institut für Kernphysik, D-69029 Heidelberg, Germany*; D. ZAJFMAN, *Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel*.

When molecules dissociate into open-shell atoms, the fine structure splitting at the atomic limit of the dissociation provides a narrow energy window where resonant dissociation processes are expected. This resonant behavior is due to non-adiabatic interactions between the split electronic states at large internuclear distances. Near-threshold photodissociation spectra are therefore sensitive probes to study the dynamics of highly excited molecular states as well as resonant collision processes. We report on the photodissociation of vibrationally cold OH⁺ ions, stored at the TSR storage ring in Heidelberg, Germany. A special interest in this process is due to the accidental coincidence of the dissociation channels:



This is considered to be the origin of an enhanced rate of the charge transfer reaction $O^+ + H \rightarrow O + H^+$ which is the main reaction responsible for the ionization of hydrogen in the earth's ionosphere.

In this measurement the resonant near-threshold structure of OH⁺ dissociation into both the $O^+ + H$ and $O + H^+$ channels was observed for the first time. The analysis of the spectrum was simplified by the *a priori* information on the spectroscopic parameters of the vibrational ground state, and by the variation of the resonance amplitudes with the storage time due to rotational cooling. Most of the lines were assigned to transitions from low rotational levels in the ground state $^3\Sigma^-(v = 0, N)$ to the spin-orbit split excited state $^3\Pi_{0,1,2}(v, J)$. All resonances in the O^+ channel are $^3\Pi_{0\pm}$ shape resonances. This is consistent with a previous measurement of high- J $^3\Pi$ shape resonances by Helm *et al.*^a. An improved value for the dissociation energy of this channel was obtained from the spectrum: $D_0 = 40410 \pm 2 \text{ cm}^{-1}$, in agreement with the previously quoted value $40384 \pm 35 \text{ cm}^{-1}$ ^a.

^aH. Helm, P. C. Cosby, and D. L. Huestis, Phys. Rev. **A30**, 851 (1984).

MB31

1 min 8:00

A CROSSED BEAM STUDY OF THE REACTIONS $C(^1D)+H_2$ AND $C(^1D)+CH_4$

A. BERGEAT, L. CARTECHINI, P. CASAVECCHIA, and G. G. VOLPI, *Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy.*

We report on the first crossed molecular beam study of the reaction dynamics of $C(^1D)+H_2$ and $C(^1D)+CH_4$. These studies were made possible by the very recent development in our laboratory of *continuous* supersonic beams of $C(^3P, ^1D)$ atoms in a high pressure radio frequency discharge beam source (the reaction of $C(^3P)$ with H_2 is strongly endoergic and that with CH_4 has a very high energy barrier). These reactions are of great fundamental and practical interest. While LIF studies of $C(^1D)+H_2$ have been reported, no dynamical studies are available for $C(^1D)+CH_4$. The reaction $C(^1D)+H_2$ at a collision energy of 3.8 kcal/mol is found to proceed by *insertion* forming an excited CH_2 (methylene) radical which decomposes into $H + CH$ (methylidene). The $CH(X^2\Pi)$ product is formed predominantly in $v'=0$, but a small fraction of $v'=1$ is also observed. The mechanism and the product energy partitioning into translation, vibration and rotation are characterized. The reaction $C(^1D)+CH_4$ at a collision energy of 7.2 kcal/mol proceeds by insertion forming an excited ethylene/ethylidene molecule which decomposes following two energetically and dynamically quite different reaction pathways: simple bond fission leads to $H + CH_2CH$ (vinyl) and concerted elimination to $H_2 +$ acetylene. The center-of-mass angular and translational energy distributions for each reaction channel are derived. Interesting comparisons are made between the unimolecular dissociation behavior of the chemically activated ethylene reaction intermediate and the UV photodissociation of the C_2H_4 molecule at comparable total energy, which has been extensively studied, both experimentally and theoretically, most notably by Y. T. Lee and coworkers.

MB32

1 min 8:01

DISSOCIATIVE RECOMBINATION OF O_2^+ AND THE GREEN AIRGLOW

M. LARSSON, A. AL-KHALILI, S. ROSN, L. VIKOR, J. SEMANIAK, A. LE PADELLEC, H. DANARED, M. AF UGGLAS, *Department of Physics, Box 6730, Stockholm University, S-113 53 Stockholm, Sweden*; R. PEVERALL, W. VAN DER ZANDE, *FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*; R. BOBBENKAMP, *Faculty of Physics, University of Bielefeld, 33615 Bielefeld*; J.R. PETERSON, *Molecular Physics Laboratory, SRI International, Menlo Park, California 94025.*

Dissociative recombination (DR) and of O_2^+ have been investigated using the ion storage ring CRYRING at the Manne Siegbahn Laboratory at Stockholm University. DR of O_2^+ plays an important role in atmospheric physics and chemistry, in particular in the F-region (above 140 km) where it gives rise to the 557.7 nm green airglow (arising from the $O(^1S) - O(^1D)$ transition). The green airglow has a long history of controversy. In 1997 two important steps forward were taken. The $O(^1S)$ quantum yield for DR of O_2^+ populating a broad vibrational distribution was measured for an electron energy of nominally 0 eV using the ASTRID storage ring and an imaging technique ^a. Despite the complication with using vibrationally hot O_2^+ , it was possible to deduce an $O(^1S)$ quantum yield of 0.05 for DR of O_2^+ ($v = 0$). A new mechanism was suggested ^b and showed to quantitatively give a yield in quite good agreement with experiment. Three experimental improvements were implemented in the present work. An ultracold electron beam allowed cross sections and quantum yields to be measured at an energy resolution of about 1 meV, a specially designed ion source supplied O_2^+ in its zeroth vibrational level, and an image intensifier was added to our three-dimensional imaging detector. The use of an image intensifier strongly reduced background events arising from collisions of O_2^+ in the rest gas. Thus, for the first time one experiment combines absolute cross section measurements with quantum yield determinations as a function of electron energy for vibrationally cold O_2^+ . A thermal rate coefficient of $2.0 \times 10^{-7} \text{ cm}^3\text{s}^{-1}$ at 300 K was obtained. The $O(^1S)$ quantum yield shows a strong dependence on the electron energy.

^aD. Kella, L. Vejby-Christensen, P. J. Johnson, H. B. Pedersen, and L. H. Andersen, *Science* 276, 1530 (1997); *ibid.* 277, 167 (1997)

^bS. L. Guberman, *Science* 278, 1276 (1997)

MB33

1 min 8:02

PREREACTIVE EVOLUTION OF SUBSTITUTED ETHYLENES EXCITED IN THE 6eV REGION

M.ELHANINE, B.SOEP, *Laboratoire de Photophysique Molculaire Bat 210 Universit Paris Sud 91405 Orsay France*; J.M.MESTDAGH, J.P.VISTICOT, *DRECAM, SPAM CE Saclay BP Gif sur Yvette France*.

It is well known that in photochemical reactions there is a preparation stage ahead of the reactive encounter. For example the reactivity of triplet states results from the intersystem crossing of molecules prepared in their singlet manifold. We have studied here the ultrafast dynamics of substituted ethylenes, namely hexenes, following their excitation at 200nm. This region corresponds to their first excited singlet states where an extensive state mixing occurs between Rydberg and valence states. We have observed by time of flight mass spectrometry the decay of the initially excited states probed at 263nm. There appears a rapid decay in the 100 fs regime followed by a slower evolution ranging from 2 to 5ps. The rapid decay has been assigned to the wave packet motion connecting the Rydberg and valence states. Rydberg states have a quasi planar geometry while the valence states exhibit a 90 eclipsed configuration corresponding to the opening of the double C=C bond and rotation about it. By comparing various isomers of the hexenes, we have observed a wealth of behaviours and assigned the ultrafast evolution to the double bond opening followed by internal conversion to the ground electronic state of the system. The constrained ones or possessing heavy substituents on both sides of the double bond exhibit a longer initial decay relative to the others with a lower moment of inertia about the initial double bond. This ultrafast evolution is very similar to the rotation observed by A.H.Zewail on stilbene yielding the formation of a diradical state.

TA. TUESDAY MORNING CARRINGTON SESSION

AUGUST 17, 1999 – 8:15 AM

Room: BALLROOM, LITTLE AMERICA HOTEL

Chair: ROBERT CURL, Rice University, Houston, TX

Alan Carrington Tribute

15 min 8:15

TA01

40 min 8:30

MICROWAVE SPECTROSCOPY AT THE DISSOCIATION LIMIT

ALAN CARRINGTON, *Department of Chemistry, University of Southampton, UK.*

An ion beam technique has been developed which allows energy levels lying close to the dissociation limit to be studied by microwave spectroscopy. Electric field dissociation provides a high degree of state selectivity, with corresponding sensitivity. The technique was originally developed to study the spectra of $\text{H}_2^{(+)}$ and its isotopes, but has since been extended to a number of rare gas dimer ions, and one triatomic ion. All of the species studied have open-shell ground states, and exhibit different angular momenta coupling schemes as dissociation is approached. The details will be discussed in this talk.

TA02

40 min 9:15

SPECTROSCOPY AND DYNAMICS OF H_2OH

DAVID C. CLARY, *Department of Chemistry, University College London, London WC1H 0J, UK.*

There has been much recent interest on the spectroscopy and dynamics of weakly-bound clusters formed between radicals and other atoms or molecules. The weakly-bound dimer H_2OH is of special interest as H_2 and OH have the potential to react to produce $\text{H}_2\text{O}+\text{H}$. This talk will present recent calculations we have performed on the vibrational predissociation (VP) dynamics of H_2OH . The VP lifetimes and rotational product distributions for initial excitation of both the OH and H_2 vibrations have been calculated. A time-dependent wavepacket method has been used in which all nine coupled degrees of freedom are treated. The potential energy surface is obtained from high-quality ab initio calculations [1]. The results compare quite favourably with time-resolved measurements made recently by M. I. Lester and co-workers. Comparison will also be made with similar calculations on the related weakly-bound molecule H_2HF . In addition, the possibility of inducing reaction by vibrationally exciting H_2OH to produce $\text{H}_2\text{O}+\text{H}$ reactive products will be discussed.

[1] S. M. Miller, D. C. Clary, A. Kliesch and H.-J. Werner, *Molec. Phys.*, 83, 405 (1994).

Intermission

TA03**40 min 10:20**

FREE RADICAL SPECTROSCOPY AND DYNAMICS BY LASER ABSORPTION TECHNIQUES

TREVOR J. SEARS, CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY, UPTON, NY 11973-5000.

Tunable continuous wave laser-based spectrometers have been used to record new spectra of molecular free radicals in the infrared and near infrared. This talk will concentrate on spectra of ethyl (C_2H_5) close to 530 cm^{-1} and a number of carbenes and other species at near infrared wavelengths. In C_2H_5 , the spectrum is due to the CH_2 out-of-plane rocking fundamental with complicated torsion-rotational structure that has now been analyzed to provide estimates for the torsional barrier and its change on vibrational excitation. At near-IR wavelengths, frequency modulation techniques can be used to increase the absorption sensitivity since the dominant noise source here is due to the probe laser; detector noise is negligible. This is not the case in the infrared where detector and laser source noise are comparable in magnitude. Examples from recent work on HCB r both at room temperature and in a jet-cooled source and simple metal containing radical species formed in an ablation source combined with a free jet expansion will be described.

Acknowledgement: This work was carried out at Brookhaven National Laboratory under contract DE-AC02-98CH10886 with the U. S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

TA04**40 min 11:05**

FAR-INFRARED LASER MAGNETIC RESONANCE

KENNETH M. EVENSON, Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO 80303-3328.

We have extended FIR LMR to the 400 cm^{-1} region (12 THz.) by developing a high finesse FIR cavity that permits many new short wavelength lines to oscillate. At these shorter wavelengths, we have been able to measure many atomic and molecular fine structure spectra in Al, P^+ , N^+ , F^+ , Si, S, Fe, Fe^+ , and FO.

We have also observed bending transitions of poly-atomic free-radicals: FeD_2 , CCN, HCCN, and DCCN. This opens up the highly sensitive technique of FIR LMR to many new species, and provides accurate frequencies of these species for radio astronomical searches for them.

The FO radical, with a dipole moment of only 4.3 milliDebye, has never been observed in the microwave region. The highly sensitive technique of FIR LMR has sufficient sensitivity to permit the observation of the magnetic dipole fine-structure spectra of FO with an excellent signal to noise. The spectra have all been analyzed, and a value of $-196.108686(50)\text{ cm}^{-1}$ for the value of A_0 has been determined along with values for rotational, centrifugal distortion, spin-orbit, lambda-doubling, magnetic hyperfine and Zeeman terms.

Bending spectra have been recorded permitting accurate determinations of the band origins of 221.14321 cm^{-1} for the ${}^5\Pi_3 \leftarrow {}^5\Delta_4$ band and 226.060 cm^{-1} for the ${}^5\Phi_3 \leftarrow {}^5\Delta_2$ band of FeD_2 . The band origin for the CCN (010) $\mu^2\Sigma^- \leftarrow (000)\tilde{X}^2\Pi_r$ transition is $179.5988176(67)\text{ cm}^{-1}$.

A new LMR spectrometer with 20 times more power is under construction and sensitivity comparisons with the previous FIR LMR spectrometer will be shown. In preliminary tests with the new pumping geometry 20 times more power was obtained and two lines at close to 400 wavenumbers oscillated. We must now search for many of the new short wavelength transitions in methanol to fill some of the spectral gaps where very few lines existed. A beam-splitter coupled double output might even improve the sensitivity more by balancing the noise in a differential detection scheme.

Far-infrared LMR has been used to measure the Zeeman spectra of 71 free-radicals up to now. Many more species remain to be measured in the future.

TB. TUESDAY POSTER PRESENTATIONS

AUGUST 17, 1999 – 7:30 PM

Room: BALLROOM, LITTLE AMERICA HOTEL

Chair: PETER BOTSCHWINA, Universitat Gottingen, Gottingen, Germany

TB01

1 min 7:30

LASER-INDUCED FLUORESCENCE DETECTION OF ATMOSPHERIC NO₂ AT PARTS PER TRILLION MIXING RATIOS: IMPLICATIONS FOR NITROGEN OXIDE PHOTOCHEMISTRY IN THE STRATOSPHERE AND TROPOSPHERE

PROFESSOR RONALD C. COHEN, *B64A HILDEBRAND, DEPARTMENT OF CHEMISTRY, AND DEPARTMENT OF GEOLOGY AND GEOPHYSICS, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720-1460.*

The NO₂ radical affects the abundance of O₃ and OH throughout the atmosphere, exerting important influence over the oxidative capacity of the atmosphere, on the distribution of compounds that contribute to the Earth's greenhouse effect, on production of organic and inorganic aerosol and on production of photochemical smog. NO₂ mixing ratios vary from 10s of parts per billion (ppb) in cities to below 10 parts per trillion (ppt) in remote regions of the atmosphere. We describe a sensitive (20ppt/10 sec, S/N=2) laser-induced fluorescence (LIF) instrument designed for accurate ($\pm 5\%$, 1σ), continuous, autonomous, in situ observations of NO₂ in any of these environs. The technique is advantageous because it is direct, in that it does not require conversion of NO₂ into another species (e.g. NO) prior to detection eliminating a class of potential interferences, and it is spectroscopically specific. The instrument weighs about 200lbs including all components necessary for operation (computers, calibration gases, . . .) and consumes about 2kW of electrical power. Performance of the instrument is illustrated with 15 weeks (July-Oct 1998) of nearly continuous observations at the University of California, Blodgett Forest field station located in the foothills of the Sierra Nevada. Ambient concentrations of NO₂ at this site varied from below 50 ppt to 4000 ppt and NO₂ ranged from 0.05 to 0.5 of total reactive nitrogen. Analysis of these observations and related NO, NO_y and O₃ measurements are used to calculate regional and local scale O₃ production rates. Analysis of observations obtained using our technique from NASA's ER-2 aircraft are used to infer quantitative uncertainties in reaction rate constants directly from stratospheric observations.

TB02

1 min 7:31

EFFECT OF WATER ON PARTICLE FORMATION IN DILUTE AROMATIC GAS MIXTURES

REGINA J. CODY, *Astrochemistry Branch, NASA's Goddard Space Flight Center, Greenbelt, MD 20771*; MARK A. IANNONE, *Department of Chemistry, Millersville University, Millersville, PA 17551*; and FRED L. NESBITT, *Department of Natural Sciences, Coppin State College, Baltimore, MD 21216.*

Particles of various organic compositions have been observed through infrared (IR) spectral features in interstellar clouds and circumstellar shells. Organic molecules are present in these entities in gas concentrations of usually no more than parts per million by volume (ppmv). A laboratory technique can generate small carbonaceous particles from gas mixtures containing small organic molecules in the ppmv range with photodissociative initiation. The photolysis source is an excimer laser at 193 nm. Since the flow area of the gas mixture is greater than that of the laser beam, reactions among radical fragments and unirradiated reactant molecules are producing the particles. A red diode laser is used to monitor the particles by scattering. Particle samples are collected on IR transmitting substrates, and their IR spectra from 2.5 - 14 or 20 microns are measured with an FTIR spectrometer. Past experiments have consisted of photolyzing a gas mixture of several ppmv of small aromatic molecules (benzene, toluene, ethylbenzene, xylenes) in each of the carrier gases (nitrogen, argon, helium) with water vapor at saturation. The water vapor adds oxidative capacity. In this poster the results will be presented of experiments with reduced water concentration from near saturation, 75% relative humidity, 50%, 25% and no water vapor. The Laboratory Astrophysics Program of NASA Headquarters is supporting this research.

TB03

1 min 7:32

HIGH-RESOLUTION INFRARED SPECTROSCOPY OF Ar-OH

MARTYN D. WHEELER, R. TIMOTHY BONN, and MARSHA I. LESTER,
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

An infrared-ultraviolet (IR-UV) double-resonance scheme has been employed to probe the vibrational spectroscopy of Ar-OH in the region of the OH fundamental stretch ($2.8 \mu\text{m}$). Using an optical parametric oscillator Ar-OH is prepared with one quantum of OH stretch ($\nu_{\text{OH}} = 1$), while a UV laser promotes Ar-OH ($\nu_{\text{OH}} = 1$) to the excited *A* electronic state resulting in laser-induced fluorescence signal. Transitions have been observed from ground state Ar-OH ($\nu_{\text{OH}} = 0$, $K=3/2$) to the pure OH fundamental stretch ($\nu_{\text{OH}} = 1$, $K=3/2$) and the first combination band ($\nu_{\text{OH}} = 1$, $K=1/2$) involving intermolecular bending excitation. The pure fundamental stretching band gives rise to PQR rotational structure typical of a parallel band of a molecule containing unquenched orbital angular momenta. The OH fundamental stretch of Ar-OH in its ground electronic state is shifted 0.64 cm^{-1} to lower energy from that in free OH. The combination band shows a rather more complicated rotational band structure due to the large splitting between rotational levels with the same total angular momentum and opposite parity in the excited intermolecular bending state. The experimental determination of the parity splitting provides a direct measure of the splitting between the *A'* and *A''* potential energy surfaces in the non-linear configurations accessed by the excited intermolecular bend. The experimental results are found to be in near quantitative agreement with recent bound state calculations on a new high-level *ab initio* potential energy surface. A direct comparison of the observed energy level structure of the $K=1/2$ state with these calculations will be presented.

TB04

1 min 7:33

CROSSED BEAM REACTIVE SCATTERING OF CONTINUOUS SUPERSONIC BEAMS OF $\text{C}(^3\text{P}, ^1\text{D})$ ATOMS AND $\text{CN}(^2\Sigma^+)$ RADICALS

A BERGEAT, L. CARTECHINI, P. CASAVECCHIA, and G. G. VOLPI, *Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy.*

Very recently, we have developed beam sources, based on a high-pressure, high-power radio-frequency discharge, able to produce, for the first time, *continuous* supersonic beams of C atoms and of CN radicals of high speed ratio (up to 9) and, most important, of intensity high enough to measure product angular and velocity distributions with high signal-to-noise in crossed beam reactive scattering experiments with mass spectrometric detection. Carbon atoms and cyanogen radicals are generated starting from dilute mixtures of CO_2/O_2 and CO_2/N_2 , respectively, in a rare gas carrier. The carbon beam is made essentially of only C atoms, with C_2 being of the order of a few percent, and C_3 absent. The C atoms are in the ground ^3P and first excited ^1D states, as demonstrated by the observation of $\text{CH}(X^2\Pi)$ product in studies of the reaction with molecular hydrogen, which is endoergic for $\text{C}(^3\text{P})$. The CN radicals are in the ground electronic state $X^2\Sigma^+$ and are expected to be vibrationally and, especially, rotationally relaxed in the supersonic expansion. We have performed preliminary crossed beam experiments on the reactive scattering of $\text{C}(^3\text{P}, ^1\text{D}) + \text{C}_2\text{H}_2$ and of $\text{CN}(^2\Sigma^+) + \text{C}_2\text{H}_2$. Detailed information on the dynamics of formation of $\text{H} + \text{C}_3\text{H}$ and of $\text{H} + \text{HC}_3\text{N}$ (cyanoacetylene), respectively, are obtained. The reactions of C and CN with unsaturated hydrocarbons are of great relevance in combustion and interstellar chemistry and have recently attracted a great deal of experimental and theoretical attention.

TB05

1 min 7:34

FLASH PYROLYSIS INFRARED LASER JET SPECTROSCOPY OF FREE RADICALS AND TRANSIENT MOLECULES

RAY J. LIVINGSTONE, ZHUAN LIU and PAUL B. DAVIES, *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom.*

We have developed a novel method of generating free radicals and transient molecules for high resolution infrared laser absorption spectroscopy. The method is based on the *flash pyrolysis* technique introduced in 1986 by Chen and co-workers to study organic free radicals by REMPI ^a.

As a test of the spectrometer we first used flash pyrolysis to form the methyl radical and measured its ν_2 out of plane bending mode ^b. The molecule was produced from one of three precursors: *tert*-butyl nitrite, di-*tert* butyl peroxide and nitromethane. Oven temperatures up to 1500 K were used and the measured rotational temperature of CH₃ was about 30 K. A study of methyl ketene is now under way. This transient molecule was produced from pyrolysis of propionyl chloride and many lines of the ν_4 fundamental, the C=C=O stretch, have been measured near 2135 cm⁻¹. The jet cooled spectrum is distinctly different from the spectrum observed at 600 K using infrared laser powered homogeneous pyrolysis reported by Russell and Hore. Another study currently under way is of propadienone (H₂C₃O), a candidate for astrophysical detection. This is produced by flash pyrolysis of acrylic anhydride. Many lines of the ν_3 C=C=C asymmetric stretch around 2130 cm⁻¹ have been measured.

^aP. Chen, S. D. Colson, W. A. Chupka and J. A. Berson, *J. Phys. Chem.*, 90, 2319 (1986).

^bZ. Liu, R. J. Livingstone and P. B. Davies, *Chem. Phys. Lett.*, 291, 480 (1998).

TB06

1 min 7:35

ALL ELECTRON AB INITIO INVESTIGATIONS OF DIATOMIC TRANSITION METAL CARBIDES

I. SHIM, *Technical University of Denmark, Department of Applied Chemistry, DTU 375 DK2800 Lyngby, Denmark*; K. A. GINGERICH, *Texas A&M University, Chemistry Department, PO Box 300012, College Station, TX 77843-3012, U.S.A.*

The low lying states of selected diatomic carbides of the first and second series transition metal atoms have been investigated using *ab initio* multi-configuration self-consistent-field (CASSCF) and multi-reference configuration interaction (MRCI) calculations.

The diatomic iron group carbide molecules have numerous low-lying electronic states. The electronic structure of these molecules have been interpreted as antiferromagnetic couplings of the localized angular momenta of the positive ions Fe⁺, Co⁺, or Ni⁺ with those of C⁻. In each of these molecules the chemical bond has triple bond character, but in the valence bond sense. The molecules are polar with charge transfer from the transition metal atom to the C atom.

For FeC the electronic ground state is confirmed to be ³Δ. The spectroscopic constants for the ground state have been derived as $r_e=1.585$ Å, and $\omega_e=859$ cm⁻¹ ^a.

For NiC the ground state is predicted as ¹Σ⁺, and this state is separated from the lowest-lying excited state by an energy gap of more than 6000 cm⁻¹. The spectroscopic constants for the ground state have been determined as $r_e=1.621$ Å, and $\omega_e=874$ cm⁻¹ ^b.

The electronic structure of the corresponding second series transition metal carbides is consistent with a molecular orbital diagram.

For the PdC molecule the electronic ground state is derived as ¹Σ⁺. The spectroscopic constants of the ground state have been determined as $r_e=1.764$ Å, and $\omega_e=744$ cm⁻¹.

^aI. Shim, and K. A. Gingerich, *European Phys. Jour. D* xx, yy (1999).

^bI. Shim, and K. A. Gingerich, *Chem. Phys. Lett.* 303, 87 (1999).

TB07**1 min 7:36**

EPR AND MO CALCULATION STUDIES ON AMINOANTHRAQUINONE ANION RADICALS

VIRPI VATANEN, JUSSI ELORANTA, MIKKO VUOLLE, *Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40351 Jyväskylä, Finland.*

The EPR spectra of electrolytically produced anion radicals of 1,4-diamino-9,10-anthraquinone (1,4-diamino-AQ), 1,4-bis-(methylamino)-AQ, 1-amino-4-hydroxy-AQ, 1,5-diamino-AQ, and 1,8-diamino-4,5-dihydroxy-AQ were measured in aprotic N,N-dimethylformamide and dimethylsulfoxide solvents. The isotropic hyperfine coupling constant (hcc) positions were assigned according to density functional (DFT; B3LYP/6-31G*) calculations and analogues found in the corresponding hydroxy-substituted AQs. These present results are somewhat different than was found for these compounds in protic solvents. Small differences in hccs were also found among the two aprotic solvents, which indicates that this latter effect is due to dielectric interaction of the solvent layer with the anion radicals. Inclusion of the dielectric solvent effect by the self-consistent isodensity polarized continuum model (SCI-PCM) into the DFT calculation improves the agreement between the calculated and experimental hccs.

TB08**1 min 7:37**OBSERVATION AND ANALYSIS OF THE ELECTRONIC EMISSION OF $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi_i$ OF THE FREE RADICAL *HCSi*.

R. CIREASA, D. COSSART, and M. VERVLOET, *Laboratoire de Photophysique Moléculaire du CNRS, Bât. 213, Université Paris-Sud, 91405 Orsay Cedex, France.*

Three new emission bands have been observed, for the first time, at around 12000 cm^{-1} from a DC discharge through a flowing mixture of Helium and Hexamethyldisilane ^a. They have been recorded under high resolution by means of a Fourier Transform spectrometer. We assigned them as the (000) (100), (000) (000), and (100) (000) of the electronic transition $\tilde{A}^2\Sigma^+ - \tilde{X}^2\Pi_i$ of the free radical *HCSi*. Analysis of this band system, together with the resulting molecular parameters, will be presented.

^aR. Cireasa, D. Cossart, and M. Vervloet, *Eur. Phys. J. D* **2**, 199 (1998).

TB09**1 min 7:38**FEMTOSECOND LASER SPECTROSCOPY ON THE VIBRATIONAL WAVE PACKET DYNAMICS OF THE $D^1\Pi_u$ STATE OF Rb_2

BO ZHANG, TONY HANSSON, LARS-ERIK BERG and RENÉE ANDERSSON, *Physics Department I, The Royal Institute of Technology, S-100 44 Stockholm, Sweden.*

The wave packet dynamics of the $D^1\Pi_u$ state of Rb_2 molecule coupling simultaneously to two pre-dissociation channels was studied by real time spectroscopy in various product channels at various excitation wavelengths from 424.5 nm to 435.5 nm but fixed probe wavelength of 630 nm . Due to widely different coupling strengths for the two pre-dissociation channels and a well-defined threshold energy for the faster process, the wave packet dynamics can be separated into three parts; the vibrational beating of the excited state, the fast drainage of the parts of the wave packet coupling to the strongest coupling state, and the slow decay of the part of the wave packet below the threshold for the fast process. The 853 fs oscillation period of the wave packet as well as the 3 ps decay time of the fast drainage are reported in this paper.

TB10

1 min 7:39

PRODUCTION OF HO₂ FROM ETHYL RADICAL + O₂ MEASURED FROM 298-700 K

E. CLIFFORD, J. FARRELL, J. DESAIN, C. TAATJES, *Combustion Research Facility, MS 9055, Sandia National Laboratories, 7011 East Avenue, Livermore, CA 94550.*

The reaction of C₂H₅ with O₂ has been studied in a time resolved fashion by infrared two tone frequency modulation spectroscopy. The product HO₂ has been observed as a function of pressure and temperature; the expected product OH was not observed. The appearance of HO₂ is fit to a single exponential from 298 K to 598 K. Above 598 K, another reaction pathway appears and the HO₂ production can only be fit as a biexponential, with a "prompt" and a "slow" rate. We have measured the yield of HO₂ as a function of temperature and observe that the two growth rates appear to be independent of each other. Analysis of the reaction channels with RRKM modeling will be presented.

TB11

1 min 7:40

ON MAPPING COMETARY MAGNETIC FIELDS BY HANLE-EFFECT MEASUREMENTS

J. E. ALLEN, JR., *Astrochemistry Branch, NASA Goddard Space Flight Center, Greenbelt, MD 20771.*

Spacecraft encounters with comet P/Halley in 1986 provided us with our most complete picture to date of a comet's magnetic-field strength and structure. Prior attempts to determine these properties via ground-based observations have been marginally successful. As a consequence many opportunities for detailed characterizations of the solar-wind interaction with comets before and after the most recent apparition of P/Halley have been missed. In this presentation the possibility of mapping cometary magnetic fields by resonance fluorescence depolarization (the excited-state Hanle effect) of emissions from the H₂O⁺ ion is examined. Using currently available molecular parameters, a model of the expected degree of polarization was developed for several H₂O⁺ transitions, and it suggests that the signal from this effect may be subtle. Nonetheless the results are sufficiently encouraging that further laboratory research and future spectropolarimetric observations of H₂O⁺ in particular are warranted, since the application of the excited-state Hanle effect to this ion may provide a viable, more accessible method by which to study the magnetic properties of a variety of comets.

TB12

1 min 7:41

THE NEAR INFRARED TRANSITION OF COPPER CHLORIDE BY INTRACAVITY LASER SPECTROSCOPY

J.J. O'BRIEN, *Department of Chemistry, University of Missouri, St. Louis, MO 63121-4499*; L.C. O'BRIEN, *Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026-1652.*

The near infrared electronic transition of CuCl occurring in the region of 13,500 cm⁻¹ has been recorded by intracavity laser absorption spectroscopy. The CuCl molecules were produced in a copper hollow cathode operating with an applied potential of 700 V, using 1.4 torr argon and a trace amount of carbon tetrachloride.

The near infrared transition previously was recorded by Balfour and Ram,^a and it was assigned as emission from a low-lying ³Σ⁺ state to the X¹Σ⁺ state. Recently, this transition has received considerable attention because of high level *ab initio* calculations^b that question whether this transition involves the X¹Σ⁺ ground state.

^aW.J. Balfour and R.S. Ram, *J. Phys. B* **17**, L19 (1984).

^bC. Sousa, W.A. de Jong, R. Broer and W.C. Nieuwpoort, *Mol. Phys.* **92**, 677 (1997).

TB13

1 min 7:42

HIGH RESOLUTION SPECTROSCOPIC STUDIES OF BENDING VIBRATIONS OF CARBON CHAIN FREE-RADICALS

MICHAEL D. ALLEN, KENNETH M. EVENSON, *Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO 80303-3328*; FUGE SUN, ROBERT F. CURL, *Department of Chemistry MS60, Rice University, 6100 South Main, Houston, TX 77005*; and JOHN M. BROWN, *The Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom*.

High Resolution spectroscopic studies of the bending vibrational transitions of CCN, HCCN, and DCCN have been carried out using far-infrared laser magnetic resonance (FIR LMR) spectroscopic techniques. These studies have resulted in an accurate determination of $\nu_0 = 179.598176(67) \text{ cm}^{-1}$ for the $(010) \mu^2\Sigma^- - (000)\tilde{X}^2\Pi_r$ transition of CCN. The $\tilde{X}^2\Pi_r$ state of the CCN radical is subject to large Renner-Teller interactions which shift the $(010) \mu^2\Sigma^-$ vibronic state down below the 200 cm^{-1} region. A complete analysis resulted in the determination vibrational, Renner-Teller, fine structure, rotational, hyperfine, and molecular g-factors for the $\tilde{X}^2\Pi_r$ state of CCN. The analysis was done using an \mathbf{N}^2 effective Hamiltonian modified to include the Renner-Teller effect. The analysis of the data for HCCN and DCCN is not complete at this time, but is expected to be by the time of the conference. The most accurate values for the X-C-C bending wavenumbers of HCCN and DCCN have been determined by Curl and co-workers and are, $\nu_5 = 128.907 \text{ cm}^{-1}$,^a and $\nu_5 = 74.845 \text{ cm}^{-1}$,^b respectively. The analysis of the HCCN and DCCN radicals will be done using an 'A' reduced asymmetric rotor Hamiltonian. Both HCCN and DCCN are considered floppy molecules. This is evident from their low energy (CCH and CCD) bending vibrations.

^aJ. Han, P. Y. Hung, W. E. Jones, J. DeSain, and R. F. Curl, in preparation.

^bF. Sun, A. Kosterev, G. Scott, V. Litosh, and R. F. Curl, *J. Chem. Phys.* **109**, 8851 (1998).

TB14

1 min 7:43

DISCRIMINATION OF PRODUCT ISOMERS IN THE PHOTODISSOCIATION OF HYDROCARBON MOLECULES (PROPYLENE, ALLENE, AND 1,3-BUTADIENE) AT 1933 Å

WEIZHONG SUN, KIICHI YOKOYAMA, JASON C. ROBINSON, AND DANIEL M. NEUMARK, *Department of Chemistry, University of California, Berkeley, CA 94720, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720*.

As the field of reaction dynamics evolves toward the study of more complex chemistry, it becomes necessary to develop new methods for probing the products of bimolecular and unimolecular reactions. The photodissociation of hydrocarbon molecules exemplifies the challenges one faces. Cleavage of the various inequivalent C-H bonds will result in chemically distinct isomers with the same mass, thereby complicating the identification of the primary photodissociation products. The well-established technique of molecular beam photodissociation with product detection by electron impact ionization cannot, in general, distinguish among isomers. While laser-based methods such as laser-induced fluorescence or resonant multiphoton ionization can in principle do better, this requires a fuller understanding of the electronic spectroscopy of polyatomic hydrocarbon radicals than is often available. On the other hand, isomers of hydrocarbon radicals often have different ionization potentials. This is exploited in the work presented here, where tunable vacuum ultraviolet (VUV) radiation from the Berkeley Advanced Light Source is used to ionize and therefore identify the product isomers of the photodissociation of allene, propyne, and 1,3-butadiene. We will present in this talk the primary dissociation channels and dynamics of photodissociation of hydrocarbon molecules (propyne, CH_3CCH ; allene, H_2CCCH_2 ; 1,3-butadiene, $\text{CH}_2\text{CHCHCH}_2$) which have been studied using the method of molecular beam photofragment translational spectroscopy following the excitation of 193 nm. Furthermore, the product isomers C_3H_3 and C_3H_2 from dissociation of propyne and allene have been discriminated by using photoionization spectroscopy. For the studies of 1,3-butadiene, photoproduct isomers were discriminated by photoionization spectroscopy as well as by employing deuterated species for further confirmation.

TB15

1 min 7:44

CALCULATION OF STATE-TO-STATE RATE COEFFICIENTS FOR $\text{H}_2(v,j) + \text{H}_2(v',j')$

M. E. MANDY, *Program in Chemistry, University of Northern British Columbia, 3333 University Way, Prince George, BC V2N 4Z9.*

Rate coefficients for transitions among the (v,j) states of molecular hydrogen as the result of collisions with other hydrogen molecules can be calculated from the corresponding cross sections. I have determined converged cross sections from quasiclassical trajectory results for the (v,j) states of molecular hydrogen with internal energy of less than 1 eV. The chemically accurate potential energy surface of Keogh, Boothroyd, Martin and Peterson (Journal of Chemical Physics 95 4331 1991) was used for the trajectory calculations. Also discussed are issues in determination of thresholds to energy transfer, microscopic reversibility and the extension of the calculation to all combinations of (v,j) states of the $\text{H}_2(v,j) + \text{H}_2(v',j')$ system. Application of the results to the master equation studies of shocked interstellar hydrogen is also considered.

TB16

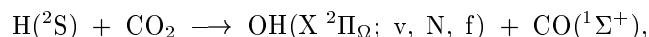
1 min 7:45

STEREODYNAMICS OF THE $\text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO}$ REACTION

M. BROUARD, W. DENZER, D. W. HUGHES, K. S. KALOGERAKIS, V. G. STAVROS, and J.P. SIMONS, *Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom.*

The goal of our experimental research is to elucidate the microscopic details of bimolecular reactions in the gas phase. We use polarised Doppler-resolved, laser-induced fluorescence spectroscopy to determine the product state-specific differential cross sections and vector correlations in the scattered products of photon-initiated bimolecular reactions. These recently developed techniques have been tested and proven to be powerful tools in unraveling the intricacies of the relation between reactants, transition state(s), and reaction products.^{a,b}

The photon initiated reaction system chosen in the present study is



which proceeds through the intermediacy of a transient collision complex. Our experiments provide measurements of the linear and angular momentum correlations in the state-resolved scattered OH fragments. The rich dynamics of this reaction is being explored by a systematic study of the scattering of the OH product for a variety of vibrational, rotational, spin-orbit, and Λ -doublet states conducted at different collision energies.^{c,d} Our studies also address the question whether electronically excited surfaces are involved.

We acknowledge financial support from the Leverhulme Trust, the EPSRC and Shell Research Plc.

^aA.J. Alexander, M. Brouard, K.S. Kalogerakis, and J.P. Simons, Chem. Soc. Rev. 27, 405 (1998).

^bA.J. Orr-Ewing and R. N. Zare, Annu. Rev. Phys. Chem., 45, 315, (1994).

^cM. Brouard, H.M. Lambert, S.P. Rayner, and J.P. Simons, Mol. Phys. 89(2), 403(1996).

^dM. Brouard, D.W. Hughes, K.S. Kalogerakis, and J.P. Simons, J. Phys. Chem. 102(47), 9559 (1998).

TB17

1 min 7:46

UV-LASER PHOTOLYSIS OF BROMOFORM: KINETIC ROTATIONAL SPECTROSCOPY OF CBr AND HCBr

MARCEL BOGEY, CLAIRE DEMUYNCK, MELINDA HASSOUNA and ADAM WALTERS, *Laboratoire PhLAM, CERLA, University of Lille 1, F-59655 Villeneuve d'Ascq, France.*

We have measured the first millimeter wave spectrum of CBr produced by excimer laser excitation of CHBr_3 at 193 nm. In our kinetic experiments, the laser radiation is pulsed and the radicals created after each shot are eliminated by collisional reactions before the next. During frequency scanning a time-dependent signal is recorded at each frequency point. These data are treated so that only the spectra of short-lived molecules are observed and the precursor spectrum is eliminated. Thanks to predictions based on recently observed IR spectrum of CBr^a we observed the millimeter wave spectrum of both ^{79}Br and ^{81}Br isotopes. The fine and hyperfine structure have been analysed. In the same experimental conditions, some transitions attributed to a b-type branch of HCBr were observed for both Br isotopes. They are in agreement with the recent observations of Marr et al. in the near infrared^b. The search for other lines belonging to a- and b-type spectra is still in progress. The measurement of the pure rotational spectrum will allow the first determination of the A rotational constant, a more precise determination of the other molecular parameters and the analysis of the quadrupolar hyperfine structure.

^aA. J. Marr, T. J. Sears and P. B. Davies *J. Mol. Spectrosc.* **184**, 413-433 (1997)

^bA. J. Marr, S. W. North, T. J. Sears, L. Ruslen and R. W. Field *J. Mol. Spectrosc.* **188**, 68-77 (1998)

TB18

1 min 7:47

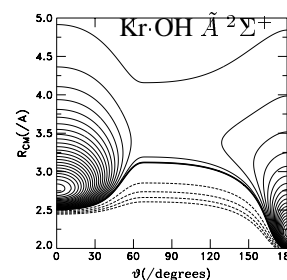
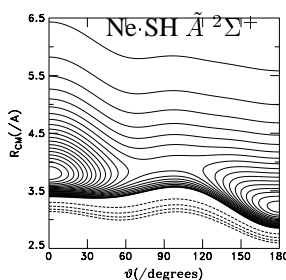
EMPIRICAL POTENTIAL ENERGY SURFACES FOR THE $\text{R}\cdot\text{XH}/\text{D}$ ($\text{R}=\text{Ne, Ar, Kr}$; $\text{X}=\text{O, S}$) FAMILY OF COMPLEXES

CHRISTOPHER C. CARTER, HEE-SEUNG LEE, ANNE B. MCCOY, EDWARD F. HAYES, AND TERRY A. MILLER, *Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.*

We have recently developed empirical potential energy surfaces (PES) for the $\text{Ne}\cdot\text{OH}/\text{D}$ complexes. This could only be accomplished with a reassignment of several of the vibronic bands. In particular those involving bending motion, that had previously been assigned to one quantum of stretch, have now been assigned to fundamentals of the bend. This reassignment results in the PES reproducing all the vibronic band origins to less than 1 cm^{-1} , and the rotational constants to within 1%.

These results complement previous work done on the $\text{R}\cdot\text{XH}/\text{D}$ ($\text{R}=\text{Ne, Ar, Kr}$; $\text{X}=\text{O, S}$) family of complexes. The PESs for all these complexes, along with the high resolution spectral data used to determine these surfaces, gives us a complete picture of this family of rare gas-open shell radical complexes both in the $\tilde{\text{A}}$ excited state and the $\tilde{\text{X}}$ ground state, albeit with somewhat lower precision in the latter case.

High resolution, rotationally resolved spectra, along with the resulting empirical PESs will be shown. Changes in bonding from the weakest van der Waals type bond found in $\text{Ne}\cdot\text{SH}$, to the strongest 'incipient' chemical bond found in $\text{Kr}\cdot\text{OH}$ will be presented. An example of these two very different PESs are shown to the right. The contours for the $\text{Ne}\cdot\text{SH}$ plot are spaced 5cm^{-1} apart while those for $\text{Kr}\cdot\text{OH}$ plot are spaced by 100cm^{-1} .



TB19

1 min 7:48

HIGH RESOLUTION STUDIES OF THE PHOTOCHEMISTRY OF THE \tilde{A}^2A_1 STATE OF THE CH_3S RADICAL

BRIAN E. APPELEGATE, MICHAEL B. PUSHKARSKY, AND TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210.*

Using the jet-cooled $\tilde{A}^2A_1 \leftarrow \tilde{X}^2E$ electronic transition, fluorescence temporal decay (FTD) and fluorescence depletion spectroscopy (FDS) techniques have been employed to investigate the photodissociation dynamics of the \tilde{A}^2A_1 state of the methylthio radical. Evidence indicating that ν_3 (C-O/S stretch) is a major promoting motion for mode selective photofragmentation, similar to earlier observations in methoxy^a, is in good agreement with the recent work of Neumark and coworkers^b. However in contrast to CH_3O and other methoxy type radicals, the FDS spectrum of CH_3S shows that ν_2 (the umbrella motion) also plays an active role in the photodissociation process. The mass-selective photodissociation spectrum of Neumark and coworkers is consistent with excitation in ν_3 promoting the photodissociation channel,



However the photodissociation spectrum shows no evidence of activity in ν_2 . Comparisons of the photodissociation dynamics of methylthio radical to other members of the methoxy family as well as possible explanations for the activity in ν_2 will be presented.

^aPowers D. E.; Pushkarsky M.; and Miller T. A., *J. Chem. Phys.*, **1997**, *106*, 6863.

^bBise R. T.; Choi H.; Pederson H. B.; Mordant D. H.; and Neumark D. M., *J. Chem. Phys.*, **1999**, *110*, 805.

TB20

1 min 7:49

CAVITY RINGDOWN SPECTROSCOPY OF HC_7H AND HC_9H

C. D. BALL, M. C. MCCARTHY, and P. THADDEUS, *Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138 and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138.*

Vibronic bands of the $^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ transitions of linear HC_7H and HC_9H have been detected in the gas phase using cavity ringdown spectroscopy in the wavelength range 500-600 nm. The 0_0^0 bands of both molecules, as well as an additional vibronic band of HC_9H , were measured. Both molecules were produced in a DC discharge through a dilute mixture of diacetylene in Ar in the throat of a supersonic nozzle. The identifications were confirmed by detecting the singly and doubly deuterated species of both molecules, and by comparison with previous matrix data^a. Neither molecule could be detected by laser-induced fluorescence. Each band exhibits expected P- and R-branches, and the band origins have been measured to 0.1 cm^{-1} or better. For HC_9H , the wavelength of the 0_0^0 band agrees to within one part in 10^4 with that of the weak diffuse interstellar band at 581.86 nm. Astronomical verification of this assignment could be achieved by detecting the expected P- and R-branches in the DIB, or by detecting the somewhat weaker ν_3 band at 521.91 nm.

^aJ. Fulara, P. Freivogel, D. Forney, and J. P. Maier, *J. Chem. Phys.* **103**, 8805 (1995).

TB21**1 min 7:50**

THE ROTATIONAL SPECTRUM OF IODINE DIOXIDE, OIO

CHARLES E. MILLER, *Department of Chemistry, Haverford College, Haverford, PA 19041-1392*; and EDWARD A. COHEN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099*.

OIO is an asymmetric prolate rotor ($\kappa = -0.690$) with a 2B_1 electronic ground state. It was formed initially from the products of a microwave discharge in O_2 passing over molecular iodine and later with greater yield in a DC discharge through a mixture of O_2 and I_2 vapor. Although the experiment was hampered by copious solid deposits and apparently inefficient production of OIO, the rotational spectrum was quite prominent in survey scans in the millimeter and submillimeter regions. Facilitated by predictions of fine and hyperfine patterns from ESR results,^a it was eventually possible to identify high J , R branch transitions with $K_c \approx J$. Over 550 ground state transitions and over 160 transitions of the excited bending state have been included in the fits. The transitions cover a wide range of rotational quantum numbers and permit the accurate determination of an extensive set of molecular parameters. The parameters will be compared to those recently published for OBrO and OCIO and will be interpreted in terms of the molecular geometry, harmonic force field, and electronic structure.

^aJ.R. Byberg, *J. Chem. Phys.* **85**, 4790-4793 (1986).

TB22**1 min 7:51**

THE ROTATIONAL SPECTRA OF IO AND BrO

CHARLES E. MILLER, *Department of Chemistry, Haverford College, Haverford, PA 19041-1392*; EDWARD A. COHEN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109-8099*; and HOLGER S. P. MÜLLER, *I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, D-50937 Köln, Germany*.

The rotational spectra of IO in vibrational states up to $v = 13$ in the $X_1^2\Pi_{3/2}$ state and up to $v = 9$ in the $X_2^2\Pi_{1/2}$ state have been observed in an O_2 DC discharge over molecular I_2 . In addition, $I^{18}O$ has been observed for both the X_1 and X_2 states up to $v = 5$. All data have been analyzed simultaneously with fixed isotopic ratios among the constants. This provides the first high resolution data for the X_2 state and for $I^{18}O$. Vibrationally hot BrO has also been observed in an O_2 DC discharge which contains a small amount of Br_2 . The BrO measurements are still in progress and have been extended to $v = 6$ for the $X_1^2\Pi_{3/2}$ state and to $v = 3$ for the $X_2^2\Pi_{1/2}$ state of the ^{16}O species. $Br^{18}O$ spectra for the vibrational ground state of both the X_1 and X_2 states as well as $v = 1$ of the X_1 state are included in a simultaneous fit of all eight isotopomers. Extensive sets of parameters have been derived for both IO and BrO. These will be interpreted in terms of the electronic structure and the interatomic potential and compared with those of related molecules.

TB23**1 min 7:52**

FOURIER TRANSFORM EMISSION SPECTROSCOPY AND AB INITIO CALCULATIONS ON OsN

P. BERNATH, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*; R. S. RAM, *Dept. of Chemistry, University of Arizona, Tucson, AZ 85721*; J. LIEVIN, *Universite Libre de Bruxelles, Laboratoire de Chimie Physique Moleculaire, CP 160/09 Av. F. D. Roosevelt 50, Bruxelles, Belgium*.

The emission spectrum of OsN has been recorded in the $3000\text{-}13000\text{ cm}^{-1}$ region using a Fourier transform spectrometer. OsN molecules were excited in an osmium hollow cathode lamp operated with neon gas and a trace of nitrogen. Six bands observed in the $8000\text{-}12200\text{ cm}^{-1}$ region have been classified into three transitions.

Ab initio calculations have been performed on OsN and the spectroscopic properties of the low-lying electronic states have been calculated. Our assignments are supported by these calculations. The ground state of OsN has been identified as a $^2\Delta$ state consistent with the observations for the isoelectronic IrC molecule. This work represents the first experimental or theoretical investigation of the electronic spectra of OsN.

TB24

1 min 7:53

ROTATIONALLY RESOLVED SPECTRA OF ISOVALENT NbCr AND VCr

SHANE M. SICKAFOOSE, JON D. LANGENBERG, AND MICHAEL D. MORSE, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112.*

Resonant two-photon ionization spectroscopy has been used to study the isovalent metal molecules NbCr and VCr. The first experimental observation of NbCr yielded a ground state rotational constant of $B_0'' = 0.14104(2) \text{ cm}^{-1}$, which corresponds to a bond length of $r_0'' = 1.8941(1) \text{ \AA}$. The excited state, which lies at 14440 cm^{-1} , has $B_0' = 0.14439(2) \text{ cm}^{-1}$ and $r_0' = 1.8720(1) \text{ \AA}$. The bond energy of $^{93}\text{Nb}^{52}\text{Cr}$ is measured as $24409(5) \text{ cm}^{-1}$ ($3.0260(6) \text{ eV}$) from the onset of predissociation in a congested vibronic spectrum. For $^{51}\text{V}^{52}\text{Cr}$ the ground state is identified as $^2\Delta_{5/2}$ with $B_0'' = 0.21991(26) \text{ cm}^{-1}$ and $r_0'' = 1.7265(10) \text{ \AA}$. The excited state, which lies at 14371 cm^{-1} , has $B_0' = 0.22153(27) \text{ cm}^{-1}$ and $r_0' = 1.7201(11) \text{ \AA}$. Finally, a comparison to related molecules is presented.

TB25

1 min 7:54

LIFETIME MEASUREMENT OF THE $C^3\Delta$ STATE OF TIS AND THE $E^3\Pi$ STATE OF TiO

CECILIA LUNDEVALL, *Department of Physics, Stockholm University, Box 6730, 11385 Stockholm, Sweden;*

Lifetime measurements of the $C^3\Delta$ electronic state of the titanium sulphide molecule and of the $E^3\Pi$ electronic state of the titanium oxide molecule have been performed using population probing with resonant two photon ionisation in a molecular beam.

The spectrum of titanium sulphide was first studied by Clements and Barrow in 1969 (1) and an extended analysis was performed by Jonsson and Launila (2). This molecule has been shown to be present in S-type Mira variables (3). In the present paper the lifetime of the $C^3\Delta$ state is reported for the first time.

Titanium monoxide was identified to belong to the characteristic bands of M-type stars already in 1904 by Fowler (4). Several studies of this molecule and its spectrum have made this molecule to one of the most well-known transition metal molecules. Theoretical calculations of the lifetimes of several electronic states of the TiO molecule were recently presented by Langhoff (5). The calculated lifetimes for the $E^3\Pi$ states were found to be considerably longer than previous experiments have indicated. The measurement in this paper shows a longer lifetime for the $E^3\Pi$ state, which supports the theoretical calculations.

References.

1. R. M. Clements and R. F. Barrow, *Trans. Faraday. Soc.* 65, 1163-1167 (1969).
2. J. Jonsson and O. Launila, *Mol. Physics.* 79, 95-103 (1993).
3. J. Jonsson, O. Launila and B. Lindgren, *Mon. Not. R. astr. Soc.* 258, 49P-51P (1992).
4. A. Fowler, *Proc. Roy. Soc. A* 73, 219 (1904).
5. S. R. Langhoff, *Astrophys. J.* 481, 1007-1015 (1997).

TB26**1 min 7:55**

REMPI SPECTROSCOPY OF TRANSITION METAL CONTAINING MOLECULES

JOHN A. DICKINSON, and TIMOTHY C. STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe, Az, 85287-1604.*

In previous work¹ by this group and A. J. Merer's group at the University of British Columbia YC_2 was tentatively identified as the carrier of an optical band assigned as an $A_1 \leftarrow \tilde{X}^2A_1$ transition, with the (0-0) band origin at $12\,889.5\text{cm}^{-1}$. This was the first observation of the electronic spectrum of a gas phase transition metal dicarbide species and was consistent with a theoretically proposed T-Shaped structure². However, that study provided no direct evidence for the identity of the carrier of the spectral features (through isotopic substitution or rotational analysis). In this work the REMPI spectrum of YC_2 in the same spectral region will be presented, confirming YC_2 as the carrier of the band system at $12\,889.5\text{cm}^{-1}$.

In addition, we have observed the time of flight mass spectra of a variety of other TM/carbon species including La_xC_y ($x=1-6$, $y=1-10$) in the products of the reaction of laser ablated La with CH_4 .

¹ T. C. Steimle, A. J. Marr, J. Xin, A. J. Merer, K. Athanassenas and D. Gillett, *J. Chem. Phys.* **106**, 2060-2066 (1996).

² S. Roszak and K. Balasubramanian, *Chem. Phys. Lett.* **246**, 20-25 (1995).

TB27**1 min 7:56**

SPECTROSCOPIC INVESTIGATION OF NiSi: IDENTIFICATION OF THE GROUND AND EXCITED ELECTRONIC STATES.

NED F. LINDHOLM, GRETCHEN K. ROTHSCOPF, DALE J. BRUGH, AND MICHAEL D. MORSE, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112.*

The electronic structure of diatomic NiSi has been examined using resonant two-photon ionization (R2PI) and dispersed fluorescence (DF) spectroscopy. Using the first technique, the ground state is determined to have $\Omega'' = 0$ and $r_0'' = 2.030 \text{ \AA}$ and transitions to upper states with $\Omega' = 0$ and 1 are identified. Based on comparisons to theoretical calculations, a closed shell $^1\Sigma^+$ ground state is likely. Dispersed fluorescence spectroscopy revealed the locations of vibrational levels $v = 0 - 13$ and $15 - 18$, and a vibrational fit of the data provided $\omega_e'' = 467.04(35) \text{ cm}^{-1}$ and $\omega_e x_e'' = 2.03(2) \text{ cm}^{-1}$ for the $^{58}\text{Ni } ^{28}\text{Si}$ isotopic modification.

TB28**1 min 7:57**

LASER SPECTROSCOPY OF SILVER-AMMONIA COMPLEXES

JUN MIYAWAKI, KO-ICHI SUGAWARA and HARUTOSHI TAKEO, *National Institute of Materials and Chemical Research, National Institute for Advanced Interdisciplinary Research, Higashi 1-1-4, Tsukuba, Ibaraki 305, Japan.*

Complexes consisting of silver and ammonia have been investigated by using laser spectroscopy. The complexes were produced with laser ablation followed by reaction and cooling in a free jet expansion. The electronic spectra of $AgNH_3$ and $Ag(NH_3)_2$ were observed through resonantly enhanced multiphoton ionization (REMPI) combined with a mass selection. The band origin of the $\tilde{A} - \tilde{X}$ band system of $AgNH_3$, located at 21410 cm^{-1} , is shifted from the corresponding atomic transition of $Ag(5p^2P_{1/2} - 5s^2S)$ to the red side by 8142 cm^{-1} , indicating a significant stabilization upon electronic excitation. The vibrational frequencies of the intermolecular stretching and bending modes in the \tilde{A} state were derived to be 380 cm^{-1} and 185 cm^{-1} , respectively. The laser induced fluorescence (LIF), and dispersed fluorescence (DF) spectra were also observed, and the frequencies of the intermolecular stretching and bending modes in the \tilde{X} state were derived to be 185 cm^{-1} and 350 cm^{-1} , respectively.

TB29

1 min 7:58

INFRARED LINESHAPES IN FINITE CLUSTERS AND MATRIX ISOLATION

JOHN S. WINN and PING HU, *Department of Chemistry, Dartmouth College, Hanover, NH 03755.*

The high resolution interferometric infrared lineshapes of the CO fundamental isolated in solid rare gases have been analyzed by a theory that uses gas-phase pair potentials to predict not only the CO lineshape but also the local matrix environment around the CO. Differences in type of matrix site (single versus double substitution) as well as in CO orientation within a site are clearly revealed. In addition to bulk matrix spectra, the theory has been applied to finite cluster spectra where it is shown that such spectra may or may not resemble spectra observed in the bulk solid. The origin of the wide variation in commonly-observed matrix isolation linewidths and line shapes is illuminated by these studies, as are the relative transition energy shifts from one type of site to another. The observed shift of transition energy with temperature is shown to be primarily due to the thermal expansion of the solid. Highly asymmetric lineshapes are predicted, in accord with experiment, and they are shown to be due to an extremum in the chromophore transition energy as a function its position in the solvent cage.

TB30

1 min 7:59

IR SPECTRUM OF HNNO IN SOLID XE MATRIX

SANDRA L. LAURSEN, *NOAA Aeronomy Lab, R/E/AL2, 325 Broadway, Boulder, CO 80303*; ALICE E. DELIA, *KWASI MITCHELL, Kalamazoo College, Kalamazoo, MI 49006.*

The novel radical intermediate HNNO has been detected at 12 K via FTIR spectroscopy. This species is formed from the reaction of NH ($X^3\Sigma^-$) with NO in solid Xe at temperatures near 40 K. The reaction is essentially activationless. The intermediate is stable indefinitely at 12 K in the dark, but visible light induces photodestruction at wavelengths as long as 550 nm. Evidence from these experiments on the thermodynamic stability of HNNO and its isomers and a comparison with theoretical predictions will be presented. This radical has been previously postulated to be an intermediate in schemes for ammonia oxidation and NO_x removal from flue gases.

TB31

1 min 8:00

ULTRAFAST REACTIVITY OF INFRARED EXCITED ELECTRON AND EARLY FORMATION OF A SULFUR-CENTERED RADICAL ANION IN SOLUTION

Y. GAUDUEL, H. GELABERT and F. GUILLOUD, *Laboratoire d'Optique Appliquée, CNRS UMR 7639 - INSERM U 451, Ecole Polytechnique-ENSTA, 91761 Palaiseau cedex, FRANCE.*

The first steps of an ultrafast radical reaction involving an infrared p-like state of excited electron and cystamine dihydrochloride (RSSR, 2HCl; R = (CH₂)₂ NH₃⁺) have been investigated by femtosecond laser spectroscopy of aqueous solution at 294K^a. An ultrafast one-electron reduction of the disulfide biomolecule exhibits a high frequency rate ($V_{ET} = 6.25 \cdot 10^{12} \text{ s}^{-1}$). This electron transfer competes with the p → s transition of trapped electron (electron hydration channel). The real-time UV spectroscopy of a primary sulfur-centered radical anion, (RS·:SR)_{aq}, is discussed in the framework of a two centers, three electron bonding formation (2c, 3e).

^a Y. Gauduel, M. Sander and H. Gelabert, *J. Phys. Chem.* **102**, 7795 (1998).

TB32

1 min 8:01

PHOTODISSOCIATION OF VINYL RADICAL (C_2H_3) VIA THE FIRST EXCITED STATE: THE $C_2H_2(\tilde{X}^1\Sigma_g^+) + H$ CHANNEL

KESHENG XU and JINGSONG ZHANG, *Department of Chemistry and Air Pollution Research Center, University of California, Riverside, CA 92521-0403.*

Photodissociation of vinyl radical via its first excited \tilde{A}^2A'' state has been studied by using high-n Rydberg-atom time-of-flight technique at 327.4 and 366.2 nm photolysis wavelengths. Center-of-mass (CM) translational energy distributions of the H atom and ground ($\tilde{X}^1\Sigma_g^+$) state acetylene photofragments reveal a small product translational energy release and two highly inverted vibrational progressions of $C_2H_2(\tilde{X}^1\Sigma_g^+)$ (most likely the C-C stretch and its combination band with C-H bend, with C-C stretch quanta up to 7). Anisotropic H-atom angular distributions are observed at the two excitation wavelengths, indicating a short excited \tilde{A}^2A'' state lifetime. Implication of the C_2H_2 vibrational state distribution and photodissociation dynamics of C_2H_3 in the first excited state are discussed. $D_0(C_2H_2-H) = 33.0 \pm 0.5$ kcal/mol is derived, in good agreement with previous studies.

TB33

1 min 8:02

ABNORMAL BEHAVIOR OF THE DEPOLARIZATION FACTOR OF BENZENE

O. ELOUTASSI, A. HAJJARI, and M. HAMEDOUN, *Faculty of Sciences Dhar Mahraz Fes, BP. 1796, Fes-Atlas, Morocco*; L. LETAMENDIA, *Bordeaux I Sciences University, CPMOH, Dept. de Recherche Physique, 33405 Talence Cedex, France.*

In this paper, we analyzed the light scattering spectra of benzene. The analyses of the spectra give a precise depolarization factor ρ value. We observe an abnormal behavior of ρ as temperature function on the range temperature $290K < T < 333K$. We observe also that the value of ρ exceed 0.75. We note that the value of ρ for some liquids which have non-cylindrical symmetric structure such as Nitrotoluene, a-chloronaphtalene^a are respectively 0.82 and 0.78 at ambient temperature. These results are abnormal since the maximum value of ρ ($\rho = 0, 75$) is deduced from the cylindrical symmetric structure hypothesis. The discrepancy between the theoretical and the experiment results occurred for benzene can be explained by one of the two considerations. The first one is that the theoretical expression of ρ is no longer exact for the benzene. The second is that the benzene structure change. Then, the depolarized factor is not linked just to the molecular structure but it can be related to the other factors. Not that we have observed an abnormal behavior of sound velocity^b and the reorientation motion^c in benzene liquid on the range temperature centered at 309K and 321K. The authors have explained this new fact as an established of long length correlation in liquid phase. This correlation is strong enough to perturb the equilibrium thermodynamic system. Thus, we can also suggest that this correlation induce a change in atom disposition on the liquid. Then, the factor ρ became more important.

^aJ. Cabannes, *La diffusion molculaire de la lumire*, Les presses Universitaires, Paris, (1929).

^bL. Letamendia, M. Belkadi, O. Eloutassi, E. Pret-Lestret, G. Nouchi, J. Rouch, D. Blaudez, F. Mallamace, and C. Vasi. *Phys. Rev. E*, 54, N 5 5327, (1996).

^cL. Letamendia, M. Belkadi, O. Eloutassi, C. Vaucamps and G. Nouchi; *Phys.Rev.E*, 48, 3572, (1993).

WA. WEDNESDAY MORNING SESSION**AUGUST 18, 1999 – 8:15 AM****Room: BALLROOM, LITTLE AMERICA HOTEL****Chair: JOHN S. WINN, Dartmouth College, Hanover, NH****WA01****40 min 8:15**

PHOTODISSOCIATION DYNAMICS OF HYDROCARBON RADICALS

PETER CHEN, Laboratorium für Org. Chemie, ETH Zürich, Zürich, Switzerland.

Laser photodissociation of the allyl, propargyl, and ethyl radicals are studied in a pump-probe experiment on both the nanosecond and picosecond timescales. In each of the radicals, initial UV excitation is followed by very rapid internal conversion, generating chemically activated radicals on the ground electronic surface with a microcanonical internal energy distribution. Hydrogen loss is monitored by Lyman- α detection of atomic hydrogen. Rates and kinetic energy release in the dissociation can be derived from the data. Comparison to rates and energy distributions calculated by statistical theories are made.

WA02**40 min 9:00**

MICROWAVE AND LASER SPECTROSCOPIC STUDIES OF CARBON-CHAIN FREE RADICALS

YASUKI ENDO, Department of Basic Sciences, The University of Tokyo, 153-8902 Tokyo, Japan.

Spectroscopy of long carbon-chain molecules has been attracting much attention in recent years, since various carbon-chain molecules have been detected in interstellar space by radio-telescopes and are also considered to be possible sources of Diffuse Interstellar Bands. So far, we have applied FTMW spectroscopy to the studies of various short lived free radicals including carbon-chain molecules. Use of a supersonic jet expansion technique, combined with a pulsed discharge nozzle consisting of two electrodes attached in front of a pulsed valve, has been proved to be a powerful method for studies of short lived species, particularly those with long carbon-chains, since the method efficiently produces short lived species in the discharge and the jet cooling of the products greatly simplifies the spectra to be observed.

Quite recently, we have successfully applied the pulsed nozzle system to laser spectroscopy in the visible and near UV regions, where various techniques including LIF, SEP, and newly developed MODR are used to elucidate detailed behaviour of electronically and/or vibrationally excited states of carbon-chain molecules. Studies of excited states are considered to have particular importance, since spectroscopic data for long carbon-chain molecules are rather limited to those in the ground electronic/vibrational states, while they are expected to show various interesting vibronic interactions.

In the present talk, we will present recent results obtained by using FTMW spectroscopy and laser spectroscopy in the visible and near UV regions.

Intermission

WA03**40 min 10:15****ELECTRONIC SPECTROSCOPY OF ATMOSPHERIC RADICALS**

PROFESSOR VERONICA VAIDA, *University of Colorado at Boulder, Department of Chemistry and Biochemistry, Boulder, CO 80309-0215.*

The photo reactivity of atmospheric radicals is investigated and illustrated here with two examples: a) chlorine dioxide (ClO) and b) alkylperoxy radicals (RO₂). The former is used to monitor the chlorine content of the polar stratosphere and is implicated in stratospheric ozone chemistry. The latter is involved in the oxidation of hydrocarbons in the troposphere and tropospheric ozone production. Electronic absorption spectra of jet cooled samples reveal complex photo chemistry. High resolution absorption spectra are used to study the excited state structure, mode coupling and photo reaction dynamics of these radicals. Consequences of the excited state reactions investigated spectroscopically are discussed using results of atmospheric models.

WA04**40 min 11:00****STUDY OF HIGHLY-PREDISSOCIATIVE STATES OF FREE RADICALS USING TWO-COLOR RESONANT FOUR-WAVE MIXING TECHNIQUE**

YUAN-PERN LEE, *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043.*

We demonstrate an application of two-color resonant four-wave mixing (TC-RFWM) spectroscopy to detect highly predissociative levels of the $C^2\Sigma^+$ AND $D^2\Pi$ states of CH in a hostile environment of an oxyacetylene flame. The 1-1 band of the $C - X$ transition is detected with the probe and the grating wavelengths in resonance with the $A^2\Delta - X^2\Pi$ and $C^2\Sigma^+ - X^2\Pi$ transitions, respectively. Six branches of the $C - X$ (1-1) system are spectrally resolved for the first time; in total 124 lines detected in this work correspond to excitation of the $C^2\Sigma^+$ ($v = 1$) state up to $N' = 23$. Observed wave numbers are fitted to yield improved spectral parameters of the $C^2\Sigma^+$ state. The D state was observed by using two grating (probe) beams in resonance with the $D^2\Pi - B^2\Sigma^-$ transition and the pump beam in resonance with a selected $B^2\Sigma^- - X^2\Pi$ transition. A total of 86 lines associated with transitions to the $D^2\Pi$ ($v = 0$) state with rotational quantum number N' up to 16 were detected; parameters for centrifugal-distortion (D , H), spin-rotation interaction (γ), and Λ -doubling (p , q , q_0) of the $D^2\Pi$ ($v = 0$) state were deduced for the first time. The predissociative line width is about 2 cm^{-1} for $N' = 1$ and gradually increases to 7 cm^{-1} for $N' = 15$. Predissociation mechanisms of both the C and the D states are discussed. If time permits, other systems will be briefly described.

WB. WEDNESDAY POSTER PRESENTATIONS

AUGUST 18, 1999 – 7:30 PM

Room: BALLROOM, LITTLE AMERICA HOTEL

Chair: MATS LARSSON, Stockholm University, Stockholm, Sweden

WB01

1 min 7:30

REMPI STUDIES OF CF AND CF₃ FREE RADICALS

Q. LI, Q. ZHANG, J. SHU, X. ZHOU, S. YU, C. CHEN, AND X. MA, *Department of Chemical Physics, Open Laboratory of Bond-Selective Chemistry of CAS, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China.*

CF and CF₃ free radicals were generated by using a dc discharge in the mixture of Ar/CF₄^a. The (2+1) resonance-enhanced multiphoton ionization spectra of CF and CF₃ have been investigated. The rotationally resolved CF(3p, v'=2-6) and CF(5p, v'=0-3) Rydberg states were observed between 260-360nm. The related vibrational and rotational constants of these two Rydberg states have been obtained. For CF₃, the band origins of 4p_σ(²A₂') and 4p_π(²E') Rydberg states were identified as 62776.8 and 62614.4 cm⁻¹. Their vibrational frequencies and quantum defect values were also estimated.

^aQ. Li, J. Shu, Q. Zhang, S. Yu, L. Zhang, C. Chen and X. Ma, *J. Phys. Chem. A*, 102, 7233(1998)

WB02

1 min 7:31

OBSERVATION OF MOLECULAR HYPERFINE QUANTUM BEATS USING NANOSECOND TRANSIENT GRATING SPECTROSCOPY

S.A. REID, J.P. SCHMIDT, Y. TANG, and B. LIANG, *Department of Chemistry, Marquette University, Milwaukee, WI 53201-1881.*

We report the observation and analysis of hyperfine quantum beats in nanosecond transient grating studies of jet-cooled NO₂ at excitation wavelengths near 488 nm. Intensity and polarization grating transients were obtained in both one-color and two-color configurations. The grating transients typically display pronounced beats, arising from excited state hyperfine coherences, which are enhanced in polarization grating configurations. Analysis of these beats yields detailed information on the excited state hyperfine level structure. The transients are compared to predictions of the grating decomposition method using Fourier transform analysis.

WB03**1 min 7:32**

VIBRATIONAL SPECTROSCOPY OF ENTRANCE CHANNEL COMPLEXES

MARTYN D. WHEELER, MICHAEL W. TODD, DAVID T. ANDERSON, MARIA TSIOURIS, and MARSHA I. LESTER,

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.

Reactions of hydroxyl radicals with hydrogen and methane play a fundamental role in combustion and atmospheric processes. The work presented here illustrates a novel approach to studying these reaction systems by trapping OH with either H₂ or CH₄ in a shallow attractive well in the entrance channel to reaction. The resultant H₂-OH and CH₄-OH complexes are then vibrationally excited by means of infrared or stimulated Raman excitation. Vibrational excitation of either the OH, H₂ or CH₄ partners provides sufficient energy to surmount the relatively low barriers to reaction or, alternatively, break the weak intermolecular bond, thereby providing access to both reactive and inelastic scattering dynamics. The spectroscopy and ensuing dissociation dynamics of these vibrationally activated complexes have been probed using a variety of double-resonance schemes. Vibrational spectroscopy offers an approach to examining structural parameters of these complexes and interesting effects due to the unquenched spin and orbital angular momenta of the OH partner. Time and frequency resolved studies of the dissociation dynamics of vibrationally excited H₂-OH and CH₄-OH complexes provides insight into the mode-selectivity of the resulting inelastic and reactive decay processes. These spectroscopic and dynamical measurements are highly sensitive to the topology of the intermolecular potential energy surface and therefore provide a rigorous test of *ab initio* theory. Comparison of experimental results with recent theoretical calculations will also be presented.

WB04**1 min 7:33**

THE VISIBLE SPECTRUM OF THE VINYL RADICAL MEASURED WITH CAVITY RING-DOWN LASER ABSORPTION SPECTROSCOPY.

J.B. HALPERN, K. PATRICK, S. ALFRED, *Department of Chemistry, Howard University, Washington, DC 20059*; C. D. PIBEL, *Department of Chemistry, American University, 4400 Massachusetts Ave. NW, Washington, D.C. 20016-8014*; A. MCILROY AND C. A. TAATJES, *Combustion Research Facility, Sandia National Laboratory, Livermore, CA 94551-0969.*

High resolution cavity ring-down spectroscopy has been used to measure the vinyl radical $\tilde{A}^2A'' \leftarrow \tilde{X}^2A'$ visible absorption spectrum between 530 and 415 nm. Vinyl radicals were formed by 193 nm photolysis of methyl vinyl ketone. Even the origin band at 20,042 cm⁻¹ is broadened (~ 1 cm⁻¹) as compared to the sub-GHz dye laser bandwidth although rotational structure can be seen in the spectral envelope of both the origin and 1₀¹ bands. The broadening increases sharply above the 1₀¹ band in the 5₀¹ and 4₀¹ bands indicating the presence of a barrier. Improved spectroscopic constants and vibrational assignments have been determined by fitting the envelopes of the various vibrational bands as a c type transition of an asymmetric top.

WB05

1 min 7:34

ELECTRONIC SPECTRA OF YOH AND YOD IN THE VISIBLE REGION; STRONG VIBRONIC COUPLING BETWEEN THE $\tilde{B}^1\Pi$ AND $\tilde{C}^1\Sigma^+$ STATES

A. G. ADAM, *Department of Chemistry, University of New Brunswick, Bag Service 45222, Fredericton, N.B. E3B 6E2, Canada*; K. ATHANASSENAS, C. T. KINGSTON, A. J. MERER, J. R. D. PEERS, S. J. RIXON, *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada*; and D.A. GILLETT, *Lambda-Physik, Inc., 3201 West Commercial Blvd., Fort Lauderdale, FL 33309*.

Laser excitation spectra of yttrium monohydroxide, YOH, have been recorded in the 500-625 nm wavelength region. Rotational analysis of bands of YOH and YOD has shown that the ground state is $\tilde{X}^1\Sigma^+$, with the structure r_0 (Y-O) = 1.948₆ Å, r_0 (O-H) = 0.920₆ Å; the bending frequency (ν_2 , π) is 313.73 cm⁻¹ (237.43 cm⁻¹ in YOD) and the Y-O stretching frequency (ν_3 , σ^+) is 673.83 cm⁻¹ (655.34 cm⁻¹).

Two excited electronic states have been identified; they are assigned as $\tilde{B}^1\Pi$ (16 449 cm⁻¹) and $\tilde{C}^1\Sigma^+$ (18 509 cm⁻¹). Unusually strong vibronic coupling through the bending vibration occurs between these two states, which causes their vibrational structures to be highly irregular; assignments have only been possible following extensive wavelength-resolved fluorescence experiments. The vibronic coupling raises the bending frequency of the $\tilde{C}^1\Sigma^+$ state to 457 cm⁻¹, and reduces that of the lower Born-Oppenheimer component of the $\tilde{B}^1\Pi$ state (which has A' symmetry in the C_s point group) to the extent that the molecule becomes non-linear, with a potential barrier at the linear configuration of about 120 cm⁻¹. The presence of the potential barrier is clearly demonstrated by the level structure of YOD, where the Σ^+ vibronic component of the 010 vibrational level (linear molecule notation) lies 1.4 cm⁻¹ below the 000 level. The upper Born-Oppenheimer component, which has A''

symmetry, is unaffected; its bending frequency is similar to that of the ground state. Perturbations occur in both the $\tilde{B}^1\Pi$ and $\tilde{C}^1\Sigma^+$ states; some of these represent local interactions between the two of them, but others are caused by higher vibrational levels of lower-lying "dark" electronic states. Over 40 ground state vibrational levels have been identified for both YOH and YOD from the wavelength-resolved fluorescence spectra.

WB06

1 min 7:35

DISPERSED FLUORESCENCE SPECTROSCOPY OF MoC, RuC, and PdC: AN EXAMINATION OF LOW-LYING ELECTRONIC STATES

RYAN S. DaBELL, RAYMOND G. MEYER, and MICHAEL D. MORSE, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112*.

Dispersed fluorescence spectroscopic studies of MoC, RuC, and PdC radicals in a supersonic expansion have recently been completed. Nine electronic states in the molecules have been identified using data from this work; seven of these states were observed here for the first time. In particular, the ground state of PdC has been identified as [...]12 σ^2 , $^1\Sigma^+$ from this work. Spectroscopic constants T_0 , ω_e , and $\omega_e x_e$ for these states have been determined. Spin-orbit coupling effects are explored. The relationship of vibrational frequency to electronic configuration is also examined for the 4d transition metal carbide series.

WB07

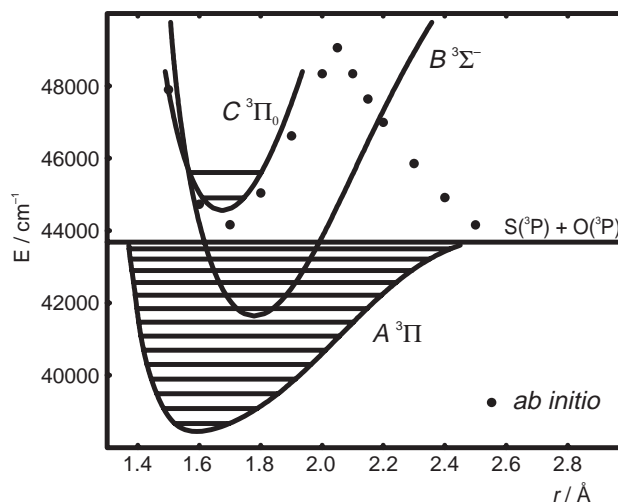
1 min 7:36

SPECTROSCOPY OF THE SO RADICAL

JOHN M. F. ELKS and COLIN M. WESTERN, *School of Chemistry, University of Bristol, Cantock's Close, Bristol. BS8 1TS. UK. (e-mail: John.Elks@bristol.ac.uk, C.M.Western@bristol.ac.uk).*

The spectroscopy of the SO radical in a jet expansion has been investigated using the techniques of laser induced fluorescence and multiphoton ionisation. Spectra of the $A^3\Pi - X^3\Sigma^-$ system have been recorded for vibrational levels up to $v' = 13$, which extends the known vibrational levels of the A state to within *ca.* 200 cm^{-1} of the dissociation limit. Collision free fluorescence lifetimes, which show a marked v dependence due to the presence of a node in the transition moment to the ground state, have been measured for the complete range of vibrational levels. Combining these measurements with previously reported data has allowed a better determination of the $A - X$ transition dipole moment in the range $1.4 - 2.0\text{ \AA}$.

Spectra have also been recorded for states with energies above the first dissociation limit, in the same region as the known $B^3\Sigma^-$ state. These reveal the existence of two interacting states of Π symmetry, one singlet and one triplet. The positions of the two vibrational levels which we have observed for the $^3\Pi$ state are shown in the potential energy diagram opposite. Also illustrated are the results of a recent *ab initio* investigation on the previously unobserved $C^3\Pi$ state, which can be seen to be in agreement with our experimental results.



WB08

1 min 7:37

UV AND VISIBLE ABSORPTION CROSS-SECTIONS OF O₂

R.COLIN, S.FALLY, M.CARLEER, *UNIVERSITE LIBRE DE BRUXELLES, LABORATOIRE DE CHIMIE PHYSIQUE MOLECULAIRE, CP160/09, 50, AV.F.D. ROOSEVELT, 1050 BRUSSELS, BELGIUM*; B.COQUART, A.JENOUVRIER, M.-F.MERIENNE, *GROUPE DE SPECTROMETRIE MOLECULAIRE ET ATMOSPHERIQUE, URAD1434, UFR SCIENCES, MOULIN DE LA HOUSSE, 51687 REIMS CEDEX 2, FRANCE*; and A.C.VANDAELE, *INSTITUT D'AERONOMIE SPATIALE DE BELGIQUE, 3 AV.CIRCULAIRE, 1180 BRUSSELS, BELGIUM*.

Absorption spectra of oxygen and its overlapping collision-induced broad bands have been measured in the laboratory under temperature and pressure conditions prevailing in the Earth's atmosphere using a Fourier Transform Spectrometer combined with a multiple reflection gas cell. Spectra were recorded in the wavenumber range 7500 to 42000 cm^{-1} (238 – 1333 nm) and at a resolution of 2 cm^{-1} . In the range 30000 – 42000 cm^{-1} , measurements were made at various pressures in order to separate the different components of the spectra, namely the discrete bands of the three Herzberg systems, the Herzberg continuum and the diffuse triplets of the Wulf bands. Oxygen spectra recorded in mixtures with N_2 and Ar demonstrate that the Wulf bands are caused by collision-induced absorption. A theoretical calculation of the spectrum in the triplet region and beyond the dissociation limit is also shown and compared to the measured spectrum. In the wavenumber region 7500 to 30000 cm^{-1} , absorption cross-sections, band centre positions and bandwidths of the O_2 collision complex are presented. The contributions from the O_2 atmospheric bands overlapping these bands at 15900 and 7900 cm^{-1} are successfully removed. A comparison with literature data is given. The use of these new spectra allow to calculate a synthetic spectrum at any desired resolution and pressure and should therefore improve the correction required in O_3 atmospheric Differential Optical Absorption Spectrometry (DOAS) measurements due to the presence of the O_2 features.

WB09

1 min 7:38

TRAPPING AND SPECTROSCOPY OF MOLECULES IN COLD HELIUM DROPLETS

FRANK RUEDIGER BRUEHL, M. KENT BALLARD, AND WOLFGANG E. ERNST, *Departments of Physics and Chemistry, The Pennsylvania State University, 104 Davey Laboratory, University Park, PA 16802.*

Helium droplets containing 5000 to 10000 atoms are generated in a supersonic expansion of about 50 bar of helium through a 5 micron nozzle at 10 to 20 K temperature. They have a diameter of about 10 nm and an internal temperature of 0.4 K and in the case of ^4He , are believed to represent finite size samples of a superfluid. By doping the droplets with spectroscopically well known atoms or molecules, their interaction dynamics can be probed. Many molecules were shown to become solvated inside the droplet and to exhibit sharp vibrational spectra. We investigated the optical $S_1 - S_0$ excitation of pentacene in large helium clusters around 18500 cm^{-1} with cw single frequency dye lasers. The total linewidth of 9 GHz for an individual vibrational band turned out to be due to both inhomogeneous and homogeneous broadening. By applying a pump-probe technique (hole burning spectroscopy), the homogeneous linewidth was shown to be about 5 GHz which may be due to overlapping rotational structure. The inhomogeneous broadening probably originates from the rather wide helium cluster size distribution. Alkali atoms, when deposited on helium droplets, reside on the surface and form molecules in cold collisions. Singlet dimers as well as aggregates of spin polarized alkali atoms were observed. Again the causes for line broadening were studied with optical pump-probe techniques and will be discussed.

WB10

1 min 7:39

PREDISSOCIATION DYNAMICS AND DYNAMICS OF HCP: DIRECT DETECTION OF CP RADICAL

HARUKI ISHIKAWA, TOSHIYUKI SASAKI, and NAOHIKO MIKAMI, *Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan.*

A presence of a predissociation of HCP molecule to $\text{H}(^2S) + \text{CP}(X\ ^2\Sigma^+)$ in excited electronic states ($\tilde{A}\ ^1A'$ and $\tilde{C}\ ^1A''$) had been suggested based on a rapid decrease in the fluorescence intensity and a broadening of the line width in an OODR spectrum in a high energy region. However, dissociation products, H atom and/or CP radical, have not yet been detected. In order to reveal a predissociation mechanism, absorption, LIF, and also CP ($X\ ^2\Sigma^+$) radicals excitation spectra were observed in the vicinity of the dissociation threshold. A $B\ ^2\Sigma^+ - X\ ^2\Sigma^+$ LIF spectrum of CP radicals was clearly observed. The dissociation threshold energy was determined to be $41\ 660 \pm 5\text{ cm}^{-1}$. The relative yield of the CP radical production does not exhibit a $J(J + 1)$ dependence on rotational quantum numbers, J . Based on this fact and results of theoretical calculations, the predissociation mechanism was discussed. Both the \tilde{A} and \tilde{C} states do not correlate to the $\text{H}(^2S) + \text{CP}(X\ ^2\Sigma^+)$ dissociation limit. Thus, the dissociation must occur after the transition from the excited electronic states to the \tilde{X} state in both case. In the case of the \tilde{A} state, an a-type Coriolis interaction is considered to cause the transition, whereas a non-adiabatic interaction along the bending coordinate for the \tilde{C} state. In addition, energy distributions of CP radicals were also measured. The rotational distribution was reproduced by that expected by the phase space theory. This may be related a fact that the dissociation occurs in the nano second time scale.

WB11

1 min 7:40

STUDY OF VINYLIDENE-ACETYLENE ISOMERIZATION BY COULOMB EXPLOSION IMAGING

J. LEVIN, *Max-Planck-Institut für Kernphysik, D-69029 Heidelberg, Germany*; H. FELDMAN, A. BAER, D. BEN HAMU, D. ZAJFMAN, Z. VAGER, *Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel*.

C_2H_2 is one of the simplest molecules that exhibit intramolecular rearrangement in a vibrationally excited state. The nature of the vinylidene-acetylene isomerization mechanism has been the focus of much theoretical investigation. The calculations predicted the existence of a vinylidene ($C=CH_2$) isomer 2 eV above the acetylene vibrational ground state. Experimentally, the vinylidene has been studied by photoelectron spectroscopy ^a revealing resonances which have been assigned as vibrational vinylidene structure. The neutral vinylidene has been predicted to decay into linear acetylene configurations due to the low isomerization barrier of < 0.2 eV. This decay time has been estimated to be 0.2-4 psec ^b.

We applied the Coulomb explosion imaging (CEI) technique to measure the structure of C_2H_2 molecules which were produced by electron photodetachment from vinylidene $C_2H_2^-$ anions ^c The nuclear density of C_2H_2 molecules as measured by CEI 3.5 μ sec after their production as vinylidene isomers shows unambiguously that a large fraction ($\sim 50\%$) of the molecules retain the vinylidene conformation. This surprising result contradicts the accepted concept of a rapidly "decaying" vinylidene isomer.

A further analysis of the CEI results suggests a different interpretation of the isomerization process. The number of total molecular eigenstates with vinylidene character is estimated to be only $N = 2 - 4$. Therefore, on a time scale shorter than the characteristic time of radiative decay, no "decay" of vinylidene into acetylenic configurations occurs. The structure of these excited states is better described as a coherent superposition of both acetylene and vinylidene amplitudes.

In this presentation, a detailed analysis of the measured structure and comparison with recent theoretical calculations will be given.

^aK. M. Ervin *et al.*, J. Chem. Phys. **91**, 5974 (1989).

^bT. Carrington *et al.*, J. Chem. Phys. **80**, 4347 (1984).

^cJ. Levin *et al.*, Phys. Rev. Lett. **81**, 3347 (1998).

WB12

1 min 7:41

INVESTIGATION OF THE FORMYL AND ISOFORMYL STRUCTURAL ISOMERS BY COULOMB EXPLOSION IMAGING

R. WESTER, U. HECHTFISCHER, L. KNOLL, M. LANGE, J. LEVIN, M. SCHEFFEL, D. SCHWALM, A. WOLF, *Max-Planck-Institut für Kernphysik, D-69029 Heidelberg, Germany*; A. BAER, Z. VAGER, D. ZAJFMAN, *Department of Particle Physics, Weizmann Institute of Science, Rehovot, 76100, Israel*.

One of the simplest molecular ions that can exist in two isomeric configurations is the formyl cation and its metastable isoformyl counterpart. A lot of information has been obtained about the formyl ion using spectroscopic techniques. The much more reactive isoformyl ion is less characterized and in particular the fundamental transition frequency of its floppy bending mode is up to now only known from ab initio calculations.

At the heavy ion storage ring TSR in Heidelberg we have investigated the structure of the deuterated isotopomers of the formyl isomers, DCO^+ and DOC^+ , by studying the foil-induced Coulomb explosion of these ions. The formyl ions were produced in the fragmentation of CD_3O^- ions and were then stored for several seconds in the TSR, which allows rovibrational excitation of the molecular ions to decay through spontaneous radiative transitions. During and after their rovibrational de-excitation, ions were continuously extracted from the storage ring and passed onto a thin target foil where they dissociate rapidly compared to the timescales of rovibrational motion. The asymptotic velocity vectors of all three atomic fragments emerging from the subsequent "Coulomb explosion" of each molecular projectile were then measured using multi-particle three-dimensional imaging detectors.

From the velocity distribution obtained for a sample of Coulomb explosion events, the presence of both isomers in the stored ion beam could be inferred. Transitions of the metastable DOC^+ ions to the DCO^+ configuration were not observed within the accessed storage times. Based on the concept of a simple Coulomb explosion the probability distribution of the bond angles for both the formyl and the isoformyl projectile ions could be derived. Deviations from a simple Coulomb potential were investigated and they were found to have only little influence on the bond angle distributions. These results will be described in detail and they will be compared to a recent ab initio calculation.

WB13

1 min 7:42

EXPERIMENTAL DETERMINATION OF BOND ANGLE DISTRIBUTION IN QUASILINEAR MOLECULES

ADAM BAER, Z. VAGER, D. ZAJFMAN, *Particle Physics, Weizmann Institute of Science, Rehovot 76100, Israel*; J. LEVIN, L. KNOLL, A. WOLF, R. WESTER, D. SCHWALM, *Max-Planck-Institut für Kernphysik, 69029 Heidelberg, Germany*.

The Coulomb Explosion Imaging (CEI) is an experimental technique which provides *images* of the nuclear configuration within small molecules. The novel combination of the CEI and storage ring techniques^a allows to probe both the structure and the relaxation dynamics of molecular ions. Highly excited molecular ions are produced by a conventional ion source, and decay radiatively while stored for several seconds. By monitoring the structure during storage we are able to follow the cooling process and identify the structure related to an excitation population distribution of 300K. This scheme has been exploited for the measurements of bond angle distributions in quasilinear molecular ions, namely NH_2^+ , ND_2^+ and CH_2^+ . The results presented here are cleaner than previous CEI measurements^b of both NH_2^+ and CH_2^+ , since with the new experimental setup the population distribution of the excited states is well defined.

We hereby present our results and compare them to such recent *ab-initio* predictions. There is an overall agreement in the shape of the measured and predicted angular distribution at 300K. However, significant discrepancies were apparent mainly near linearity where a larger population was measured. The discrepancies appearing both in NH_2^+ and ND_2^+ indicate that there are significant non-adiabatic effects neglected in the theory. Similer characteristics were observed^c in CH_2^+ , leading to the conclusion that non-adiabatic effects beyond the Renner-Teller effect must be included in theory.

^aR. Wester, F. Albrecht, M. Grieser, L. Knoll, R. Repnow, D. Schwalm, A. Wolf, A. Baer, J. Levin, Z. Vager and D. Zajfman, *Nucl. Instrum. Methods A*, **413**, 379 (1998)

^bT. Graber, E. P. Kanter, J. Levin, D. Zajfman, Z. Vager, *Phys. Rev. A*, **56**, 738 (1997).

^cA. Baer, M. Grieser, L. Knoll, J. Levin, R. Repnow, D. Schwalm, Z. Vager, R. Wester, A. Wolf and D. Zajfman, *Phys. Rev. A*, **A59**, 1865 (1999)

WB14

1 min 7:43

COLLISIONAL PROCESSES NEAR THE CH B $^2\Sigma^-v' = 0, 1$ PREDISSOCIATION LIMIT AND THEIR APPLICATION TO LASER-INDUCED FLUORESCENCE FLAME DIAGNOSTICS

ROBERT J.H. KLEIN-DOUWEL, JORGE LUQUE, JAY B. JEFFRIES, GREG P. SMITH, and DAVID R. CROSLY, *Molecular Physics Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025*.

Excitation and dispersed laser induced fluorescence (LIF) spectra of CH B $^2\Sigma^-v' = 0, 1$ in methane flames are analyzed using rotational energy transfer (RET) models. The existence of non-predissociative and highly predissociative rotational levels in the same vibrational state provides a prime opportunity to test the effects of RET in LIF measurements. A statistical power gap law fits the spectra, showing that levels with collision-free lifetimes as short as 100 ps have apparent fluorescence yields larger than expected because of the extent of RET at atmospheric pressure. Also, vibrational ($1 \rightarrow 0$) and electronic energy transfer ($\text{B } ^2\Sigma^-v' = 1 \rightarrow \text{A}^2\Delta$) are competitive with RET, and account for 24 % and 20 %, respectively, of the total collisional removal rate from CH B $^2\Sigma^-v' = 1$. The electronic transfer branching ratio into different v in the A state depends on the initial rotational level pumped, and can be explained by energy gap considerations. These results are then used to select the most practical excitation - detection scheme for CH LIF in an atmospheric pressure, partially premixed methane/air flame. The choice optimizes between maximum signal size and minimum overall collisional effects on quantitative measurements. CH is excited at the Q₁(8) line of the B-X (1,0) band and fluorescence over the entire B-X (1,1) band is collected and calibrated to obtain CH number densities. Planar LIF measurements are performed for various flame stoichiometries and geometries.

WB15

1 min 7:44

INVESTIGATION OF THE ROTATIONAL SPECTRUM OF BiO IN THE $X^2\Pi$ ELECTRONIC STATE

EDWARD A. COHEN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109-8099*; DAMIAN M. GOODRIDGE and KENTAROU KAWAGUCHI, *Nobeyama Radio Observatory, Minamimaki, Minamisaku, Nagano 384-1305, Japan.*

A recent, far reaching study of the BiO radical by Shestakov *et al*^a, has provided spectroscopic constants for a total of nine of its electronic states. The rotational constants calculated for the $X^2\Pi$ state have been used as the basis for a further investigation by microwave spectroscopy at Nobeyama Radio Observatory. BiO was produced in a flow system by heating Bi to 1120 K in a Knudsen cell and reacting the resulting vapor with an approximately 1:1 mixture of O₂ and Argon in the presence of a dc discharge.

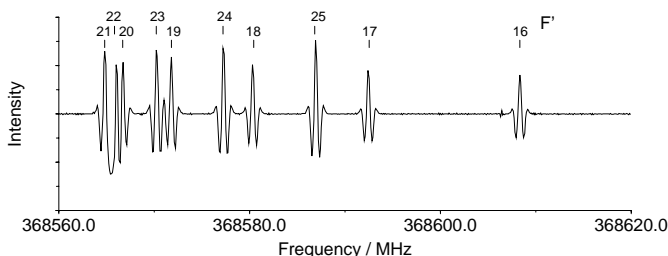


Figure 1: The BiO $X_1^2\Pi_{1/2}$ ($v=0$) $\Delta F = +1$, $J = 41/2 - 39/2$ transitions.

A useful side-effect of this method of production is the population of highly excited vibrational states of BiO. This is presumably due to collisional energy transfer from the metastable $a^1\Delta_g$ electronic state of O₂. As a result, rotational transitions within vibrationally excited levels up to $v = 9$ in the $X_1^2\Pi_{1/2}$ electronic state and $v = 5$ in the $X_2^2\Pi_{3/2}$ state have been observed. A sample microwave spectrum of the BiO radical is given in Figure 1, which illustrates the hyperfine pattern that is associated with the presence of the $I = 9/2$ ²⁰⁹Bi nucleus.

Thus far, a total of 575 lines have been assigned and fitted with an RMS of 27 kHz, using an effective Hamiltonian similar to that of Brown *et al*^b. There is excellent agreement between the microwave parameters and those obtained in the optical study. In addition, the hyperfine parameters for both the X_1 and X_2 electronic states have been determined.

^aO. Shestakov, R. Breidohr, H. Demes, K. D. Setzer and E. H. Fink, *J. Mol. Spectrosc.* **190**, 28-77 (1998)

^bJ. M. Brown, E. A. Colbourn, J. K. G. Watson and F. D. Wayne, *J. Mol. Spectrosc.* **74**, 294-318 (1979)

WB16

1 min 7:45

SOLVATION OF MAGNESIUM AND SINGLY IONISED MAGNESIUM ATOMS IN NH₃ CLUSTERS, THEORY AND EXPERIMENT

M.ELHANINE, B.SOEP, *Laboratoire de Photophysique Molculaire Bat 210 Universit Paris Sud 91405 Orsay France*; L. DUKAN, P. MAITRE, *Laboratoire de Chimie Thorique, Universite Paris-Sud, Bt. 490*; W.H.BRECKENRIDGE, S. MASSICK, *Department of Chemistry University of Utah Salt Lake city.*

The solvation of group II metals has not been studied in great details as compared to alkali metals and we show that due to the closed shell nature of these metals, the clusters possess unique features. Besides clusters allow the observation of singly ionised solvated ions that do not exist in solution and the characterisation of their properties is important since many of these singly ionised systems are reactive. The ionisation thresholds of magnesium atom solvated by ammonia have been investigated by tuneable laser ionisation of clusters prepared in a simple pick-up source. The ionisation potential IP of clusters Mg(NH₃)_n have been measured for n=1 up to 35. The solvation of the magnesium ion is more efficient than for the closed shell neutral atoms resulting in a steep decrease of the ionisation energy of clusters with ammonia of increasing sizes (1.3 eV for n=1, 2.4 eV for n=2 and 3.2 eV for n=3 etc...). The effect becomes smaller large clusters (n_i>20) for higher order clusters but the potential continues to decrease and the asymptote does not appear to be reached at n=35, corresponding to increased electrostatic stabilisation of the ion cluster with these sizes. Quantum chemical calculations have been performed which reveal the unique features of the solvation of the neutral closed shell metal, ns² and the metal ion ns¹ by ammonia molecules. The formation of neutral clusters are dominated by singly coordinated cyclic sub-units containing 3 ammonia, while the ion is best stabilised in triply coordinated magnesium. The experimental ionisation energies are in excellent agreement with calculated values for singly coordinated, neutral cluster ionised to locally adiabatic states, doubly coordinated with ammonia.

WB17**1 min 7:46****ISOTOPE EFFECTS ON STRUCTURE AND DYNAMICS OF SOME RADICAL CATIONS STUDIED BY AB INITIO AND DFT CALCULATIONS AND ESR SPECTROSCOPY**

S. LUNELL and T. FÄ NGSTRÖ M, *Department of Quantum Chemistry, Uppsala University, Box 518, S-751 20 Uppsala, Sweden*; P. WANG, and M. SHIOTANI, *Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739, Japan*.

Deuterium isotope effects on conformation and ESR spectra of some selectively deuterated radical cations are studied using accurate ab initio and density functional theory (DFT) quantum chemical methods, and compared with experimental data obtained with matrix-isolation ESR techniques. The temperature dependence of the ESR spectra is studied in the temperature range 4K - 100 K. The applicability and limitations of different computational methods are illustrated by results on partially deuterated dimethyl ether and cyclohexane radical cations.

WB18**1 min 7:47****A THEORETICAL STUDY OF THE ACETYLIDE ANION, HCC⁻**

MIRJANA MLADENović, PETER BOTSCHWINA, *Institut für Physikalische Chemie, Universität Göttingen, Tammannstraße 6, D-37077 Göttingen*; PETER SEBALD, *Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany*; STUART CARTER, *Department of Chemistry, University of Reading, Reading RG6 2AD, United Kingdom*.

The results of various ab initio calculations are reported for the electronic ground state of the acetylide anion. An "Eyring's lake" in the T-shaped configuration is identified with six different methods (SCF, MP2, CCSD, CCSD-T, CCSD(T), and CEPA-1). The equilibrium bond lengths of HCC⁻ are estimated to be $r_e(\text{CH})=1.0689(3)$ Å and $R_e(\text{CC})=1.2464(2)$ Å and the ground-state rotational constant is predicted to be $B_0 = 41636(20)$ MHz. The large permanent dipole moment of $\mu_0 = -3.093$ D should facilitate detection of the anion by microwave spectroscopy. The band centers are predicted to be 3211.3 cm⁻¹ (ν_1), 511.1 cm⁻¹ (ν_2), and 1805.0 cm⁻¹ (ν_3). A large transition dipole moment of 0.477 D is calculated for the ν_2 band.

Rovibrational levels of HCC⁻ up to ~ 20000 cm⁻¹ are calculated with the DVR-DGB and FBR methods on the basis of a previous CEPA-1 potential energy surface. Several types of energy patterns are identified and discussed. The appearance of rotor-like characteristics in the vicinity of an adiabatic barrier is clearly shown for bending levels with identical stretching excitation. The coupling between the rotational and vibrational degrees of freedom is a prominent factor in the internal dynamics of HCC⁻ and leads to complicated energy patterns with particularly strong Coriolis resonances at those energies where the eigenstates display the onset of rotor-like structure. Anharmonic resonances depend sensitively on rotational excitation.

WB19**1 min 7:48****THE ELECTRONIC STATES OF THE FeH RADICAL : A PROGRESS REPORT**

JOHN M BROWN, RICHARD F. BARROW, DANIEL F. HULLAH and CATHERINE WILSON, *The Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, OX1 3QZ, United Kingdom*.

The electronic spectrum of the FeH radical in the visible region has been studied using the techniques of laser excitation spectroscopy and dispersed fluorescence^{a b}. We have recently made good progress in the definition and understanding of the low-lying states below 5000 cm⁻¹. In particular, the lowest three spin-orbit components of the b⁶Π state have been identified together with the lowest spin component of C⁴Φ state ($\Omega = 7/2$). As a result, all three of the expected low-lying sextet states have now been located. Some other sets of rotational terms have also been identified but it has not yet proved possible to assign them to particular electronic states. We have also been able to characterize the excited vibrational level ($v = 1$) of the e⁶Π state at about $22\,400$ cm⁻¹ which gives a vibrational interval of about 1715 cm⁻¹ in this state.

^aD. M. Goodridge, R. T. Carter, J. M. Brown and T. C. Steimle, *J. Chem. Phys.*, **106**, 4823 (1997)

^bD. M. Goodridge, D. F. Hullah and J. M. Brown, *J. Chem. Phys.*, **108**, 428 (1998)

WB20**1 min 7:49****PURE ROTATIONAL AND FINE-STRUCTURE TRANSITIONS OF NITRIC OXIDE (NO) IN ITS GROUND VIBRATIONAL STATE**

THOMAS D. VARBERG, *Department of Chemistry, Macalester College, St. Paul, MN 55105*; FRED STROH, *Institute for Stratospheric Chemistry, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*; KENNETH M. EVENSON, *Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO 80303*.

We have made highly accurate measurements of the absorption spectra of the ^{14}NO and ^{15}NO isotopomers of nitric oxide by tunable far-infrared (TuFIR) spectroscopy. Pure rotational transitions up to $J'' = 37.5$ within the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin components and several $^2\Pi_{3/2} \leftarrow ^2\Pi_{1/2}$ fine-structure transitions were recorded within the ground vibrational state. The hyperfine structure was resolved for many of the low- J lines. A least-squares fit to these data combined with some measurements of previous workers has resulted in accurate values for the rotational, fine and hyperfine parameters of these two isotopomers. The set of calculated frequencies, which have uncertainties of less than 10 kHz, will be useful in astronomy and atmospheric science as well as for spectral calibration.

WB21**1 min 7:50****IDENTIFICATION OF NEW LOW-LYING ELECTRONIC STATES OF THE TiCl^+ AND TiF^+ MOLECULAR IONS BY DISPERSED LASER INDUCED FLUORESCENCE**

C. FOCSA ^a, B. PINCHEMEL, and M. BOGEY, *Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523, Centre d'Etudes et de Recherches Lasers et Applications, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France*.

The dispersed laser-induced fluorescence technique has been applied for the first time to metallic molecular ions. The TiCl^+ and TiF^+ ions were produced by a high-voltage discharge in helium with traces of TiCl_4 or TiF_4 , respectively. A c.w. dye-laser and a grating spectrometer were used to record low-resolution spectra of these species in the visible region. This led to the observation of new low-lying electronic states of these ions: the $C^3\Pi$ ($\sim 1535\text{ cm}^{-1}$) state of TiCl^+ , the $B^3\Delta$ ($\sim 2040\text{ cm}^{-1}$) and $C^3\Pi$ ($\sim 2200\text{ cm}^{-1}$) states of TiF^+ . The identification of these new states contributes to a better characterization of the first 3000 cm^{-1} of the energy level diagram of these molecules. The experimental position of the $C^3\Pi$ state of TiCl^+ is in good agreement with theoretical predictions given by a Ligand Field Theory model.^a We have extended these calculations to the TiF^+ isovalent ion, taking advantage of the new experimental data. Both experimental and theoretical new results presented here are expected to help future high-resolution investigations on these species.

^aPresent address: Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

^aC. Focsa, M. Bencheikh, and L. G. M. Pettersson, *J. Phys. B: At. Mol. Opt. Phys.* **31**, 2857-2869 (1998).

WB22**1 min 7:51****MILLIMETER-WAVE SPECTROSCOPY OF ALKALI AND ALKALINE-EARTH AMIDE SPECIES**

M. A. BREWSTER, P. M. SHERIDAN, J. M. THOMPSEN, J. XIN, and L. M. ZIURYS, *Department of Chemistry, Department of Astronomy, and the Steward Observatory, University of Arizona, Tucson, AZ 85719*.

The pure rotational spectra of several alkali and alkaline-earth amide species have been recorded using millimeter/sub-millimeter direct absorption techniques. These molecules were created by the reaction of metal vapor, generated in a Broida-type oven, with ammonia gas. Eight transitions of CaNH_2 were measured in the frequency range 320-530 GHz, for $K_a=0,1,2,3,4$, and 5. CaNH_2 had been studied previously by optical spectroscopy^a. For NaNH_2 the $K_a=0,1,2,3,4$, and 5 components in ten separate rotational transitions were recorded. This study is the first gas phase detection of this molecule. The spectra of both amides were analyzed using the S-reduced Hamiltonian and rotational, centrifugal distortion, and, in the case of CaNH_2 , fine structure parameters determined. Both molecules appear to be planar species with C_{2v} symmetry. Studies are currently being carried out for magnesium and strontium analogs.

^aA. J. Marr, M. Tanimoto, D. Goodridge, and T.C. Steimle *J. Chem. Phys.* **103**(4466), 1995.

WB23

1 min 7:52

LIF STUDIES ON THE UNIMOLECULAR DECOMPOSITION OF CHEMICALLY ACTIVATED SILANOL

ATSUKO TAKAHARA, RYUTA ARAKI, ATSUMU TEZAKI, and HIROYUKI MATSUI, *The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656 Japan.*

Silanol (SiH_3OH) is prepared by a chemical activation technique using two reaction processes; $\text{O}(^1\text{D}) + \text{SiH}_4 \rightarrow \text{SiH}_3\text{OH}^* \rightarrow \text{SiO} + 2\text{H}_2$ (1) ($\Delta H_{298} = -575 \text{ kJ mol}^{-1}$) and $\text{OH} + \text{SiH}_3 \rightarrow \text{SiH}_3\text{OH}^* \rightarrow \text{SiO} + 2\text{H}_2$ (2) ($\Delta H_{298} = -341 \text{ kJ mol}^{-1}$). It is confirmed that SiO and $\text{Si}(^3\text{P})$ are directly produced in the unimolecular decomposition of SiH_3OH^* ^a, and a kinetic analysis coupled with vibrational relaxation yields nascent vibrational distribution of SiO ($v=0-8$). The measured vibrational distributions for (1) and (2) are approximated as vibrational temperatures, $T^v = 5200 \pm 500$, and 2800 ± 790 K, respectively. Vibrational distributions of SiO calculated by a quasi-statistical theory (BIM) are compared with the experimental results. Here, the energies and the structures of the transition states are given by ab initio calculations for the multi-step decomposition processes leading to SiO formation^b. The statistical model gives a reasonable agreement with the measured vibrational distributions; this result is consistent with the recent crossed molecular beam study for the reaction $\text{O}(^1\text{D}) + \text{SiH}_4$ ^c.

^aA. Takahara, A. Tezaki, and H. Matsui, *J. Phys. Chem.*, (under submission).

^bE. R. Zachariah and W. Tsang, *J. Phys. Chem.*, **99**, 5308 (1995).

^cJ. J. Lin, Y. T. Lee, and X. Yang, *Abstract 15th Symp. Chem. Kinet. Dynamics*, 34 (1999).

WB24

1 min 7:53

FAST-SCAN, PULSED-JET SUBMILLIMETER WAVE ABSORPTION SPECTROSCOPY OF TRANSIENT SPECIES

DMITRY G. MELNIK, SANDHYA GOPALAKRISHNAN, TERRY A. MILLER, *The Ohio State University, Dept. of Chemistry, Laser Spectroscopy Facility, 120 W. 18th Avenue, Columbus, Ohio 43210*; and FRANK C. DE LUCIA, *The Ohio State University, Dept. of Physics, Microwave Laboratory, 174 W. 18th Avenue, Columbus OH 43210.*

A newly developed pulsed jet spectrometer utilizing an extension of the previously reported FASSST technique^a is presented. The technique extends rapid-scan submillimeter wave absorption spectroscopy to a pulsed mode rendering feasible synchronous production and probing of transient species, including free radicals. The output beam from a backward wave oscillator (BWO) is focused on a pulsed supersonic jet and rapidly scanned in frequency (up to 10^5 Doppler linewidths per second), covering the entire accessible spectrum range. The absolute frequency calibration and system synchronization is performed in real time by linking the output signal to a computer running appropriate software. The apparatus is designed to be flexible and suitable for a broad range of applications and is optimized for searching for weak molecular lines. Initial results obtained in experiments with transient species like Van der Waals molecules, Ar·CO and Ar·ND₃, are discussed.

^aPetkie D. T.; Goyette T. M.; Bettens R.P. A.; Belov S. P.; Albert S.; Helminger P; and De Lucia F. C., *Rev. Sci. Instrum.*, **1997**, 68(4), 1675

WB25

1 min 7:54

OPTICAL STARK MEASUREMENT OF THE $\text{C}^3\Delta - \text{X}^3\Delta$ BAND OF TiS AND THE $\text{C}^1\Sigma^+ - \text{X}^1\Sigma^+$ BAND OF ZrS

ROBERT R. BOUSQUET, KEI-ICHI C. NAMIKI and TIMOTHY C. STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe, Az, 85287-1604.*

The high resolution laser induced fluorescence spectra of TiS and ZrS were recorded and optical Stark measurements were performed. The species were produced by the laser ablation of a titanium or zirconium rod in the presence of a supersonic expansion of CS_2 and Ar. The $\text{C}^3\Delta - \text{X}^3\Delta$ spectrum for TiS was fit to within reasonable agreement with the parameters determined by Jonsson and Launila^a. For ZrS, the $\text{C}^1\Sigma^+ - \text{X}^1\Sigma^+$ Stark analysis was performed with the rotational parameters constrained to those determined by Jonsson, Wallin, and Lindgren^b. The permanent electric dipole moments obtained for the ground and excited states of the two species will be reported and discussed.

^aJ. Jonsson and O. Launila, *Mol. Phys.* **79**, 95,(1993)

^bJ. Jonsson, S. Walin, and B. Lindgren, *J. Mol. Spec.* **192**, 198,(1998)

WB26**1 min 7:55**THE PERMANENT ELECTRIC DIPOLE MOMENTS OF THE $A''^1\Sigma^+$ AND $A'^1\Pi$ STATES OF PtC

SARA BEATON, ROBERT BOUSQUET AND TIMOTHY STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604.*

The (0,0) bands of the $A'^1\Pi-X^1\Sigma^+$ ($13\,200\text{cm}^{-1}$) and $A''^1\Sigma^+-X^1\Sigma^+$ ($12\,640\text{cm}^{-1}$) transitions of PtC have been re-recorded^{ab} via laser induced fluorescence at high resolution (FWHM $\sim 35\text{MHz}$). The molecule was produced by the ablation of a solid platinum rod in the presence of a supersonic expansion of CH_4 in argon. The permanent electric dipole moment for each excited state has been determined from optical Stark measurements. The dipole moments will be discussed in terms of a plausible molecular orbital correlation diagram that has been used to describe the molecular properties of several Pt containing diatomics^c. Also, an unusually large value for the nuclear spin-rotation constant, C_I , for the $A''^1\Sigma^+$ state of the ^{195}PtC isotopomer ($I=1/2$) has been determined and will be discussed.

^aO.Appelblad, C.Nilsson and R.Sculman, *Physica Scripta* **7**, 65 (1973)

^bT.C.Stiemle, K.Y.Jung and B.-Z.Li, *J.Chem.Phys.* **102**, 5937 (1995)

^cT.C.Stiemle, K.Y.Jung and B.-Z.Li, *J.Chem.Phys.* **103**, 1767 (1995)

WB27**1 min 7:56**

LIF JET SPECTROSCOPY OF METAL-BEARING FREE RADICALS

MASARU FUKUSHIMA and TAKASHI ISHIWATA, *Department of Information Sciences, Hiroshima City University, Asa-Minami, Hiroshima 731-3194, Japan.*

The rotationally resolved laser induced fluorescence spectra of metal-containing free radicals, such as AINC and AICN, were measured in supersonic free expansions. The metal cyanide and metal isocyanide radicals were prepared by reacting the CN fragments from CH_3CN in an Ar plasma with metal atoms evaporated using laser ablation of the metal surface. The spectra were measured in the collision free region, about 40 mm downstream from the reaction point. The electronic spectrum of AINC and AICN have been already identified by molecular structures obtained by the rotational analysis of the observed spectra. We are also trying to observe the other free radicals containing silicon, magnesium and iron. The analyses of the observed spectra are under way.

WB28**1 min 7:57**EFFECTS DETERMINING THE $1+1'$ PFI-ZEKE PHOTOELECTRON SPECTRUM OF ACETYLENE

SHUENN-JIUN TANG, JIM JR-MIN LIN, AND YEN-CHU HSU, *Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 107, Taiwan, R. O. C. and Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O. C.*

$1+1'$ two-color photoionization spectrum of C_2H_2 via a single rovibrational level of \tilde{A}^1A_u as the intermediate was recorded under nearly field-free condition in the range of $91900\text{-}92700\text{cm}^{-1}$. If the first color was frequency-tuned to excite a single rotational level ($J' = 1 - 4$, e parity) of V_4K_1 of the \tilde{A}^1A_u state, sharp autoionizing spectral lines with the line width of $\Delta\nu = 0.13\text{-}0.20\text{cm}^{-1}$ were obtained except that where near the ionization threshold, extensive diffuseness ($\Delta\nu = 2.1\text{-}4.1\text{cm}^{-1}$) was observed. The prominent autoionizing features have been assigned as two Rydberg series converging to the vibronic state ($K^+ = 0^-, V_4^+ = 1$) of $\text{C}_2\text{H}_2^+(\tilde{X}^2\Pi_u)$. However, if a single rotational level ($J' = 2 - 4$, e parity) of V_4K_2 of the \tilde{A} state was chosen as the doorway state, no autoionizing Rydberg series was possibly assigned. Unusual spectral intensities and spectral line shapes of the PFI-ZEKE Photoelectron spectrum were only observed if V_4K_1 of the \tilde{A}^1A_u state was chosen as the intermediate. We attributed these observations to the interchannel coupling among the vibronic autoionizing states, the ZEKE states and the continuum. The photoionization selection rules of from the \tilde{A} state of acetylene to various vibronic levels of the acetylene cation and Stark effect on the PFI-ZEKE spectrum will also be presented.

WB29

1 min 7:58

TRANSITION STATE DYNAMICS OF THE $\text{OH} + \text{OH} > \text{O} (^3\text{P}) + \text{H}_2\text{O}$ REACTION

HANS-JUERGEN DEYERL and R. E. CONTINETTI, *Department of Chemistry and Biochemistry, University of California San Diego (UCSD), 9500 Gilman Drive, La Jolla CA 92093.*

The transition state region of the $\text{OH} + \text{OH} > \text{O} (^3\text{P}) + \text{H}_2\text{O}$ have been studied at 266, 258 and 355 nm by photoelectron - photofragment coincidence spectroscopy of the $\text{O}^- (\text{H}_2\text{O})$ and $\text{O}^- (\text{D}_2\text{O})$ anions. Photoelectron-photofragment kinetic energy spectra reveal vibrationally resolved product translational energy distributions and allows measurement of the correlation between them. From our experimental data the dissociation energy for the $\text{O}^- (\text{H}_2\text{O})$, $D_0 (\text{O}^- \text{H}_2\text{O}) = 1.00$ eV, was determined.

The data were interpreted by ab initio calculations of both the anion and the neutral surface at the CASSCF level of theory. Comparison with experimental results confirms that the experiment accesses photodetachment from both the $\text{O}^- (\text{D}_2\text{O})$ isomer of D_2O_2^- producing $\text{O} (^3\text{P}) + \text{D}_2\text{O}$ and the higher energy $\text{OD}^- (\text{OD})$ isomer yielding $\text{OD} + \text{OD}$. The latter channel is not energetically accessible and was not observed using 355 nm light.

WB30

1 min 7:59

THE CONSERVATION OF ANGULAR MOMENTUM IN POLYATOMIC PHOTOCHEMICAL REACTIONS: H_2CO AND D_2CO

SIOBHAN E. WAUGH, ONDREJ VOTAVA and SCOTT H. KABLE, *School of Chemistry, University of Sydney Sydney, NSW, 2006, Australia.*

The photodissociation dynamics of the unimolecular dissociation of H_2CO and D_2CO have been investigated. Initially, both the formaldehyde and deuterated formaldehyde are excited into specific J , K_a , K_c rotational states of several vibrational levels in the first excited states. The ensuing distribution of rotational energy in the HCO and DCO fragments are measured as a function of the N , K_a , K_c and $J = N - S$ quantum numbers of the fragment, and also the initial v , J , K_a , K_c quantum numbers of the parent. In a previous publication we investigated the dynamics of the formaldehyde reaction at low available energy (vibrational state $2^1 4^3$) and concluded that when only the N and K_a quantum numbers of both formaldehyde and the formyl radical are considered, the distributions are modelled well by phase space theory (PST) including a centrifugal barrier. However, resolution of K_c in the parent and product gave large deviations from the PST model. A correlation between this K_c preference and the initial state was observed: odd K_c formaldehyde states produce K_c (lower) preference in HCO and vice versa for initially even K_c states. We have also done experiments with different laser polarisation to explore whether the effect is caused by a vector correlation, however the product state distributions are invariant to pump and probe laser polarisation and thus we can rule out vector correlations as a cause for the distributions. Experiments have also been performed that extend the number of vibrational states toward the triplet barrier to show that the same " K_c effect" holds. Various vibrational bands have been chosen with different symmetries and have shown the same effect to hold regardless of the vibronic symmetry. The experiments are being undertaken presently on the photodissociation dynamics of D_2CO to explore whether the " K_c effect" is also evident in the deuterated analogue or perhaps nuclear spin factors play a role. The theoretical interpretation of these results is not yet complete and we hope to provide more details by the time of the conference.

WB31**1 min 8:00****CROSSED BEAM STUDIES OF THE REACTION DYNAMICS OF NITROGEN ATOMS WITH SATURATED AND UNSATURATED HYDROCARBONS: $N(^2D)+CH_4$, C_2H_2 , AND C_2H_4**

M. ALAGIA, N. BALUCANI, A. BERGEAT, L. CARTECHINI, P. CASAVECCHIA, and G. G. VOLPI,
Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy.

We report on the investigation of the reaction dynamics of excited nitrogen atoms $N(^2D)$ with both saturated and unsaturated hydrocarbons, such as methane, acetylene, and ethylene, using the crossed molecular beam scattering technique with mass spectrometric detection. These reactions are significant in a wide variety of systems, in particular in the atmosphere of Saturn's moon Titan, where CH_4 is the most abundant hydrocarbon, followed by C_2H_2 , C_2H_4 and C_2H_6 . We exploit the capability to generate continuous supersonic beams of N atoms by radio-frequency discharge in high pressure N_2 /rare gas mixtures through a quartz nozzle. The beams are characterized by Stern-Gerlach magnetic analysis: 72% of the N atoms are found in the ground 4S state, and 21% and 7% in the first excited 2D and 2P states (lying 2.39 eV and 3.56 eV, respectively, above the ground state). The reactions of $N(^4S)$ with CH_4 , C_2H_2 and C_2H_4 are either endoergic or have high barriers, while the reactions of $N(^2P)$ are much slower than those of $N(^2D)$, as indicated by recent rate constant measurements. From product angular and velocity distribution measurements we have found that the reaction $N(^2D)+C_2H_2$ leads to $H+HCCN$ (cyanomethylene) formation, the reaction $N(^2D)+C_2H_4$ to $H+C_2H_3N$ (in different isomeric forms: azirine, ketenimine, acetonitrile), and the reaction $N(^2D)+CH_4$ to $H+CH_2NH$, $H+CHNH_2$ and possibly $H+CH_3N$. The dynamics of these pathways are elucidated and the results discussed at the light of recent theoretical calculations by Takayanagi and coworkers on the relevant potential energy surfaces. For $N(^2D)+CH_4$, recent studies by Umemoto and coworkers in pump-probe experiments with LIF detection are noted. This is the first time that product angular and velocity distributions are measured in crossed beam experiments for bimolecular N-atom reactions.

WB32**1 min 8:01****ELECTRONIC SPECTROSCOPY OF THE $CN-H_2/D_2$ VAN DER WAALS COMPLEX**

YALING CHEN, ALEXEY L. KALEDIN, and MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

A preliminary spectroscopic study of the $CN-H_2/D_2$ van der Waals complex was reported recently^a. A bound-free continuum spectrum was observed for the B-X transition, while the A-X system exhibited resolved rotational structure. Ground state dissociation energies of $D_0''=38$ ($CN-H_2$) and 42 cm^{-1} ($CN-D_2$) were deduced from the onset of the B-X continuum and the A state predissociation dynamics. Anomalous isotope effects were noted for the dissociation energies and the rotational structures of the A-X bands (which were not assigned).

In recent work we have assigned the A-X bands and detected bound levels of $CN(B)-H_2/D_2$. Analyses of bands associated with the CN monomer 2-0 transition yielded ground state rotational constants of $B''=0.245$ ($CN-H_2$) and 0.229 cm^{-1} ($CN-D_2$). The $CN(X)-H_2$ constant was much smaller than would be predicted using typical van der Waals radii. A similar discrepancy, but less pronounced, was present for $CN(X)-D_2$. High-level ab initio calculations predict ground state constants of 0.518 ($CN-H_2$) and 0.292 cm^{-1} ($CN-D_2$). However, these predictions were for $J=0$ complexes. Theoretical calculations show that the zero-point levels are mixed (via Coriolis coupling) to the first excited internal rotor states. This mixing can account for the small values for the rotational constants and the anomalous isotope effects (for both D_0 and B). The rotational structure is consistent with a collinear $CN-H_2$ equilibrium structure for the ground state.

Bound levels of $CN(B)-H_2/D_2$ were observed by action spectroscopy. Excitation to the B state resulted in rapid $CN(B)-H_2 \rightarrow CN(A) + H_2$ predissociation, so the B-X absorption was detected via A-X fluorescence. The B-X bands were homogeneously broadened and did not show rotational structure. Vibrational structure was evident in the $CN-D_2$ spectrum. The bound B-X bands cut-off at energies that exactly coincided with the onset of the bound-free continua. This observation validates our previous use of the thresholds to determine ground state dissociation energies.

^aY. Chen and M. C. Heaven, *J. Chem. Phys.* 109, 5171 (1998)

WB33

1 min 8:02

DETERMINATION OF MOLECULAR CONSTANTS OF CS^+ BY VELOCITY MODULATION LASER SPECTROSCOPY

YUYAN LIU, HONGPING LIU, HUI GAO, CHUANXI DUAN, *Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, PRC*; P. A. HAMILTON, *Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London, UK E1 4NS*; P. B. DAVIES, *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW*.

A new differential velocity modulation spectrometer operating in the near infrared region has been constructed and used to obtain the (1,0) band of $A^2\Pi - X^2\Sigma^+$ transition of CS^+ . Although the transient CS molecule has been observed in both the earth's atmosphere and the interstellar medium, the corresponding ion, CS^+ , has proved elusive, due in part to the lack of precise ground state molecular constants. In this CS^+ was produced by discharging a trace amount of CS_2 in He and the spectrum observed in absorption using the velocity modulation technique. The use of a balanced differential system substantially reduces noise due to laser power variation and vibration. The spectrum was recorded with high signal to noise ratios and Doppler limited resolution using a Ti:Sapphire laser over the 12400-13000/cm region.

Assignment of the spectra was straightforward using previously available lower resolution data. The local perturbation in the $A^2\Pi$ state ($v=1$) due to the $X^2\Sigma^+$ ($v=10$) state was treated quantitatively in the fitting procedure to provide molecular constants (in cm^{-1}) for the perturbing state. The precise unperturbed molecular constants determined for the ground $^2\Sigma^+$ state and the excited $A^2\Pi$ state of CS^+ are summarised in the table below. The ground state rotational constant is now determined to better than 0.1MHz which should aid in the search for this species in interstellar space.

	$A^2\Pi$	$X^2\Sigma(v = 10)$	$X^2\Sigma(v = 10)$
B	0.7089859(21)	0.8642486(25)	0.799991(62)
$D/10^{-6}$	1.4662(45)	1.3605(47)	
A	-302.0369(23)		
$A_d/10^{-6}$	6.6(35)		
T	12805.827010(66)		12908.288(13)
α			9.0098(37)
β			-0.000413(90)
γ		0.0975146(13)	

RA. THURSDAY MORNING SESSION

AUGUST 19, 1999 – 8:15 AM

Room: BALLROOM, LITTLE AMERICA HOTEL

Chair: MICHAEL MORSE, University of Utah, Salt Lake City, UT

RA01

40 min 8:15

RAPID EVAPORATIVE COOLING SUPPRESSES FRAGMENTATION IN MASS SPECTROMETRY: SYNTHESIS OF “UNPROTONATED” WATER CLUSTER IONS

RIENK T. JONGMA, YUHUI HUANG, SHIMING SHI, and ALEC WODTKE, *Department of Chemistry, University of California, Santa Barbara, CA 93106.*

Hydrogen bonded water clusters were formed with inert gasses adsorbed to them in a strong molecular beam expansion. Upon photo-ionization of such mixed clusters, fragmentation of the substrate water cluster ion is markedly suppressed. Experimental evidence is presented, showing that the rapid evaporation of the inert gas from the newly formed water cluster ion efficiently removes internal energy on a time scale much faster than the usual fragmentation reactions present in pure water cluster, i.e., rates of fragmentation that are normally $>10^9 \text{ s}^{-1}$. This phenomenon is exploited to produce “unprotonated” water clusters, formally $(\text{H}_2\text{O})_n^+$. Using post source decay reflectron time-of-flight mass spectrometry, the structure of the “unprotonated” water cluster ions is experimentally determined for the first time. The structure determined, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_k \cdot \text{OH}$ where the hydroxyl radical is found outside the first solvation shell of the charge, is consistent with recent *ab initio* calculations. This simple approach to the control of fragmentation in mass spectrometry appears to have promise in applications to other interesting polymeric samples, for example biopolymers.

RA02

40 min 9:00

ON THE PHOTOIONIZATION OF STATE-SELECTED ACYL RADICALS: CATION STRUCTURE AND VIBRATIONAL RELAXATION DYNAMICS

R. J. FOLTYNOWICZ, E. ZUCKERMAN, J. D. ROBINSON, H. G. HEDDERICH, and E. R. GRANT, *Department of Chemistry, Purdue University, West Lafayette, IN 47907.*

Many open-shell free radicals exhibit complex electronic structure as neutral molecules, but form electronically simple closed-shell cations. As a result, higher excited states often conform with an elementary Rydberg separation. Bound intermediate states commonly found in such systems provide convenient gateways for double-resonant photoionization using ultraviolet and visible laser radiation. Distinctive spectra of photoselected Rydberg series reflect state-to-state electron-ejection dynamics of super-excited neutrals and yield structural information on corresponding cations. We illustrate this principle with new results on formyl radical that characterize anharmonic terms in the vibrational potential of the cation.

Intermission

RA03

40 min 10:05

METAL-LIGANDS AND METAL-METAL INTERACTIONS: SPECTROSCOPY AND KINETICS

BENOIT SIMARD, *Molecular Spectroscopy Program, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6.*

The first part of the talk will focus on complexations and oxydative addition reactions at metal centers. Three examples will be reviewed and discussed: $Y + NH_3$, $Al + NH_3$, and $Zr + O(CH_3)_2$. The reaction of yttrium with ammonia proceeds without the formation of a stable adduct. The N-H bond is readily activated and the reactions proceeds with the elimination of molecular hydrogen to produce yttrium imide, $YNH(D)$. We have studied the visible spectrum of yttrium imide at medium and high resolution using laser induced fluorescence (LIF). Following a brief survey of the visible spectrum, the presentation will focus on the origin band of the $\tilde{B}^2\Sigma^+ - \tilde{X}^2\Sigma^+$ system for which rotational, fine and nuclear magnetic hyperfine structure has been recently analyzed in detail. The reaction of aluminum with ammonia proceeds with the formation of a stable adduct, $Al(NH_3)$, which we have recently studied using photoionization spectroscopy. Resonant two-photon ionization (R2PI) yielded a vibronically resolved spectrum in the $18000-21000\text{ cm}^{-1}$, which is beleived to be due to four electronic band systems. Photoionization efficiency (PIE) spectroscopy yielded Rydberg spectra whose limits provided information on the ground state of the cation. All of these observations will be summarized in the presentation. The reaction of zirconium with dimethylether also leads to the formation of an adduct. We have studied the adduct using a combination of pulsed field ionization-zero electron kinetic energy (PFI-ZEKE) photoelectron spectra, density functional calculations and kinetic measurements. The latter yielded a binding energy of 16 kcal/mol. Detail of these measurements and calculations will be provided. A novel apparatus for the rapid acquisition of absorption spectra for metal-containing complexes will be introduced. The apparatus consists of a fast-flow reactor coupled to a multipass absorption cell and a Fourier transform spectrometer.

The second part of the presentation will focus on the structures of small ligated yttrium and niobium clusters. The structures of these species have been determined using a combinations of PFI-ZEKE measurements and density-functional calculations. Detail of these experiments and calculations will be given.

FA. FRIDAY MORNING SESSION

AUGUST 20, 1999 – 8:15 AM

Room: BALLROOM, LITTLE AMERICA HOTEL

Chair: PETER BERNATH, University of Waterloo, Waterloo, Ontario, Canada

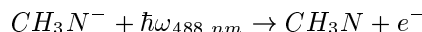
FA01

40 min 8:15

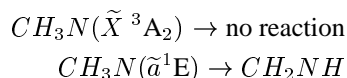
PHOTOELECTRON STUDIES OF METHYLNITRENE, CH₃N

BARNEY ELLISON, *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215.*

Complex organic radicals are important intermediates in many combustion and environmental processes. In combustion processes, the organic radical CH is known to cleave N₂ into HCN and N atoms. Most N atoms are further oxidized to NO which exhausts into the atmosphere. Thus the reaction of CH with N₂ to produce N atoms connects internal combustion engines with NO production. Some fraction of these N atoms, however, reacts with CH₃ in the flame to produce CH₃N. Methylnitrene is very unstable and decomposes to generate CH₂NH or H₂ + HCN. We will discuss the use of negative ion photoelectron spectroscopy to characterize methylnitrene.



We find $EA(CH_3N) = 0.022 \pm 0.009$ eV. In addition to detaching the methylnitrene anion to the ground state of CH₃N (\tilde{X}^3A_2), we also detect the first electronically excited state of methylnitrene, \tilde{a}^1E . We measure $\Delta E(\tilde{a}^1E - \tilde{X}^3A_2) = 1.352 \pm 0.011$ eV. The reaction dynamics of nitrene rearrangements will be discussed:



FA02

40 min 9:00

THE INFRARED SPECTRUM OF CH₅⁺

TAKESHI OKA, *Department of Chemistry, Department of Astronomy and Astrophysics, and the Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637.*

Protonated methane, CH₅⁺, has unusual C-H bondings and is a new prototype of spectroscopic specimen. While all of the five protons are strongly bound to the central carbon atom with well defined C-H stretch potentials, angles between C-H bonds are highly fluxional. Ab initio theory predicts lowest energy for an "equilibrium structure" with C_s symmetry but the barriers separating the 24 equivalent structures are extremely low and almost non-existent when zero point vibrations are taken into account.^{ab}

We have identified nearly 1000 spectral lines of CH₅⁺ in a liquid N₂-cooled hydrogen dominated plasma using a gas mixture of H₂:CH₄ ~ 100:1.^c The spectral lines are weak and do not show obvious symmetry or regular pattern. The identification required extensive studies of the spectra of other carbocations CH₃⁺ (and CH₂⁺) and C₂H₃⁺ (and C₂H₂⁺) whose spectra appear in the same wavelength region with much higher intensities. Spectroscopy and plasma chemistry of those carbocations will be discussed and the raw observed spectrum of CH₅⁺ will be presented without assignment nor even qualitative understanding.

^aP. R. Schreiner et al., *J.Chem.Phys.* **99**, 3716 (1993)

^bH. Mueller et al., *J.Chem.Phys.* **106**, 1863 (1997)

^cE. T. White, J. Tang and T. Oka, *Science* **284**, 135 (1999)

Intermission

FA03

40 min 10:05

SPECTROSCOPY OF CARBON CHAINS AND THEIR IONS

J. P. MAIER, *Institute for Physical Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland.*

The electronic spectra of neutral carbon chains, their anions and cations are being observed in the gas-phase. Three different approaches are used. The transitions of the chain radicals, C_nH $n=6,8,10$ have been detected by cavity ring down spectroscopy in a slit jet discharge. Carbon chain anions of the type C_n^- , C_nH^- have been studied by a two colour resonant photodetachment approach. The electronic transitions of the polyacetylene cations, like HC_6H^+ and its cyanoderivative HC_4CN^+ , have been measured at high resolution in cell and jet discharges using frequency modulation absorption spectroscopy.

FA04

40 min 10:50

FREE RADICAL REACTION DYNAMICS WITH CROSSED BEAMS

PIERGIORGIO CASAVECCHIA, *Departimento di Chimica, Università di Perugia, 06123 Perugia, Italy.*

During the last decade, tremendous advancements in molecular beam and laser spectroscopic techniques, as well as in theoretical methodologies and computer capabilities, have brought to maturity the understanding of the dynamics of simple prototype reactions involving three-atoms.^a At the same time, this progress has permitted to tackle the dynamics of a larger variety of atom and small radical reactions of interest from both fundamental points of view and in areas of practical importance, such as atmospheric, combustion and astrophysical chemistry.^{a,b} The crossed beam scattering technique with mass spectrometric detection has continued to play a very important role in studies of reaction dynamics.^a Central to studies of free radical reactions with crossed beams is the production of supersonic beams of the transient reactants of sufficient intensity to carry out product angular and velocity distribution measurements. Over the past ten years there have been considerable developments in the generation of free radical beams, most notably by using pulsed laser photolysis or ablation. However, only *pulsed* beams of $O(^1D)$, $C(^3P)$ and $CN(X^2\Sigma^+)$ have been used in "classic" crossed beam experiments with mass spectrometric detection. In our laboratory, we have pursued the development of *continuous* supersonic beams of transient species for reactive scattering studies, since they best couple with a *continuous* "universal" detector. By using a high-pressure radio-frequency discharge source, we have been able to produce intense beams of $O(^3P, ^1D)$, $Cl(^2P)$, $OH(^2\Pi)$ and recently, for the first time, of $N(^4S, ^2D)$, and have studied a variety of important reactions of these species.^{a,b} Very recently, the same approach has been successfully extended to the production of *continuous* beams (for the first time) of other important free radicals, such as $C(^3P, ^1D)$ and $CN(X^2\Sigma^+)$, and this has allowed us to tackle the dynamic study of reactions which are of relevance from hydrocarbon combustion and synthesis to astrochemistry. The recent progress in studies of free radical reaction dynamics with crossed beams will be discussed.

^aP. Casavecchia, N. Balucani, and G.G. Volpi, *Annu. Rev. Phys. Chem.* **50**, 347 (1999).

^bP. Casavecchia, N. Balucani, M. Alagia, L. Cartechini, and G.G. Volpi, *Acc. Chem. Res.* (June 1999), in press.

Closing Remarks

15 min 11:35

AUTHOR INDEX

A

ADAM, A. G. – WB05
 AL-KHALILI, A. – MB32
 ALAGIA, M. – WB31
 ALDENER, M. – MB09
 ALFRED, S. – WB04
 ALLEN JR., J. E. – TB11
 ALLEN, M. D. – TB13
 ANDERSON, D. T. – WB03
 ANDERSSON, R. – TB09
 APPLGATE, B. E. – MB21, TB19
 APPONI, A. J. – MB17, MB18
 ARAKI, R. – WB23
 ATHANASSENAS, K. – WB05
 ATKINSON, D. B. – MB20

B

BAER, A. – WB11, WB12, WB13
 BALFOUR, W. J. – MB04
 BALL, C. D. – TB20
 BALLARD, J. – MB10
 BALLARD, M. K. – WB09
 BALUCANI, N. – WB31
 BARCKHOLTZ, T. A. – MB21
 BARROW, R. F. – WB19
 BEATON, S. – WB26
 BERG, L. – TB09
 BERGEAT, A. – MB31, TB04, WB31
 BERNATH, P. – MB16, TB23
 BOBBENKAMP, R. – MB32
 BOGEY, M. – TB17, WB21
 BONN, R. T. – TB03
 BOTSCHWINA, P. – MB19, WB18
 BOUSQUET, R. – WB26
 BOUSQUET, R. R. – WB25
 BRECKENRIDGE, W. H. – WB16
 BREWSTER, M. A. – WB22
 BROUARD, M. – TB16
 BROWN, J. M. – TB13, WB19
 BRUEHL, F. R. – WB09
 BRUGH, D. J. – TB27

C

CARLEER, M. – WB08
 CARRINGTON, A. – TA01
 CARTECHINI, L. – MB31, TB04,
 WB31

CARTER, C. C. – TB18
 CARTER, S. – WB18
 CASAVECCHIA, P. – MB31, TB04,
 WB31, FA04
 CHEN, C. – WB01
 CHEN, M. H. – MB06
 CHEN, P. – WA01
 CHEN, W. – MB01
 CHEN, Y. – WB32
 CHRISTENSEN, L. – MB15
 CIREASA, R. – TB08
 CLARY, D. C. – TA02
 CLIFFORD, E. – TB10
 CODY, R. J. – TB02
 COHEN, E. A. – TB21, TB22, WB15
 COHEN, P. R. C. – TB01
 COLIN, R. – WB08
 CONTINETTI, R. E. – WB29
 COQUART, B. – WB08
 COSSART, D. – TB08
 CRIM, F. F. – MA02
 CROSLY, D. R. – WB14
 CURL, R. F. – MB08, TB13

D

DABELL, R. S. – WB06
 DANARED, H. – MB32
 DAVIES, P. B. – MB28, TB05, WB33
 DAVIS, S. J. – MB29
 DE LUCIA, F. C. – WB24
 DELIA, A. E. – TB30
 DEMUYNCK, C. – TB17
 DENZER, W. – TB16
 DESAIN, J. – MB08, TB10
 DEYERL, H. – WB29
 DICKINSON, J. A. – TB26
 DING, X. D. – MB03
 DUAN, C. – WB33
 DUKAN, L. – WB16

E

ELHANINE, M. – MB33, WB16
 ELKS, J. M. F. – WB07
 ELLISON, B. – FA01
 ELORANTA, J. – TB07
 ELOUTASSI, O. – TB33
 ENDO, Y. – WA02
 ERNST, W. E. – MB13, WB09
 EVENSON, K. M. – TA04, TB13,
 WB20

F

FALLY, S. – WB08
 FAN, W. Y. – MB07, MB28
 FARRELL, J. – TB10
 FELDMAN, H. – WB11
 FINK, E. H. – MB05
 FOCSA, C. – WB21
 FOLTYNOWICZ, R. J. – RA02
 FOUGERE, S. G. – MB04
 FUJIWARA, H. – MB23
 FUKUSHIMA, M. – MB23, WB27
 FÄNGSTRÖM, T. – WB17

G

GAO, H. – WB33
 GAUDUEL, Y. – TB31
 GELABERT, H. – TB31
 GIELEN, R. – MB05
 GILLET, D. A. – WB05
 GINGERICH, K. A. – TB06
 GOLONZKA, O. – MB13
 GOODRIDGE, D. M. – WB15
 GOPALAKRISHNAN, S. – WB24
 GOTTLIEB, C. A. – MB17, MB18
 GRAHAM, W. R. M. – MB03
 GRANT, E. R. – RA02
 GUILLOUD, F. – TB31
 GUSS, J. – MB26

H

HAJJARI, A. – TB33
 HALPERN, J. B. – WB04
 HAMEDOUN, M. – TB33
 HAMILTON, P. A. – WB33
 HAMU, D. B. – WB11
 HAN, J. – MB08
 HANSSON, T. – TB09
 HASSOUNA, M. – TB17
 HAYES, E. F. – TB18
 HEAVEN, M. C. – MB29, WB32
 HECHTFISCHER, U. – MB30,
 WB12
 HEDDERICH, H. G. – RA02
 HEMERT, M. C. V. – MB22
 HEUFF, R. F. – MB04
 HINKLE, K. – MB16
 HOWIE, W. H. – MB11

HSU, Y. – MB24, WB28
 HU, P. – TB29
 HUANG, Y. – RA01
 HUGHES, D. W. – TB16
 HULLAH, D. F. – WB19
 HUNG, P. Y. – MB08
 HUNT, N. T. – MB28

I

IANNONE, M. A. – TB02
 ISHIKAWA, H. – WB10
 ISHIWATA, T. – MB23, WB27

J

JACOX, M. E. – MB02
 JEFFRIES, J. B. – WB14
 JENOUVRIER, A. – WB08
 JONES, W. E. – MB08
 JONGMA, R. T. – RA01

K

KABLE, S. H. – MB26, WB30
 KAGI, E. – MB23
 KALIEDIN, A. L. – WB32
 KALINOVSKI, I. – MB07
 KALOGERAKIS, K. S. – TB16
 KAWAGUCHI, K. – WB15
 KELLERMAN, T. L. – MB14
 KINGSTON, C. T. – WB05
 KLEIN-DOUWEL, R. J. H. – WB14
 KNEPP, P. – MB26
 KNOLL, L. – MB30, WB12, WB13
 KODA, S. – MB27
 KOMISSAROV, A. V. – MB29

L

LANE, I. C. – MB10, MB11
 LANGE, M. – MB30, WB12
 LANGENBERG, J. D. – TB24
 LARSSON, M. – MB32
 LAURSEN, S. L. – TB30
 LE PADELLEC, A. – MB32
 LEE, H. – TB18
 LEE, Y. – WA04
 LESTER, M. I. – TB03, WB03
 LETAMENDIA, L. – TB33
 LEVIN, J. – MB30, WB11, WB12,
 WB13
 LI, G. – MB16

LI, Q. – WB01
 LIANG, B. – WB02
 LIEVIN, J. – TB23
 LIN, J. J. – MB24, WB28
 LINDGREN, B. – MB09, MB12
 LINDHOLM, N. F. – TB27
 LIU, H. – WB33
 LIU, Y. – WB33
 LIU, Z. – MB28, TB05
 LIVINGSTONE, R. J. – TB05
 LUGEZ, C. L. – MB02
 LUNDEVALL, C. – MB12, TB25
 LUNELL, S. – WB17
 LUQUE, J. – WB14

M

MA, X. – WB01
 MAIER, J. P. – FA03
 MAITRE, P. – WB16
 MANDY, M. E. – TB15
 MANKE II, G. C. – MB29
 MANN, A. M. – MB07
 MASSICK, S. – WB16
 MATSUI, H. – WB23
 MCCARTHY, M. C. – MA04, MB01,
 MB17, MB18, TB20
 MCCOY, A. B. – TB18
 MCILROY, A. – WB04
 MELNIK, D. G. – WB24
 MERER, A. J. – WB05
 MERIENNE, M. F. – WB08
 MESTDAGH, J. M. – MB33
 MEYER, R. G. – WB06
 MIKAMI, N. – WB10
 MILLER, C. E. – TB21, TB22
 MILLER, T. A. – MB21, MB25,
 TB18, TB19, WB24
 MITCHELL, K. – TB30
 MIYAWAKI, J. – TB28
 MLADENOVIC, M. – WB18
 MOORE, C. B. – MB07
 MORSE, M. D. – TB24, TB27,
 WB06
 MÜLLER, H. S. P. – TB22

N

NAMIKI, K. C. – WB25
 NESBITT, F. L. – TB02
 NEUMARK, D. M. – TB14
 NEWMAN, S. M. – MB10, MB11
 NEWNHAM, D. A. – MB10

NOVICK, S. E. – MB01

O

O'BRIEN, J. J. – TB12
 O'BRIEN, L. C. – MB14, TB12
 OKA, T. – FA02
 OKUMURA, M. – MB15
 ORR-EWING, A. J. – MB10, MB11
 OSHIMA, Y. – MB27
 OTOMO, J. – MB27

P

PATRICK, K. – WB04
 PEERS, J. R. D. – WB05
 PETERSON, J. R. – MB32
 PETTERSSON, A. – MB09, MB12
 PEVERALL, R. – MB32
 PIBEL, C. D. – WB04
 PINCHEMEL, B. – WB21
 PUSHKARSKY, M. B. – MB25,
 TB19

Q

QIAN, C. X. W. – MB04
 QIN, Q. Z. – MB06

R

RAM, R. S. – MB16, TB23
 REID, S. A. – WB02
 RITTBY, C. M. L. – MB03
 RIXON, S. J. – WB05
 ROBBINS, D. L. – MB03
 ROBINSON, J. C. – TB14
 ROBINSON, J. D. – RA02
 ROTHSCHOPF, G. K. – TB27

S

S. ROSN – MB32
 SAATHOF, G. – MB30
 SANDER, S. – MB15
 SASAKI, T. – WB10
 SASSENBERG, U. – MB09, MB12
 SCHEFFEL, M. – WB12
 SCHMIDT, J. P. – WB02
 SCHMIDT, T. – MB26
 SCHWALM, D. – MB30, WB12,
 WB13
 SEARS, T. J. – TA03

SEBALD, P. – WB18
 SEMANIAK, J. – MB32
 SHERIDAN, P. M. – WB22
 SHESTAKOV, O. – MB05
 SHI, S. – RA01
 SHI, W. – MB12
 SHIM, I. – TB06
 SHIOTANI, M. – WB17
 SHU, J. – WB01
 SICKAFOOSE, S. M. – TB24
 SIMARD, B. – RA03
 SIMONS, J. P. – TB16
 SMITH, G. P. – WB14
 SOEP, B. – MB33, WB16
 SOMMERDIJK, H. T. – MB22
 STAKHURSKY, V. L. – MB25
 STAVROS, V. G. – TB16
 STEIMLE, T. – WB26
 STEIMLE, T. C. – TB26, WB25
 STROH, F. – WB20
 SUGAWARA, K. – TB28
 SUN, F. – TB13
 SUN, W. – TB14

T

TAATJES, C. – TB10
 TAATJES, C. A. – WB04
 TAKAHARA, A. – WB23
 TAKAMI, A. – MB27
 TAKEO, H. – TB28
 TANG, S. – MB24, WB28
 TANG, Y. – WB02
 TEMPS, F. – MA01

TEZAKI, A. – WB23
 THADDEUS, P. – MB01, MB17,
 MB18, TB20
 THOMPSEN, J. M. – WB22
 THOMPSON, W. E. – MB02
 TODD, M. W. – WB03
 TSIOURIS, M. – WB03

U

UGGLAS, M. A. – MB32

V

VAGER, Z. – WB11, WB12, WB13
 VAIDA, P. V. – WA03
 VANDAELE, A. C. – WB08
 VARBERG, T. D. – WB20
 VATANEN, V. – TB07
 VERVLOET, M. – TB08
 VIKOR, L. – MB32
 VISTICOT, J. P. – MB33
 VOLPI, G. G. – MB31, TB04, WB31
 VOTAVA, O. – WB30
 VUOLLE, M. – TB07

W

WALLACE, L. – MB16
 WALTERS, A. – TB17
 WANG, P. – WB17
 WANG, S. L. – MB03
 WANG, X. F. – MB06
 WAUGH, S. E. – WB30

WESTER, R. – MB30, WB12, WB13
 WESTERN, C. M. – WB07
 WHEELER, M. D. – TB03, WB03
 WILSON, C. – WB19
 WINN, J. S. – TB29
 WINNEWISSER, G. – MA03
 WODTKE, A. – RA01
 WOLF, A. – MB30, WB12, WB13

X

XIN, J. – WB22
 XU, K. – TB32

Y

YOKOYAMA, K. – TB14
 YU, S. – WB01

Z

ZAJFMAN, D. – MB30, WB11,
 WB12, WB13
 ZANDE, W. V. D. – MB32
 ZHANG, B. – TB09
 ZHANG, J. – TB32
 ZHANG, L. N. – MB06
 ZHANG, Q. – WB01
 ZHENG, Q. K. – MB06
 ZHOU, C. – MB04
 ZHOU, X. – WB01
 ZIURYS, L. M. – WB22
 ZUCKERMAN, E. – RA02

Participant List

Marc Airola
Department of Chemistry
University of Utah
315 S. 1400 E. Rm. DOCK
Salt Lake City, UT 84112-0850 USA
airola@chemistry.chem.utah.edu

Ismail Al-Jihad
Steward Observatory
University of Arizona
933 N. Cherry St.
Tucson, AZ 85719 USA
ialjihad@u.arizona.edu

Mattias Aldener
Department of Physics
Stockholm University
Box 6730
Stockholm S-11385 Sweden
aldener@physto.se

John E. Allen
NASA Goddard Space Flight Center
Code 691
Greenbelt, MD 20771 USA
john.e.allen@gsc.nasa.gov

Michael D. Allen
Time and Frequency Division, 847
NIST
325 Broadway
Boulder, CO 80303 USA
mallen@boulder.nist.gov

Brian Applegate
Department of Chemistry
Ohio State University
120 W. 18th Ave.
Columbus, OH 43210 USA
apple@chemistry.ohio-state.edu

Aldo Apponi
DEAS
Harvard University
Pierce Hall Rm. B4
29 Oxford St.
Cambridge, MA 02138 USA
aapponi@cfa.harvard.edu

Dean Atkinson
Chemistry Department
Portland State University

Portland OR 97207-0751 USA
atkinsond@pdx.edu

Adam Baer
Department of Particle Physics
Weizmann Institute of Science
Rehovot 76100 Israel
fnadam@physics.weizmann.ac.il

Walter J. Balfour
Department of Chemistry
University of Victoria
PO Box 3055
Victoria, B.C. V8W 3V6 Canada
balfour@uvvm.uvic.ca

Christopher Ball
Harvard-Smithsonian Center for As-
trophysics
M.S. 72, 60 Garden St.
Cambridge, MA 02138 USA
cball@cfa.harvard.edu

Sara Beaton
Department of Chemistry
Arizona State University
Tempe, AZ 85287-1604 USA
beaton@imap3.asu.edu

Astrid Bergeat
Dipartimento Di Chimica
Universita Di Perugia
Perugia 06123 Italy
astrid@dyn.unipg.it

Peter F. Bernath
Department of Chemistry
University of Waterloo
Waterloo, Ontario N2L 3G1 Canada
bernath@uwaterloo.ca

Marcel Bogey
Laboratoire PhLAM
Universite de LILLE 1
Bat P5
Villeneuve d'Ascq, Cedex F-59655
France
marcel.bogey@univ-lille1.fr

Dharshi Bopegedera
Department of Chemistry
Evergreen State College

Olympia, WA 98505 USA
bopegedd@evergreen.edu

Peter Botschwina
Inst. fur Physik. Chemie
Universität Göttingen
Tammannstrasse 6
Göttingen D-37077 Germany
pbotsch@gwdg.de

Robert Bousquet
Department of Chemistry
Arizona State University
Tempe, AZ 85287-1604 USA
r.bousquet@juno.com

John M. Brown
Physical Chem. Lab.
Oxford University
South Parks Road
Oxford OX1 3QZ England
jmb@physchem.ox.ac.uk

Alan Carrington
Department of Chemistry
University of Southampton
Hampshire SO17 1BJ England
ac@soton.ac.uk

Chris Carter
Department of Chemistry
Ohio State University
Columbus, OH 43210 USA
ccarter@chemistry.ohio-state.edu

Piergiorgio Casavecchia
Dipartimento di Chimica
Universita di Perugia
Perugia 06123 Italy
piero@dyn.unipg.it

Kelly Chance
Center for Astrophysics
60 Garden Street
Cambridge, MA 02138 USA
kchance@cfa.harvard.edu

Peter Chen
Laboratorium fur Org. Chemie
ETH-Zurich
Universitatstrasse 16
Zurich CH-8092 Switzerland

chen@org.chem.ethz.ch

Lance Christensen
Department of Chemistry
CalTech
Pasadena CA 91125 USA
lance@its.caltech.edu

David C. Clary
Department of Chemistry
University College London
20 Gordon Street
London WC1H 0AJ England
d.c.clary@ucl.ac.uk

Eileen Clifford
Sandia National Laboratories
7011 East Ave., MS 9055
Livermore, CA 94550 USA
epcliff@ca.sandia.gov

Regina J. Cody
Goddard Space Flight Center
NASA
Code 691
Greenbelt, MD 20771 USA
regina.cody@gssc.nasa.gov

Edward A. Cohen
Jet Propulsion Lab
California Institute of Technology
M.S. 183-301
Pasadena, CA 91109-8099 USA
eac@spec.jpl.nasa.gov

Ronald C. Cohen
Department of Chemistry
UC Berkeley
B64A Hildebrand
Berkeley, CA 94720-1460 USA
cohen@cchem.berkeley.edu

Reginald Colin
Lab. de Chimie Phys. Molec.
Universite Libre de Bruxelles
50 av. F.D. Roosevelt
Brussels 1050 Belgium
rcolin@ulb.ac.be

Steven D. Colson
Pacific Northwest National Laboratory
P.O. Box 999 MSIN K8-88
Richland, WA 99352 USA
steven.colson@pnl.gov

F. Fleming Crim
Department of Chemistry
University of Wisconsin-Madison
Madison WI 53706 USA
fcrim@chem.wisc.edu

Robert Curl
Department of Chemistry
Rice University
PO Box 1892
Houston, TX 77005-1892 USA
rfcurl@rice.edu

Ryan DaBell
Department of Chemistry
University of Utah
315 S. 1400 E. Rm. DOCK
Salt Lake City, UT 84112-0850 USA
rsdabell@chemistry.chem.utah.edu

Paul B. Davies
Dept. of Chemistry
University of Cambridge
Lensfield Road
Cambridge CB2 1EW England
pbd2@cus.cam.ac.uk

Wolfgang Denzer
Physical & Theoretical Chemistry Lab
Oxford University
South Parks Road
Oxford OX1 3QZ England
denzer@physchem.ox.ac.uk

John DeSain
Sandia National Laboratories
P.O. Box 969, M.S. 9055
Livermore, CA 94551-0969 USA
jddesai@sandia.gov

Hans-Juergen Deyerl
Department of Chemistry
UCSD
9500 Gilman Dr.
LaJolla, CA 92093-0340 USA
hdeyerl@checks2.ucsd.edu

John A. Dickinson
Department of Chemistry
Arizona State University
Tempe, AZ 85287-1604 USA
johnd@asu.edu

Michael Eastman
Department of Chemistry
Northern Arizona University
Box 5698
Flagstaff, AZ 86011-5698 USA
michael.eastman@nau.edu

Mohammed Elhanine
LPPM
Universite Paris-XI
Batiment 210
Orsay, Cedex 91405 France
mohammed.elhanine@ppm.u-psud.fr

John Elks
School of Chemistry
University of Bristol
Cantock's Close
Bristol BS8 1TS England
john.elks@bristol.ac.uk

Barney Ellison
Department of Chemistry
University of Colorado
Boulder, CO 80309-0215 USA
barney@jila.colorado.edu

Jussi Eloranta
Revontie 5 A 2
Jyvaskyla 40250 Finland
eloranta@jyu.fi

Yasuki Endo
Dept. of Basic Science
Graduate School of Arts and Sciences
University of Tokyo
Meguro-ku 381
Tokyo 153-8902 Japan
endo@bunshi.c.u-tokyo.ac.jp

Wolfgang E. Ernst
Department of Physics
The Pennsylvania State Univ.
104 Davey Laboratory
University Park, PA 16802 USA
weel@psu.edu

Kenneth M. Evenson
NIST
325 Broadway
Boulder, CO 80303 USA
evenson@bldrdoc.gov

Wai Yip Fan

Dept. of Chemistry
University of California at Berkeley
D40 Hildebrand Hall
Berkeley, CA 94720 USA
waif@socrates.berkeley.edu

Ewald H. Fink
Fachbereich Chemie
Universität Wuppertal
Gauss-Strasse 20
Wuppertal D-42097 Germany
fink@mailgate.urz.uni-wuppertal.de

Masaru Fukushima
Department of Information Sciences
Hiroshima City University
Asa-Minami
Hiroshima 731-3194 Japan
fukushim@im.hiroshima-cu.ac.jp

Eva Garland
CalTech
Mail Code 127-72
Pasadena, CA 91125 USA
garland@its.caltech.edu

Yann Gauduel
L.O.A. INSERM U451
Ecole Polytechnique - ENSTA
Chemin de a Hunigre
Palaiseau, Cedex 91761 France
gauduel@enstay.ensta.fr

Damian Goodridge
Nobeyama Radio Observatory
Nobeyama, Minamimaki
Minamisaku, Nagano 384-1305 Japan
damian@nro.nao.ac.jp

Robert Gordon
Department of Chemistry
Queen's University
Kingston, Ontario K7L 3N6 Canada
gordonr@chem.queensu.ca

William R. M. Graham
Department of Physics and Astronomy
Texas Christian University
PO Box 298840
Forth Worth, TX 76129 USA
w.graham@tcu.edu

Edward R. Grant
Department of Chemistry

Purdue University
West Lafayette, IN 47907 USA
egrant@chem.purdue.edu

Joshua Halpern
Department of Chemistry
Howard University
Washington, D.C. 20059 USA
jhb@scs.howard.edu

John Hardwick
Department of Chemistry
University of Oregon
Eugene, OR 97403-1253 USA
hardwick@oregon.uoregon.edu

Michael Heaven
Department of Chemistry
Emory University
Atlanta, GA 30322 USA
heaven@euch4c.chem.emory.edu

Wendy Howie
School of Chemistry
University of Bristol
Cantock's Close
Bristol BS8 ITS UK
w.howie@bris.ac.uk

Yen-Chu Margaret Hsu
Institute of Atomic & Molecular Sci-
ences
Academia Sinica
PO Box 23-166
Taipei 107 Taiwan, R.O.C.
ychsu@po.iams.sinica.edu.tw

Pui Yee Hung
Rice University
6500 South Main, #C22
Houston, TX 77030 USA
hungp@ruf.rice.edu

Neil Terence Hunt
Fitzwilliam College
Cambridge CB3 ODG England
nth20@hermes.cam.ac.uk

Haruki Ishikawa
Department of Chemistry
Graduate School of Science
Tohoku University
Aoba-ku, Sendai 980-8578 Japan
haruki@qclhp.chem.tohoku.ac.jp

Marilyn Jacox
Molecular Physics Div.
National Institute of Standards and
Technology
Mail Stop 8441
Gaithersburg, MD 20899-8441 USA
marilyn.jacox@nist.gov

Alexandria Janczyk
Department of Chemistry
Arizona State University
Tempe, AZ 85287-1604 USA

Scott Kable
Department of Physical Chemistry
University of Sydney
Sydney 2006 Australia
s.kable@chem.usyd.edu.au

Eriko Kagi
Information Sciences
Hiroshima City University
3-4-1, Ozuka-Higashi 3-4-1, Asa-
Minami
Hiroshima 731-3194 Japan
kagi@im.hiroshima-cu.ac.jp

Ilia Kalinovski
Department of Chemistry
University of California
Berkeley, CA 94720 USA
ilia@socrates.berkeley.edu

Konstantinos Kalogerakis
Physical and Theoretical Chemistry
Laboratory
Oxford University
South Parks Road
Oxford OX1 3QZ England
kostas@physchem.ox.ac.uk

Robert J. H. Klein-Douwel
Molecular Physics Laboratory
SRI International
333 Ravenswood Avenue
Menlo Park, CA USA
robertkd@crvax.sri.com

Seiichiro Koda
Department of Chemical System Engi-
neering
University of Tokyo
Hongo 7-3-1

Bunkyo-ku, Tokyo 113-8656 Japan
koda@chemsys.t.u-tokyo.ac.jp

Ian Lane
School of Chemistry
University of Bristol
Cantock's Close
Bristol BS8 ITS England
ian.lane@bris.ac.uk

Mats Larsson
Department of Physics
Stockholm University
Box 6730
Stockholm S 11385 Sweden
mats.larsson@physto.se

Sandra Laursen
R/E/AL2 NOAA
325 Broadway
Boulder CO 80303 USA
slaursen@al.noaa.gov

Yuan-Pern Lee
Department of Chemistry
National Tsing Hua University
101, Sec 2, Kuang-Fu Rd
Hsinchu 30043 Taiwan
yplee@chem.nthu.edu.tw

Jacob Levin
Max-Planck Institute
Fur Kernphysik
Heidelberg 69029 Germany
yasha@mickey.mpi-hd.mpg.de

Bosse Lindgren
Department of Physics
University of Stockholm
PO Box 6730
Stockholm S 11385 Sweden
bol@physto.se

Ned Lindholm
Department of Chemistry
University of Utah
315 S. 1400 E. Rm. DOCK
Salt Lake City, UT 84112-0850 USA
wolfman@chemistry.chem.utah.edu

Raymond Jeremy Livingstone
Christ's College
Cambridge CB2 3BU England
rjl36@cus.cam.ac.uk

Henrik Ludwigs
Department of Chemistry
University of California
337 Rowland Hall
Irvine, CA 92697 USA
ludwigs@chili.ps.uci.edu

Cecilia Lundevall
Department of Physics
Stockholm University
Box 6730
Stockholm S 11385 Sweden
cia@physto.se

Sten Lunell
Department of Quantum Chemistry
Uppsala University
Box 518
Uppsala S-751 20 Sweden
lunell@kvac.uu.se

John P. Maier
Inst. for Physical Chemistry
University of Basel
Klingelbergstrasse 80
Basel CH-4056 Switzerland
maier@ubaclu.unibas.ch

Margot Mandy
Department of Chemistry
UNBC
3333 University Way
Prince George, BC V2N 4Z9 Canada
mandy@unbc.ca

C. Weldon Mathews
Department of Chemistry
Ohio State University
100 West 18th Avenue
Columbus, Ohio 43210 USA
mathews.6@osu.edu

Hiroyuki Matsui
Dept of Mechanical Engineering
University of Tokyo
7-3-1 Hongo, Bunkyo-ku
Tokyo 113 Japan
matsui@mech.t.u-tokyo.ac.jp

Michael C. McCarthy
Center for Astrophysics
Harvard University
60 Garden St, Mail Stop 14

Cambridge, MA 02138 USA
mccarthy@cfa.harvard.edu

Dmitry Melnik
Department of Chemistry
The Ohio State University
Columbus, OH 43210 USA
melnik@chemistry.mps.ohio-state.edu

Anthony Merer
Department of Chemistry
University of British Columbia
2036 Main Mall
Vancouver, BC V6T 1Z1 Canada
merer@chem.ubc.ca

Terry A. Miller
Department of Chemistry
The Ohio State University
120 West 18th Ave.
Columbus, OH 43210-1173 USA
tamiller+@osu.edu

Jun Miyawaki
National Institute of Materials and
Chem. Research
1-1-4 Higashi
Tsukuba Ibaraki 305-8565 Japan
miyawaki@nair.go.jp

Michael D. Morse
Department of Chemistry
University of Utah
315 S. 1400 E. Rm. DOCK
Salt Lake City, UT 84112-0850 USA
morse@chemistry.chem.utah.edu

Chris Mullen
Department of Chemistry
University of Arizona
1306 E. University Dr.
Tuscon, AZ 85721 USA
cmullen@u.arizona.edu

Stewart Novick
Department of Chemistry
Wesleyan University
Lawn Avenue
Middleton, CT 06459 USA
snovick@wesleyan.edu

James O'Brien
Department of Chemistry
University of Missouri - St. Louis

St. Louis, MO 63121-4499 USA
obrien@jinx.umsl.edu

Leah O'Brien
Department of Chemistry
Southern Illinois University
Box 1652
Edwardsville, IL 62026-1652 USA
lobrien@siue.edu

Takeshi Oka
Department of Chemistry
University of Chicago
5735 S. Ellis Ave.
Chicago, IL 60637-1403 USA
t-oka@uchicago.edu

Anders Pettersson
Department of Physics
Stockholm University
Box 6730
Stockholm S 11385 Sweden
anders.petterson@physto.se

Michael Pushkarsky
Department of Chemistry
The Ohio State University
Columbus, OH 43210 USA
mpush@chemistry.ohio-state.edu

Qi-Zong Qin
Laser Chemistry Institute
Fudan University
220 Handan Road
Shanghai 200433 P. R. China
qzqin@srcap.stc.sh.cn

Donald A. Ramsay
Steacie Institute for Molecular Sciences
National Research Council
100 Sussex Drive
Ottawa, Ontario K1A 0R6 Canada
donald.ramsay@nrc.ca

Scott A. Reid
Department of Chemistry
Marquette University
P.O.Box 1881
Milwaukee, WI 53201-1881 USA
reids@marquette.edu

Magnus Rittby
Dept. of Physics & Astronomy

Texas Christian University
Box 298840
Fort Worth, TX 76129 USA
m.rittby@tcu.edu

Marin Robinson
Department of Chemistry
Northern Arizona University
Box 5698
Flagstaff; AZ 86011 USA
marin.robinson@nau.edu

Peder Royen
Dept. of Physics
Stockholm University
Box 6730
Stockholm S 11385 Sweden
pr@physto.se

Thomas Ruchti
Department of Chemistry
University of California
337 Rowland Hall
Irvine, CA 92697 USA
truchti@uci.edu

Trevor Sears
Department of Chemistry
Brookhaven National Laboratory
Building 555
Upton, NY 11973-5000 USA
sears@bnl.gov

Phillip Sheridan
Steward Observatory
University of Arizona
933 W. Cherry St.
Tucson, AZ 85719 USA
pmsherid@u.arizona.edu

Irene Shim
Department of Applied Chemistry
Technical University of Denmark
DTU 375
Lyngby DK2800 Denmark
irene.shim@ifak.dtu.dk

Shane Sickafoose
Department of Chemistry
University of Utah
315 S. 1400 Rm. DOCK
Salt Lake City, UT 84112-0850 USA
ssickafo@chemistry.chem.utah.edu

Benoit Simard
Steacie Institute for Molecular Sciences
National Research Council of Canada
100 Sussex Dr.
Ottawa, Ontario K1A 0R6 Canada
benoit.simard@nrc.ca

H. T. Sommerdijk
Leiden University
Arendshorst 116
Leiden 2317CW Netherlands
harry@rulgle.leidenuniv.nl

Timothy C. Steimle
Department of Chemistry
Arizona State University
Tempe, AZ 85287-1604 USA
tsteimle@asu.edu

Weizhong Sun
Department of Chemistry
Lawrence Berkeley National Laboratory
Latimer 402 Neumark
Berkeley, CA 94704 USA
wzs@radon.cchem.berkeley.edu

Shuenn-Jiun Tang
Institute of Atomic and Molecular Sciences
Academia Sinica
P.O. Box 23-166
Taipei Taiwan
tangsj@po.iams.sinica.edu.tw

Friedrich Temps
MPI für Physikalische Chemie
CAU Kiel
Ohlshausenstr 40
Kiel 24098 Germany
temps@phc.uni-kiel.de

Brian A. Thrush
Department of Chemistry
University of Cambridge
Lensfield Road
Cambridge CB2 1EW England
bat1@hermes.cam.ac.uk

Adrian Tuck
NOAA Aeronomy Laboratory
325 Broadway, R/E/AL6
Boulder, CO 80303-3328 USA

tuck@al.noaa.gov

Zeev Vager
Department of Particle Physics
Weizmann Institute of Science
Rehovot 76100 Israel
fzvager@wicc.weizmann.ac.il

Veronica Vaida
Department of Chemistry and Bio-
chemistry
University of Colorado
Campus Box 215
Boulder, CO 80309-0215 USA
vaida@colorado.edu

Marc C. van Hemert
Leiden Institute of Chemistry
Gorlaeus Laboratories
Leiden University
P.O. Box 9502
Leiden 2300 RA Netherlands
marc@rulgle.leidenuniv.nl

Tom Varberg
Department of Chemistry
Macalester College
1600 Grand Ave.
St. Paul, MN 55105-1899 USA
varberg@macalester.edu

Michel Vervloet
Lab. Photophys. Moleculaire

Universite Paris-Sud
Batiment 213
Orsay, Cedex 91405 France
michel.vervloet@ppm.u-psud.fr

Siobhan Waugh
Dept. of Physical Chemistry
Sydney University
407/187 Liverpool St.
Sydney NSW 2000 Australia
s.waugh@chem.usyd.edu.au

Martyn Wheeler
Department of Chemistry
University of Pennsylvania
250 South 33rd Street
Philadelphia, PA 19104-6323 USA
martynw@sas.upenn.edu

John. S. Winn
Department of Chemistry
Dartmouth College
6128 Burke Laboratory
Hanover, NH 03755-3564 USA
jwinn@dartmouth.edu

Gisbert Winnewisser
I. Physicalisches Institut
Universitat zu Koln
Zulpicher Str. 77
Koln D-50937 Germany
winnewisser@ph1.uni-koeln.de

Alec Wodtke
Department of Chemistry
University of California
Santa Barbara, CA 93106 USA
wodtke@chem.ucsb.edu

Shuqin Yu
Department of Chemical Physics
University of Science and Technology
of China
Jinzhai Road 96
Hefei, Anhui 230026 P. R. China
suyu@ustc.edu.cn

Bo Zhang
Department of Physics I
Royal Institute of Technology
Stockholm 10044 Sweden
zhang@atom.kth.se

Jingsong Zhang
Department of Chemistry
University of California
Riverside, CA 92521 USA
jszhang@ucr.ac1.ucr.edu

Lucy M. Ziurys
Steward Observatory
University of Arizona
933 W. Cherry Avenue
Tucson, AZ 85719 USA
lziurys@as.arizona.edu

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