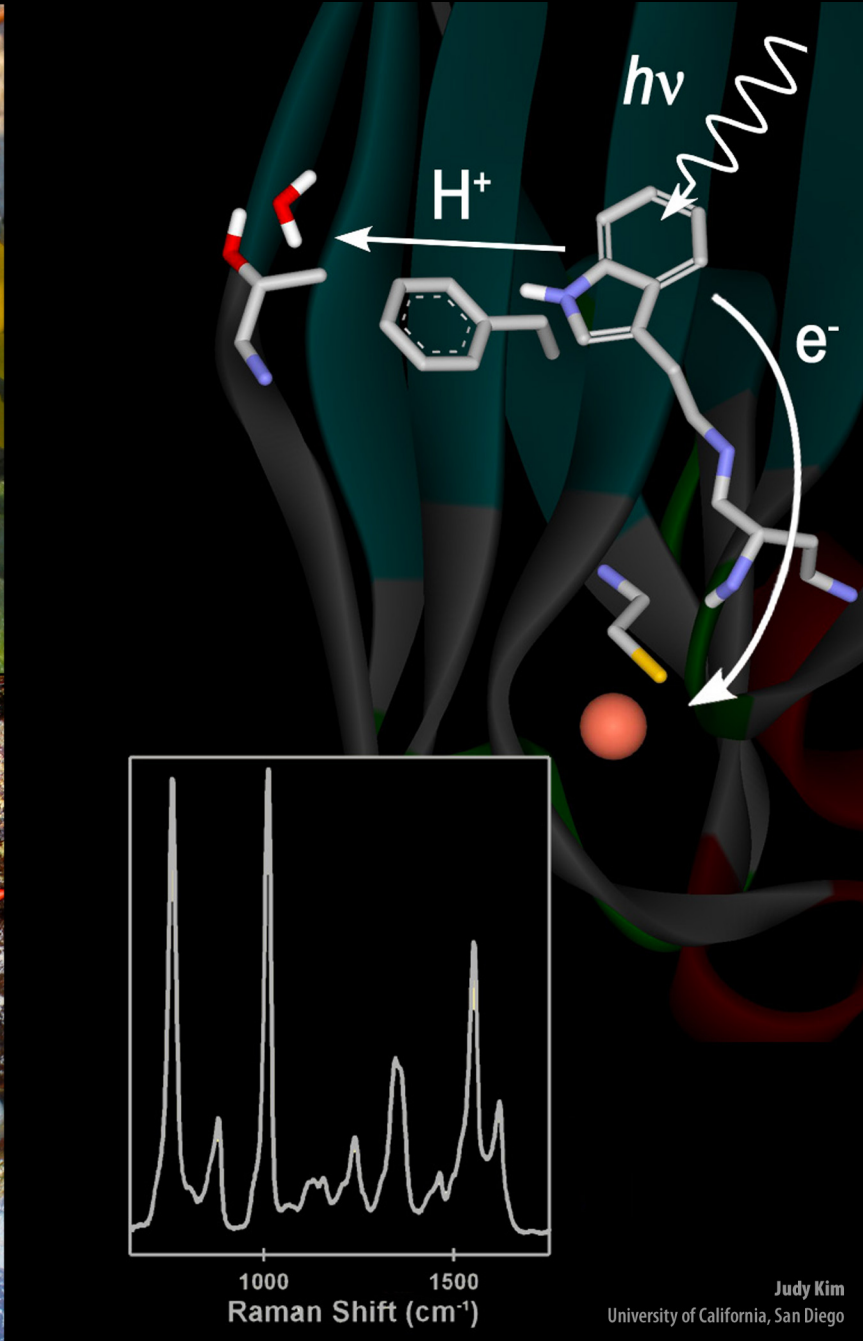




# 57<sup>th</sup> Annual Western Spectroscopy Association Conference

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February 3<sup>rd</sup> - 5<sup>th</sup>, 2010, Asilomar Conference Center, Pacific Grove, California



Judy Kim  
University of California, San Diego





February 3<sup>rd</sup> - 5<sup>th</sup>, 2010, Asilomar Conference Center, Pacific Grove, CA

## Meeting Schedule

All talks and poster sessions will be in *the Chapel*.  
All meals will be served in *Crocker Dining Hall*.

### Wednesday, February 3<sup>rd</sup>

- |                 |   |
|-----------------|---|
| 3:30-6:00 p.m.  | Registration in Main Lodge  |
| 4:00-5:00 p.m.  | Set up for Poster Session I   |
| 5:00-6:00 p.m.  | Poster Session I  |
| 6:00-7:00 p.m.  | Dinner  |
| 7:45-9:00 p.m.  | Registration Continues in the Chapel  |
| 7:55-9:05 p.m.  | <i>Session A Lectures &amp; Welcoming Remarks in the Chapel</i>   |
| 7:55-8:00 p.m.  | <b>Tim Steimle (Arizona State University)</b><br>WSA Program Chair  |
| 8:00-8:45 p.m.  | <b>Prof. Martin Zanni (Univ. of Wisconsin Madison, Chemistry)</b><br>“We Need Help! Deficiencies in the Vibrational Coupling Models of Peptides Used to Simulate 2D IR Spectra”                                     |
| 8:45-9:05 p.m.  | <b>David Long (Cal Tech, Chemistry)</b><br>“Quantitative Measurements of Magnetic Dipole and Electric Quadrupole Transitions in the O <sub>2</sub> A-band Using Frequency-stabilized Cavity Ring-down Spectroscopy” |
| 9:05-11:45 p.m. | Poster Session I Continues  |

## Thursday, February 4<sup>th</sup>

7:30 a.m.	Breakfast
8:30-9:00 a.m.	Registration in continues in the Chapel
9:00-10:30 a.m.	<i>Session B Lectures</i> <i>Chair: C. Bradley Moore</i>
9:00-9:45 a.m.	<b>Prof. Lucy Ziurys (Univ. of Arizona, Chemistry &amp; Astronomy)</b> “Molecules Beyond the Solar System: New Insights into the Spectroscopy of Transient Species”
9:45-10:30 a.m.	<b>Prof. Gerard Meijer (Fritz-Haber Institut der max-Planck-Gesellschaft)</b> “Taming Molecular Beams; Towards a Molecular Laboratory on a Chip”
10:30-10:50 a.m.	Coffee Break
10:50-12:20 p.m.	<i>Session C Lectures</i> <i>Chair: Trevor Sears</i>
10:50-11:35 a.m.	<b>Prof. Benjamin Schwartz (UCLA, Chemistry)</b> “Watching the Solvation of Atoms in Liquids, One Solvent Molecule at a Time”
11:35 -11:55 a.m.	<b>Paul Raston (Univ. of Alberta, Chemistry)</b> “Microwave Spectroscopy of ( <i>para</i> -H <sub>2</sub> ) <sub>N</sub> -OCS and ( <i>para</i> -H <sub>2</sub> ) <sub>N</sub> -CO Clusters”
11:55-12:15 p.m.	<b>Emily Fenn (Stanford University, Chemistry)</b> “Water Dynamics at Neutral and Ionic Interfaces”
12:20-1:30 p.m.	Lunch

## Thursday, February 4<sup>th</sup>

- 1:30-3:20 p.m. *Session D Lectures*  
*Chair: Craig Taatjes*
- 1:30-2:15p.m. **Prof. R. W. Field (MIT, Chemistry)**  
“Acetylene: Just Large Enough”
- 2:15 -2:35 p.m. **Dr. Oleg Kornilov (LBNL & UC-Berkeley)**  
“Femtosecond Photoionization Dynamics of Pure Helium Droplets”
- 2:35-3:20 p.m. **Prof. Alexander Benderskii (USC, Chemistry)**  
“Hydrogen Bonding, Vibrational, and Rotational Dynamics at Aqueous Interfaces”
- 3:20-5:00 p.m. Break
- 5:30-6:00 p.m. Set up for Poster Session II
- 6:00-7:00 p.m. Banquet (Seascape)
- 7:30-8:30 p.m. Banquet Address in the Chapel:  
**Dr. John C. Pearson (JPL & Cal Tech)**  
“Laboratory Spectroscopy in the Era of Big Science Data Users”
- 8:30-11:45 p.m. Poster Session II Continues

## Friday, February 5<sup>th</sup>

- 7:30 a.m. Breakfast
- 9:00-10:15 a.m. *Session E Lectures*  
*Chair: Anne Myers Kelley*
- 9:00-9:20 a.m. **Marie N. van Staveren (UC-Irvine, Chemistry)**  
“Solid-like Coherent Vibronic Dynamics in a Room Temperature Liquid: Resonance Raman and Absorption Spectroscopy of Liquid Bromide”
- 9:20-10:05 a.m. **Prof. Cheuk Y. Ng (UC-Davis, Chemistry)**  
“Spectroscopy and Dynamics of Neutrals and Ions by VUV and UV Photoionization and Photodissociation Methods”
- 10:05-10:25 a.m. **Yingdi Liu (UC-Riverside, Chemistry)**  
“Measurements of Peroxy Radicals Using Chemical Amplification-Cavity Ringdown Spectroscopy”
- 10:25-10:45 a.m. Break  
**Remember to check out by 12:00 noon!**
- 10:45-11:50 am *Session F Lectures*  
*Chair: Fred Grieman*
- 10:45-11:05 a.m. **Melissa Hill (UC-Davis, Chemistry)**  
“Triplet State Chemistry of Biologically Relevant Pyridoxal 5'-Phosphate Schiff Base as Determined by Transient Absorption Spectroscopies”
- 11:05-11:50 a.m. **Prof. Judy E. Kim (UC-San Diego, Chemistry)**  
“Photochemistry, Photophysics, and Structures of Functional Tryptophan Residues: Radical Intermediates and Protein Anchors”
- 11:50-12:00 a.m. Closing Remarks, **Judy Kim, WSA Program Vice-Chair**
- 12:00 p.m. Lunch

## Poster Session I (Wednesday, February 3)

5-6PM, 9-11 PM

- 1) **Kathryn A. Colby**, Jonathan J. Burdett, Robert F. Frisbee, Lingyan Zhu, Robert J. Dillon, Kerry M. Hanson, and Christopher J. Bardeen  
*Energy migration in dye-doped polymer films: Evidence for anomalous exciton diffusion*  
University of California, Riverside
- 2) **Ryan M. Young**, Graham B. Griffin, and Daniel M. Neumark  
*Electronic relaxation dynamics in acetonitrile cluster anions*  
Department of Chemistry, University of California, Berkeley  
Chemical Sciences Division, Lawrence Berkeley National Laboratory
- 3) **W.A. Hale** (1), N.C. Freyschlag (2), K.A. Martin (2), and A.M. Nishimura (1)  
*Evidence for Quenching of Methylanthalene Fluorescence by Cyclopentanone on Al<sub>2</sub>O<sub>3</sub>*  
(1) Department of Chemistry, Westmont College  
(2) Department of Chemistry, Point Loma Nazarene University
- 4) **Shanshan Yu** (1), John C. Pearson (1), Brian J. Drouin (1), Olivier Pirali (2), Michel Vervloet (2), Marie-Aline Martin (2), and Christian P. Endres (3)  
*Terahertz and far-infrared spectroscopy of high-J transitions of ammonia*  
(1) Jet Propulsion Laboratory, California Institute of Technology  
(2) Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, France  
(3) I. Physikalisches Institut, Universität zu Köln, Germany
- 5) **Cesar S. Contreras**, Claire L. Ricketts, and Farid Salama  
*Laboratory Studies of the Formation Processes of Interstellar PAHs*  
NASA Ames Research Center, Space Science Division, and Oak Ridge Associated Universities
- 6) **Amy Cordones, Teresa Bixby**, and Steve Leone  
*Power and Wavelength Dependent Studies of Fluorescence Blinking in Single CdSe/ZnS Nanoparticles*  
Department of Chemistry, University of California, Berkeley  
Chemical Sciences Division, Lawrence Berkeley National Laboratory
- 7) **David S. Medina**, Yingdi Liu, and Jingsong Zhang  
*Detection of Nitrate Radical Using Cavity Enhanced Absorption and Off-Axis Cavity Ringdown Spectroscopy*  
University of California, Riverside
- 8) **Xinchuan Huang**, David W. Schwenke, and Timothy J. Lee  
*Spectroscopically Accurate Potential Energy Surface and Rovibrational Energy Levels of <sup>14</sup>NH<sub>3</sub> and <sup>15</sup>NH<sub>3</sub>*  
SETI Institute; NASA Ames Research Center

- 9) Darcy H. Tarrant** (1), Peter B. Kelly (2), and Gary W. Scott (1)  
*The Excited States of Dianthracenes*  
(1) Department of Chemistry, University of California, Riverside  
(2) Department of Chemistry, University of California, Davis
- 10) Molly A. Taylor**, Jordan M. Pio, Wytze E. van der Veer, and Kenneth C. Janda  
*Competition Between Electronic and Vibrational Predissociation Dynamics of the HeBr<sub>2</sub> and NeBr<sub>2</sub> van der Waals Molecules*  
University of California, Irvine
- 11) Adam L. Sturlaugson** (1), Kendall S. Fruchey (1), Stephen R. Lynch (1), Sergio R. Arag (2), and Michael D. Fayer (1)  
*Orientalional and Translational Dynamics of Polyether/Water Solutions*  
(1) Stanford University  
(2) San Francisco State University
- 12) Zsolt Gengeliczki**, Daniel E. Rosenfeld, and Michael D. Fayer  
*Orientalional motion of molecules at interfaces*  
Stanford University
- 13) Hana Cho**, Nils Huse, Tae-Kyu Kim, and Robert W. Schoenlein  
*Ultrafast Dynamics of Photoinduced Iron(II) Spin Crossover Reaction in Solution by Time-Resolved Soft X-ray Spectroscopy*  
Chemical Sciences Division, Lawrence Berkeley National Laboratory  
Department of Chemistry, Pusan National University, Geumjeong-gu Busan, Korea
- 14) John B. Randazzo** (1), Philip Croteau (1), Oleg Kostko (2), Musahid Ahmed (2), and Kristie A. Boering (3)  
*Measurement of the photoionization of <sup>14</sup>N<sub>2</sub>, <sup>15</sup>N<sub>2</sub>, and <sup>14</sup>N<sup>15</sup>N between 15.5 and 18.9 eV using synchrotron radiation*  
(1) Department of Chemistry, University of California, Berkeley  
(2) Chemical Sciences Division, Lawrence Berkeley National Laboratory;  
(3) Departments of Chemistry and Earth and Planetary Sciences, University of California, Berkeley
- 15) O. Kornilov**, O. Gessner, C. Wang, O. Buernemann, S. Leone, and D. Neumark  
*Femtosecond photoionization dynamics of pure helium droplets*  
Lawrence Berkeley Laboratory, University of California, Berkeley
- 16) Xianfeng Zheng, Yu Song**, Jingze Wu, and Jingsong Zhang  
*H-atom product channel and mode specificity in the near-UV photodissociation of thiomethoxy radical via the A<sup>2</sup>A<sub>1</sub> state*  
Department of Chemistry and Air Pollution Research Center, University of California



- 17) Edward T. Branigan**, Marie N. van Staveren, V. Ara Apkarian  
*Solid-like coherent vibronic dynamics in a room temperature liquid: Resonant Raman and absorption spectroscopy of liquid bromine*  
University of California, Irvine
- 18) Amelia W. Ray** (1), David L. Osborn (2), Craig A. Taatjes (2), Giovanni Meloni (1)  
*Vinyl Alcohol: A Major Product of the Ethene + OH Reaction*  
(1) Department of Chemistry, University of San Francisco  
(2) Combustion Research Facility, Sandia National Laboratories
- 19) F. Goulay** (1), L. Nemes (2), P. E. Schrader (1), and H. A. Michelsen (1)  
*Spectrally Resolved Laser-Induced Incandescence of Soot Particles*  
(1) Combustion Research Facility, Sandia National Laboratories  
(2) Chemical Research Centre of the Hungarian Academy of Sciences, Budapest, Hungary
- 20) Anh Le** and T. C. Steimle  
*Spectroscopy in support of parity non-conservation measurements:  $^{87}\text{SrF}$  and  $^{137}\text{BaF}$*   
Department of Chemistry and Biochemistry, Arizona State University
- 21) Fang Wang** and T. C. Steimle  
*Molecular beam Stark spectroscopy of  $\text{CuF}$  and  $\text{CuOH}$*   
Department of Chemistry and Biochemistry, Arizona State University
- 22) Maria A. Garcia**, Michael D. Morse  
*Resonant two photon ionization (R2PI) spectroscopy of jet-cooled osmium nitride*  
University of Utah, Department of Chemistry
- 23) Fangyuan Han**, Jie Zhang, and Wei Kong  
*Polarization Spectroscopy of Tetracene Embedded in He Droplets and Aligned by a Laser Field*  
Department of Chemistry, Oregon State University
- 24) Jeffrey J. Kay**, Kevin E. Strecker, and David W. Chandler  
*Production of cold atoms by collisional cooling*  
Sandia National Laboratories
- 25) Hiroaki Maekawa** (1), Matteo De Poli (2), Alessandro Moretto (2), Claudio Toniolo (2), and **Nien-Hui Ge** (1)  
*Two-Dimensional Infrared Spectroscopy Reveals Amide-I/II Couplings between Hydrogen-Bonded Peptide Linkages in a 3(10)-Helix*  
(1) Department of Chemistry, University of California, Irvine  
(2) Institute of Biomolecular Chemistry, CNR, Padova Unit, Department of Chemistry, University of Padova, Italy

**26) W. Atom Yee (1), James W. Lewis (2), and Yaopeng Zhao (3)**

*Low Temperature Photochemistry of 1,4-Diphenylbutadiene*

(1) Department of Chemistry & Biochemistry, Santa Clara University

(2) Department of Chemistry & Biochemistry, University of California, Santa Cruz

(3) Department of Chemistry, University of Miami

## Poster Session II (Thursday, February 4)

5:15-6:30 PM, 9-11 PM

- 1) Hiroaki Maekawa (1), Matteo De Poli (2), Alessandro Moretto (2), Claudio Toniolo (2), and **Nien-Hui Ge** (1)  
*Two-Dimensional Infrared Spectroscopy Reveals Amide-I/II Couplings between Hydrogen-Bonded Peptide Linkages in a 3(10)-Helix*  
(1) Department of Chemistry, University of California, Irvine  
(2) Institute of Biomolecular Chemistry, CNR, Padova Unit, Department of Chemistry, University of Padova, Italy
- 2) **Kilyoung Kim** and Eric T. Sevy  
*The study of State-specific Energy Gain by N<sub>2</sub>O during Collisions with Vibrationally Excited Pyrazine*  
Department of Chemistry and Biochemistry, Brigham Young University
- 3) C. McRaven, M. Cich, G. V. Lopez, and **T. J. Sears**  
*Near infrared spectroscopy referenced to a frequency comb*  
University of Oklahoma  
Stony Brook University  
Brookhaven National Laboratory
- 4) R. J. Gates, C. Sheffield, **M. C. Asplund**  
*Comparison of DFT measured properties of weak agostic metal complexes*  
Department of Chemistry and Biochemistry, Brigham Young University
- 5) **O. Krechkivska**, Michael D. Morse  
*Resonant two-photon ionization spectroscopy of 5d carbides*  
University of Utah, Department of Chemistry
- 6) **E. Vehmanen**, J. Eloranta, and V.A. Apkarian  
*LIF spectroscopy of Cu<sub>2</sub>-He*  
Department of Chemistry, University of California, Irvine
- 7) **Ming Sun** (1), Dennis J. Clouthier (2), and Lucy M. Ziurys (1)  
*Fourier Transform Microwave spectrum of the AlCCH radical and its <sup>13</sup>C/D isotopologues*  
(1) Departments of Chemistry and Astronomy, Arizona Radio Observatory and Steward Observatory, University of Arizona  
(2) Department of Chemistry, University of Kentucky

- 8) **Shanshan Yu** (1), John C. Pearson (1), Brian J. Drouin (1), Adam Walters (2), Holger S. P. Müller (3), and Sandra Brünken (3)  
*Terahertz spectroscopy of excited water*  
(1) Jet Propulsion Laboratory, California Institute of Technology  
(2) Centre d'Etude Spatiale des Rayonnements, Toulouse University, France  
(3) I. Physikalisches Institut, Universität zu Köln, Germany
- 9) **Jie Zhang**, Fanyuan Han, and Wei Kong  
*ZEKE spectroscopy of PAHs*  
Oregon State University
- 10) **Lisa Marshall**, Jian Cui, Xavier Brokmann, and Mounji Bawendi  
*Interferometric FCS for measuring spectral dynamics of single particles in solution*  
Massachusetts Institute of Technology
- 11) **James E. Patterson**, Alexander D. Curtis, and Arthur D. Quast  
*In Situ Spectroscopy of Model Liquid Chromatography Stationary Phases*  
Department of Chemistry and Biochemistry, Brigham Young University
- 12) **Lindsay N. Zack**, Brent J. Harris, and Lucy M. Ziurys  
*Studies in 3d Hydroxides: The Pure Rotational Spectrum of ZnOH ( $X^2A'$ )*  
Departments of Chemistry and Astronomy, Arizona Radio Observatory and Steward Observatory, University of Arizona
- 13) **Casey Davis-Van Atta**, **Kira Watson**, Fred Grieman, Aaron Noell, Stanley Sander, and Mitchio Okumura  
*Study of the HO<sub>2</sub>/Acetone Reaction Approaching Tropospheric Temperatures Using Infrared Kinetic Spectroscopy (IRKS)*  
Pomona College and Jet Propulsion Laboratory, California Institute of Technology
- 14) **Xiujuan Zhuang** and T. C. Steimle  
*The visible spectrum of gas-phase titanium dioxide*  
Department of Chemistry and Biochemistry, Arizona State University
- 15) **Daniel R. B. Sluss**, **Paul H. Davis**, Becky L. Munoz, Larry F. Scatena, and Michael W. Hill  
*A Molecular Level View of Chem/Bio Protective Materials: Vibrational Sum Frequency Generation Spectroscopy of Polymer Surfaces & Chemical Weapons Simulants*  
Boise Technology, Inc.
- 16) **Craig Bieler**, Culver Redd, and Andrew Fidler  
*The Ultraviolet/Visible Absorption Spectra of Benzoic Acid Derivatives*  
Albion College

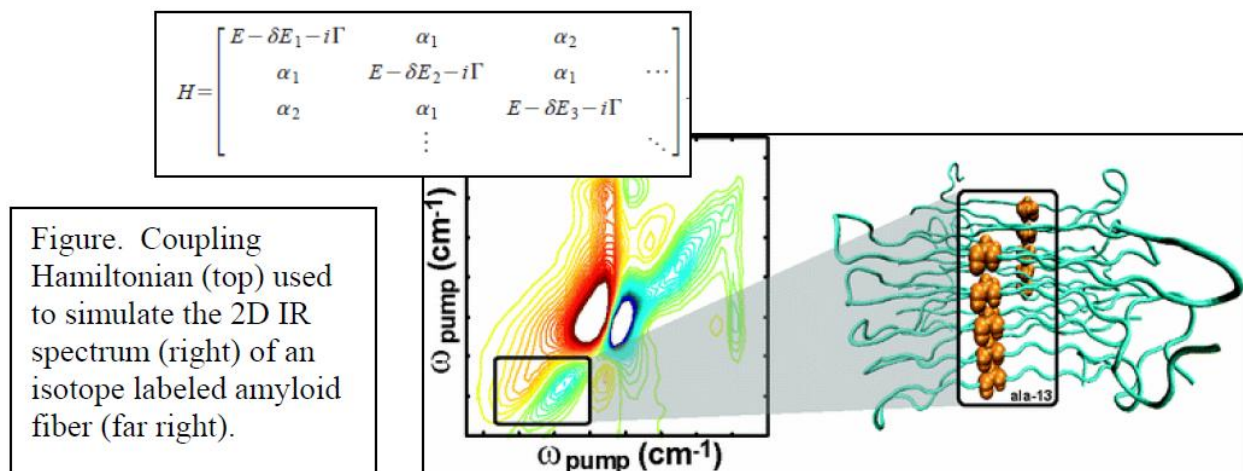
- 17) Fariba Allyasin, Sarah McGovern, and **Alfred Leung**  
*Low-cost Frequency-domain Fluorescence Lifetime Measurements*  
California State University, Long Beach
- 18) **C.L. Binkley** (1), N.C. Freyschlag (2), M.L. Gross (1), W.A. Hale (1), T.C. Judkins (1), K.A. Martin (2), and A.M. Nishimura (1)  
*Disubstitutional Effect on Naphthalene Fluorophores on Al<sub>2</sub>O<sub>3</sub>*  
(1) Department of Chemistry, Westmont College  
(2) Department of Chemistry, Point Loma Nazarene University
- 19) **Dharmalingam Kurunthu**, Yaobing Wang, Gary W. Scott, and Christopher J. Bardeen  
*Fluorescence Quenching in Conjugated Polymers/Reduced Graphitic Oxide blends*  
Department of Chemistry, University of California, Riverside
- 20) T. Pfeifer, M. J. Abel, P. Nagel, W. Boutu, **M. J. Bell**, H. Mashiko, C. P. Steiner, A. R. Beck, D. M. Neumark, and S. R. Leone  
*Molecular Attosecond Dynamics*  
Department of Chemistry, University of California, Berkeley  
Chemical Sciences Division, Lawrence Berkeley National Laboratory
- 21) **Qian He** (1), David L. Osborn (2), Craig A. Taatjes (2), and Giovanni Meloni (1)  
*OH Initiated Oxidation of Gamma Valerolactone*  
(1) Department of Chemistry, University of San Francisco  
(2) Combustion Research Facility, Sandia National Laboratories
- 22) **Kendall Fruchey** and Michael D. Fayer  
*Rotational Dynamics in Ionic Liquids*  
Stanford University
- 23) **Jordan M. Pio**, Molly A. Taylor, Wytze E. van der Veer, Craig R. Bieler, and Kenneth C. Janda  
*Real-time dissociation dynamics of the Ne<sub>2</sub>Br<sub>2</sub> van der Waals complex*  
University of California, Irvine
- 24) **Beth E. Reed**, Luis A. Cuadra-Rodriguez, and G. Barney Ellison  
*A Water Droplet Spectrometer*  
University of Colorado, Boulder
- 25) **Marina Stavtyska-Barba** and Anne Myers Kelley  
*Surface enhanced Raman study of the interaction of PEDOT:PSS with silver and gold nanoparticles*  
University of California, Merced
- 26) **Haifeng Huang**, Daniel J. Merthe, Judit Zádor, Leonard E. Jusinski, and Craig A. Taatjes  
*New experiments and validated master-equation modeling for OH production in propyl/ethyl + O<sub>2</sub> reactions*  
Combustion Research Facility, Sandia National Laboratories

## We Need Help! Deficiencies in the Vibrational Coupling Models of Peptides Used to Simulate 2D IR Spectra.

Martin T. Zanni  
*University of Wisconsin-Madison*

Two-dimensional infrared spectroscopy is proving to be a very useful tool in structural biology because it has a combination of structure- and time-resolution that is unique among standard structural tools. While 2D IR spectroscopy is providing new insights protein structural kinetics, the accuracy that structural information can be obtained from 2D IR spectra is limited by our understanding of the vibrational coupling in proteins. To extract structural information from 2D IR spectra, or to test structures against 2D IR spectra, a coupling model must be used to relate the measured frequencies and anharmonicities to the protein structure and its environment. Existing models are largely based on ab initio calculations with little or no experimental verification. They are difficult to test against solution-phase peptide structures because small model peptides amenable to ab initio calculations do not have well-defined structures in solution (or multiple structures). Furthermore, their infrared spectra are too broad to distinguish between frequency shifts caused by differences in peptide structures versus those caused by solvation effects. What is needed are infrared spectra of peptides with known conformations and controllable solvation states. We believe that gas-phase studies of small peptides could provide an important data set from which to test existing coupling models and develop new ones.

This talk will provide an overview of the experimental methods used to obtain 2D IR spectra and the coupling models that are being used to convert between protein structures and infrared spectra. Experiments currently underway in our laboratory will be presented for which the accuracy of the structural models have a direct impact. We aim to stimulate a discussion on future experiments that could be used to improve existing peptide coupling models.



# Quantitative Measurements of Magnetic Dipole and Electric Quadrupole Transitions in the O<sub>2</sub> A-band Using Frequency-Stabilized Cavity Ring-Down Spectroscopy

D.A. Long,<sup>1</sup> D.K. Havey,<sup>2</sup> M.Okumura,<sup>1</sup> H.M. Pickett,<sup>3</sup> C.E. Miller,<sup>3</sup> and J.T. Hodges<sup>2</sup>

<sup>1</sup>*Division of Chemistry and Chemical Engineering,*

*California Institute of Technology, Pasadena, CA 91125*

<sup>2</sup>*Process Measurements Division, National Institute of Standards and Technology,*

*100 Bureau Drive, Gaithersburg, MD 20899*

<sup>3</sup>*Jet Propulsion Laboratory, California Institute of Technology,*

*4800 Oak Grove Drive, Pasadena, CA 91109*

Frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) was employed to make quantitative, laboratory-based measurements of magnetic dipole and electric quadrupole transitions in the O<sub>2</sub> A-band ( $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-(0,0)$ ). The A-band is triply forbidden by quantum mechanical selection rules, but allowed as a magnetic dipole or electric quadrupole transition. Despite this inherent weakness, the A-band is the most prominent, near-infrared absorbance in the atmosphere and has been extensively utilized in remote sensing measurements to determine optical pathlengths and optical properties of clouds and aerosols.

FS-CRDS differs from traditional single mode, *cw*-CRDS by actively stabilizing the optical cavity length through the use of a co-resonant reference beam (1). This length stabilization leads to an extremely linear and stable spectral frequency axis. This allows transition frequencies and pressure shifting coefficients to be measured at the sub-MHz ( $<3 \times 10^{-5}$  cm<sup>-1</sup>) and 0.5% levels, respectively. In addition, FS-CRDS possesses the high sensitivity inherent to all cavity enhanced techniques, with low loss mirrors enabling a short term noise equivalent absorption coefficient of  $2.5 \times 10^{-10}$  cm<sup>-1</sup> Hz<sup>-1/2</sup>. Long-term averaging is also possible, due to the stable frequency axis, allowing for a detection limit of  $2.5 \times 10^{-31}$  cm molec.<sup>-1</sup>.

Through the use of this long-term averaging we have been able to quantitatively measure (uncertainties in the line intensity measurements of less than 9%) nine ultraweak electric quadrupole transitions having intensities of  $3 \times 10^{-30}$  to  $2 \times 10^{-29}$  cm molec.<sup>-1</sup> (2). Seven of these transitions had not previously been observed.

Magnetic dipole transitions have also been extensively measured with FS-CRDS. Line intensities and lineshape parameters have been reported with uncertainties at the 0.1% and 1% level, respectively (3). Room-temperature measurements have been of transitions up to  $J=50$ , corresponding to line strengths at the  $1 \times 10^{-30}$  cm molec.<sup>-1</sup> level. These measurements have allowed us to examine the validity of present spectroscopic databases at high rotational energy. Recent measurements have shown evidence of a subtle Herman-Wallis rotational-vibrational interaction.

## References:

- (1) J.T. Hodges, *et al.*, Rev. Sci. Instrum. **75** (2004) 849.
- (2) D.A. Long, *et al.*, Phys. Rev. A **80** (2009) 042513.
- (3) D.J. Robichaud, *et al.*, J. Mol. Spectrosc. **248** (2008) 1.

# Molecules Beyond the Solar System: New Insights into the Spectroscopy of Transient Species

L.M. Ziurys  
*University of Arizona*

At present, over 140 different chemical compounds have been detected in interstellar space, primarily via their pure rotational spectra, measured with radio telescopes. Over half of these molecules are free radicals, molecular ions, or metastable isomers, namely, species that are transient under terrestrial conditions. High resolution laboratory molecular spectroscopy has played a critical role in the discovery and study of interstellar molecules, by providing the necessary “fingerprints” for identification in astronomical data. Therefore, the compounds that are discovered in space are highly correlated with those that can be measured in the laboratory, and the success of synthetic techniques in creating unusual species. The sensitivity, stability and spectral coverage of heterodyne receivers at radio telescopes are naturally other critical factors. With the technological advances fostered by the development of the upcoming Atacama Large Millimeter Array, or ALMA, improvements in receivers at radio telescopes have been substantial. New interstellar molecular compounds are being discovered that suggest ever increasing complexity in interstellar synthesis. Some of these recent identifications include phosphorus-bearing species, such as PO, CCP, and HCP. For many years, few phosphorus-containing species were known in interstellar gas. Possible “pre-biotic” organic molecules are also being found, such as glycolaldehyde and acetamide. There are interesting chemical trends concerning the types of organic molecules that are present, or absent, in interstellar space. Unexpected metastable isomers, such as HSCN, are also being identified in the interstellar medium, as well as unusual inorganic compounds like AlO. Some of these recent molecular detections will be discussed, as well as the laboratory spectroscopic work that made them possible. As these studies and others show, it has become increasingly apparent that chemical synthesis occurs even under some of the most extreme interstellar conditions. Furthermore, it is now well-recognized that solar systems form out of molecular material, linking our origins to interstellar chemistry. In fact, we have only begun to evaluate the molecular content outside our solar system. The impact of the emerging field of astrochemistry for molecular spectroscopy will be discussed, and future directions suggested for the laboratory study of “non-terrestrial” molecules.

## References:

“Detection of the CCP Radical ( $X^2\Pi_r$ ) in IRC+10216: A New Interstellar Phosphorus-Containing Species,” D.T. Halfen, D.J. Clouthier, and L. M. Ziurys, *Ap.J.(Letters)*, **677**, L101 (2008)

“Millimeter Detection of AlO ( $X^2\Sigma^+$ ): Metal Oxide Chemistry in the Envelope of VY Canis Majoris,” E.D. Tenenbaum and L. M. Ziurys, *Ap.J.(Letters)*, **694**, L59 (2009)

“Detection of a New Interstellar Molecule: Thiocyanic Acid HSCN, ” D. T. Halfen, L. M. Ziurys, S. Brünken, M. C. McCarthy, C. A. Gottlieb, and P. Thaddeus, *Ap.J.(Letters)*, **702**, L124 (2009)



# Taming Molecular Beams; Towards a Molecular Laboratory on a Chip

Gerard Meijer

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Getting ever better control over gas-phase molecules is an important research theme and drives progress in the field of molecular physics. The motion of neutral molecules in a beam can be manipulated with inhomogeneous electric and magnetic fields. Static fields can be used to deflect or focus molecules, whereas time-varying fields can be used to decelerate or accelerate beams of molecules to any desired velocity. I will give an overview of the possibilities that this molecular beam technology presently offers, ranging from ultrahigh-resolution spectroscopy and novel scattering experiments to lifetime measurements on trapped molecules [1].

I will report in particular on our recent experiments demonstrating trapping of carbon monoxide molecules on a chip [2] using direct loading from a supersonic beam [3,4]. Upon arrival above the chip, the molecules are confined in tubular electric field traps of about 20 micrometer diameter, centered 25 micrometer above the chip, that move along with the molecular beam at a velocity of several hundred meters per second. By using the  $^{13}\text{CO}$  isotopologue, losses due to nonadiabatic transitions [5] near the center of the tubular traps are prevented. An array of these miniaturized moving traps can be brought to a complete standstill over a distance of only a few centimeters. After a certain holding time, the molecules can be accelerated off the chip again for detection. This loading and detection methodology is applicable to a wide variety of polar molecules, and enables the creation of a molecular laboratory on a chip. Many of the gas phase molecular physics experiments that are currently being performed in large beam machines might be performed in a compact vacuum machine on a surface area of a few square centimeters in the future and new experiments will become possible.

## References:

- [1] S.Y.T. van de Meerakker, H.L. Bethlem, and G. Meijer, *Nature Physics* **4**, (2008) 595.
- [2] S.A. Meek, H. Conrad, and G. Meijer, *Science* **324**, (2009) 1699.
- [3] S. A. Meek, H.L. Bethlem, H. Conrad, and G. Meijer, *Phys. Rev. Lett.* **100**, (2008) 153003.
- [4] S.A. Meek, H. Conrad, and G. Meijer, *New J. Phys.* **11**, (2009) 055024.
- [5] M. Kirste, B.G. Sartakov, M. Schnell, and G. Meijer, *Phys. Rev. A* **79**, (2009) 051401(R).

## Watching the Solvation of Atoms in Liquids, One Solvent Molecule at a Time

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When chemical reactions take place in liquids, it is generally assumed that molecular details of how the liquid interacts with reacting solutes don't matter: electron transfer and other solvent-driven reactions are usually described by treating the liquid as a continuum. In this talk, we present the results from a combination of quantum molecular dynamics simulations and ultrafast spectroscopy aimed at studying the motions of solvent molecules around sodium atoms in a room-temperature organic liquid. Our MD simulations reveal that the sodium solute's electronic absorption spectrum correlates with the number of nearest solvent molecules that interact with it. Our experiments explore this correlation by measuring the spectral dynamics accompanying the fluctuations that change the number of coordinating solvent molecules at equilibrium. We find that the rearrangement of the solvent molecules around the atoms occurs discretely – we are able to spectroscopically identify and temporally resolve the arrival of individual solvent molecules in the first solvent shell around the atom. Moreover, our results suggest that atoms coordinated by different numbers of solvent molecules behave as (albeit quite transiently) chemically distinct species, so that a continuum description of the solvent would lead to an entirely incorrect description of the molecular relaxation. Finally, we note that our results also allow us to explain the breakdown of Linear Response for atomic solvation dynamics that we observed previously [*Science* **321**, 1817 (2008)].

# Microwave Spectroscopy of (*para*-H<sub>2</sub>)<sub>N</sub>-OCS and (*para*-H<sub>2</sub>)<sub>N</sub>-CO Clusters

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Rotational spectra of both carbon monoxide (CO) and carbonyl sulfide (OCS) solvated with  $N \leq 10$  *para*-hydrogen (*p*H<sub>2</sub>) molecules have been collected using pulsed nozzle Fourier transform microwave spectroscopy. The clusters were generated in a supersonic expansion by forcing a high pressure (up to 200 bar) mixture consisting of about 0.01% CO or OCS and 2-5% *p*H<sub>2</sub> in helium through a pinhole nozzle. The observed transitions were assigned to clusters with specific *N*-values based on the dependence of the signal intensity on the sample composition and backing pressure, and by comparison with infrared data.<sup>1,2</sup> The *end-over-end* rotational frequency (proportional to the inverse moment of inertia) decreases with increasing cluster size for (*p*H<sub>2</sub>)<sub>N</sub>-OCS as is expected classically. For (*p*H<sub>2</sub>)<sub>N</sub>-CO, the rotational frequency decreases to a minimum at  $N=6$ , then increases in going to  $N=7$ ; this could indicate a significant decoupling of *p*H<sub>2</sub> density from CO rotation. By measuring the pure rotational frequencies of the (*p*H<sub>2</sub>)<sub>N</sub>-CO clusters we are able to separate the rotational and vibrational contributions to the infrared line positions.

## References:

- 1 J. Tang, A. R. W. McKellar, *J. Chem. Phys.*, 2004, **121**, 3087
- 2 S. Moroni, M. Botti, S. De Palo, A. R. W. McKellar, *J. Chem. Phys.*, 2005, **122**, 094314

## Water Dynamics at Neutral and Ionic Interfaces

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The hydrogen bonding properties of water often deviate from their bulk behaviors in the presence of an interface. Whether the interface is hydrophilic, hydrophobic, charged, or neutral, it has the ability to disrupt the concerted reorientational motions of water molecules that are necessary for hydrogen bond network rearrangement. Measuring how quickly the hydrogen bond network randomizes affords information about how confined or hindered a system is. Such considerations are important, for example, in fuel cell membranes which require efficient pathways for proton transport. An important question is whether the chemical composition or solely the presence of an interface plays the dominant role in affecting the hydrogen bonding dynamics of interfacial water. To answer this question, ultrafast infrared pump-probe techniques are used to measure water orientational relaxation dynamics at the water/head group interfaces of two same-size reverse micelles systems made from either an ionic or neutral surfactant. The ionic reverse micelles are made from bis(2-ethylhexyl) sulfosuccinate (AOT), and the nonionic micelles are made from Igepal CO-520. AOT contains a sulfonate head group with a sodium counterion while Igepal has a hydroxyl head group. In each micelle there is a large region of mostly bulk-like water molecules, but there is also a significant fraction of water that hydrates the surfactant head groups. Previous comparisons between water dynamics in AOT and Igepal looked at the collective reorientations of water molecules; now we present a method that separates the dynamics of interfacial water molecules from the bulk-like water interior. It is found that the orientational relaxation dynamics for interfacial water molecules are similar in magnitude for AOT and Igepal systems, with Igepal being slightly faster. These results suggest that while the presence of the interface is the dominant factor in determining the dynamics, the chemical composition may play a secondary role.

## Acetylene: Just Large Enough

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What can acetylene ( $\text{H-C}\equiv\text{C-H}$ ) do that a diatomic molecule cannot? It can undergo bond-breaking isomerization. The minimum energy isomerization path from acetylene to vinylidene is a very large-amplitude local-bend. How are large-amplitude motions encoded in a spectrum? At high vibrational excitation, anharmonic interactions between vibrational normal-modes become very strong and all of the textbook energy level patterns, upon which assignments are based, are shattered. Most vibrational eigenstates are complex, one might even say “ergodic,” mixtures of many normal-mode basis-states. However, large-amplitude-motion states comprise a tiny fraction of all eigenstates. How does one **gain access** to these rare large-amplitude states? How does one **distinguish** a large-amplitude state from an ergodic state in a spectrum? How does one **use** large-amplitude states to map the chemically interesting isomerization path on the  $S_0$  potential energy surface? Access is provided by a “local-bender pluck” state, which exploits anharmonic interactions on the  $S_1$  potential energy surface to escape Franck-Condon restrictions in the  $S_1 \rightarrow S_0$  Stimulated Emission Pumping (SEP) spectrum. A relatively low *trans-cis* isomerization barrier on  $S_1$  provides spectroscopic access to eigenstates proximal to a high barrier on  $S_0$ . Electronic properties (such as the electric dipole transition moment) serve as embedded reporters on the existence and extent of large-amplitude motions. However, electronic properties give rise to minuscule level splittings. How does one combine a survey over a wide spectral region in search of rare large-amplitude local-bender states yet simultaneously achieve the extremely high resolution necessary to read what the embedded reporter has written? Brooks Pate (University of Virginia) has developed “Chirped Pulse Microwave Spectroscopy (CPMW),” which combines the previously unimaginable combination of survey (10GHz), high-resolution (100kHz), and accurate relative-intensity (1 part in  $10^4$ ) capabilities. The CPMW scheme is perfectly suited to 20 Hz repetition rate pulsed supersonic jet molecular beams and Q-switched Nd:YAG pumped pulsed tunable lasers, upon which most small-molecule spectroscopists depend.

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# Femtosecond Photoionization Dynamics of Pure Helium Droplets

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Superfluid helium droplets possess properties, which make them targets of active research in diverse fields of science: from nuclear physics to high-resolution molecular spectroscopy. Apart from fundamentally important collective quantum effects the droplets show ability to efficiently pick-up foreign atoms, molecules and complexes. The latter serves as a basis for a number of matrix isolation spectroscopy techniques including rotational, vibration and electronic excitation spectroscopy. Complementary to these studies in energy domain, novel time-domain experiments will be presented emphasizing dynamics of photoionization of a pure helium droplets via photoelectron spectroscopy. These experiments follow up on a recent photoelectron spectroscopy study in energy domain using synchrotron radiation, which discovered a peculiar feature: all photoelectrons emitted from the droplets upon ionization below atomic IP have very low energies (less than 1 meV). In the present experiments the dynamics of ionization is studied by exciting droplets by a pulsed VUV radiation generated using the high-order harmonic generation technique. The droplets are subsequently probed by an IR pulse, which leads to change of photoelectron kinetic energy distributions. The results show femtosecond and picosecond relaxation dynamics involving localization of initial VUV excitation in the bulk of the droplet or in the surface region. Bulk excitations tend to quickly relax to a long-lived excited state, while the surface excitations lead to an autoionization channel possibly competing with emission of excited atoms and molecules. Dynamics at longer times (>10 ps) indicate that bulk excitons are likely to emerge on the surface.

## References:

[1] D. Peterka et al, *Phys. Rev. Lett.* **91**, 043401 (2003)

# Hydrogen Bonding, Vibrational, and Rotational Dynamics at Aqueous Interfaces

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This talk will review recent results on the rotational relaxation time scales and vibrational couplings at the air/water interface probed by the surface-selective sum frequency generation (SFG) spectroscopy. Rotational time scales of a small, linear rigid probe molecule (propionic acid) were inferred from the SFG spectral line shapes recorded using different (SFG-vis-IR) polarization combinations. The time scales are found nearly an order of magnitude faster than expected for similar molecules in bulk water. A combination of heterodyne-detected sum frequency generation (HD-SFG) vibrational spectroscopy and isotopic dilution studies was used to probe intra- and intermolecular vibrational couplings of the OD-stretch modes at the air-water interface of H<sub>2</sub>O:HOD:D<sub>2</sub>O mixtures. The “free OD” mode couples effectively only to the “other OD” mode on the same molecule, whose frequency can be extracted from the measurement. This reports on the average H-bond strength in the top-most layer at the water surface, which is found to be slightly weaker than the bulk average.

## **Laboratory Spectroscopy in the Era of Big Science Data Users**

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Historically spectroscopy has been performed by small research groups interested in experimentally investigating fundamental chemical and physical aspects of nature. Subsequently, the spectroscopically derived constants of nature have proven to be exquisitely useful in a variety of applied science investigations including chemical detection, process control, environmental monitoring, Earth science, planetary science and Astrophysics. Many of the applications which utilize spectroscopic data have grown into (multi)billion dollar class enterprises often desiring very specific spectral information to successfully address their scientific goals. In the mean time spectroscopy has become a mature field, with the fundamental principles and many aspects of fundamental chemistry and physics having been fully elucidated. The result is a different landscape for spectroscopy between specific big project driven data needs and the often difficult fundamental chemical and physical investigations that remain. Spectroscopists need to understand that big projects actually offer a number of unique and often surprising opportunities so that humble servitude is rarely even an option. Spectroscopists with their broad technical background in instrumentation, measurements and fundamental physics and chemistry should not assume that the engineering specialists developing big projects understand the nuances of spectroscopic measurements, the full implications or propagation of measurement errors, or even how to accurately make basic measurements. If spectroscopists are willing to adapt to the new political and technical reality, they can assure that there will be plenty of interesting fundamental molecular physics research that must be done as well as a steady stream of funding. The path to remaining kings of the new landscape will be discussed.



# **Solid-like Coherent Vibronic Dynamics in a Room Temperature Liquid: Resonant Raman and Absorption Spectroscopy of Liquid Bromine**

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UV-Vis absorption and resonance Raman (RR) spectra of liquid bromine are presented, and rigorously interpreted. The RR spectrum, which shows an anharmonic vibrational progression of thirty overtones, defines the ground state potential in the range  $2.05 \text{ \AA} < r < 3.06 \text{ \AA}$ . The excited state A, B, C potentials are extracted from the absorption spectrum. The spectrum is first inverted under the assumption of the classical reflection approximation, then corrected by forward simulations through quantum time correlations. While the quantum to classical correction for individual electronic transitions are small ( $\sim 200 \text{ cm}^{-1}$  in the Franck-Condon window), corrections for quantum interference between overlapping bands are significantly larger (on the order of  $1000 \text{ cm}^{-1}$  displacements of potentials in the Franck-Condon window). The extrapolated B and C potentials are used to simulate an RR spectrum. Remarkably, the RR lineshapes are skewed toward the red, indicating up-chirp in frequencies that develop over a period of 400 fs. Evidently, the molecular vibrations adiabatically follow the solvent cage, which is impulsively driven into expansion during the  $\sim 20 \text{ fs}$  evolution on the electronically excited state. Despite the strong electronic intermolecular interactions, vibrational dynamics in liquid bromine retain coherence in ordered, sluggish local cages – dynamics akin to molecules isolated in structured cryogenic rare gas solids.

# Spectroscopy and Dynamics of Neutrals and Ions by VUV and IR-VUV Photoionization and Photodissociation Methods

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Recent developments of single-photon vacuum ultraviolet (VUV) and two-color infrared (IR)-VUV and VUV-IR photoionization and photoelectron methods for spectroscopy and reaction dynamics studies will be presented.<sup>1-5</sup> The application of the VUV pulsed field ionization (PFI) methods has allowed the determination of thermochemical data of many small molecules with unprecedented precision. By preparing molecules in single rovibrational states using a single-mode IR laser (optical resolution = 0.007 cm<sup>-1</sup>) prior to VUV photoion-photoelectron measurements, we have demonstrated that rotationally selected and resolved IRVUV-PFI-photoelectron (PFI-PE) spectra for polyatomic molecules can be obtained. Using VUV photoionization as a probe and by scanning the IR laser frequency, we have shown that high-resolution IR spectra for many neutral polyatomic species can be measured with high sensitivity. Two-color VUV-IR photo-induced Rydberg ionization experiment, in which high-*n* Rydberg states are prepared by VUV-photoexcitation followed by IR-induced autoionization, has also been found to be applicable for IR spectroscopic measurement of molecules in excited Rydberg states. High-*n* Rydberg tagging time-of-flight measurements for nascent H, O, and S atomic photofragments formed in laser photodissociation have also been successfully made using singlephoton VUV excitation.<sup>4</sup>

## References:

1. C. Y. Ng, "Vacuum Ultraviolet Spectroscopy and Chemistry Using Photoionization and Photoelectron Methods", *Ann. Rev. Phys. Chem.* **53**, 101-140 (2002).
2. C. Y. Ng, "Two-Color Photoionization and Photoelectron Studies by Combining Infrared and Vacuum Ultraviolet", *J. Electron Spectroscopy & Related Phenomena* (invited review), **152**, 142-179 (2004).
3. Kai-Chung Lau and Cheuk-Yiu Ng, "Benchmarking state-of-the-art *ab initio* thermochemical predictions with accurate pulsed-field ionization photoion-photoelectron measurements", *Accounts of Chemical Research*, **39**, 823-829 (2006).
4. B. Jones, J. Zhou, L. Yang, and C. Y. Ng, "High-resolution Rydberg tagging time-of-flight measurements of atomic photofragments by single-photon vacuum ultraviolet Laser Excitation", *Rev. Sci. Instrum.* **79**, 123106 (2008).
5. C. Y. Ng, "Spectroscopy and Dynamics of Neutrals and Ions by high-resolution infrared vacuum ultraviolet photoionization and photoelectron methods", in "Frontiers of Molecular Spectroscopy", edited by Jaan Laane (Elsevier, 2009) Chap. 19, page 659-691.

## Measurements of Peroxy Radicals Using Chemical Amplification-Cavity Ringdown Spectroscopy

Yingdi Liu, Rodrigo Morales-Cueto, James Hargrove, David Medina, and Jingsong Zhang\*  
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The peroxy radical chemical amplification (PERCA) method is combined with cavity ringdown spectroscopy (CRDS) to detect peroxy radicals HO<sub>2</sub> and RO<sub>2</sub>. In the PERCA method, HO<sub>2</sub> and RO<sub>2</sub> are first converted to NO<sub>2</sub> via reactions with NO, and the OH and RO co-products are then recycled back to HO<sub>2</sub> in subsequent reactions with CO and O<sub>2</sub>; the chain reactions of HO<sub>2</sub> are repeated and amplify the level of NO<sub>2</sub>. The amplified NO<sub>2</sub> is then monitored by CRDS, a sensitive absorption technique. The PERCA-CRDS method is calibrated using a HO<sub>2</sub> radical source (0.5-3 ppbv), which is generated by thermal decomposition of H<sub>2</sub>O<sub>2</sub> vapor (permeated from 2% H<sub>2</sub>O<sub>2</sub> solution through a porous Teflon tubing) up to 600 °C. Using a 2-meter long 6.35-mm o.d. Teflon tubing as the flow reactor and 2.5 ppmv NO and 2.5-10% vol/vol CO, the PERCA amplification factor or chain length,  $\Delta[\text{NO}_2]/([\text{HO}_2]+[\text{RO}_2])$ , is determined to be 150±50 (90% confidence limit) in this study. The peroxy radical detection sensitivity by PERCA-CRDS is estimated to be ~10 pptv/60 s. Ambient measurements of the peroxy radicals are carried out at Riverside, California from March to October in 2007 to demonstrate the PERCA-CRDS technique.

## **Triplet State Chemistry of Biologically Relevant Pyridoxal 5'-Phosphate Schiff Base as Determined by Transient Absorption Spectroscopies**

Melissa P. Hill, Lucy H. Freer, Elizabeth C. Carroll, Michael D. Toney and Delmar S. Larsen  
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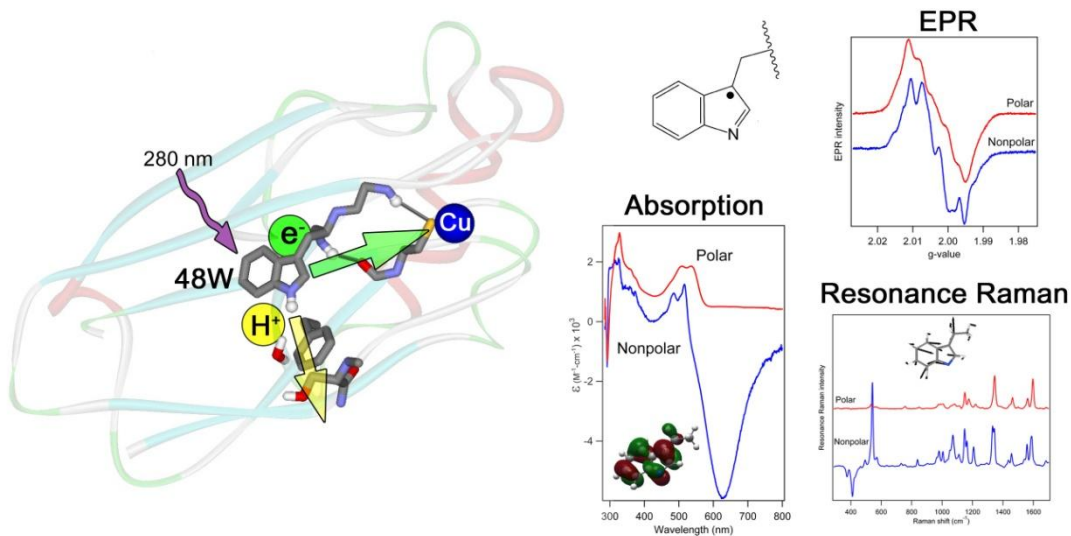
Excited state dynamics of the pyridoxal 5'-phosphate (PLP) Schiff base (SB) blue absorbing cofactor in solution have been resolved using pump-probe and pump-dump-probe transient absorption spectroscopies spanning 18 decades ( $10^{-14}$  –  $10^4$  s). Femtosecond pump-probe studies showed formation of a SB triplet state within picoseconds following 400-nm excitation; nanosecond pump-probe experiments revealed decay of this triplet state within microseconds. We show that the triplet state has lower C-H pKa\* compared to ground state pKa, inducing rapid formation of a quinonoid intermediate that is essential in the thermally-activated reaction of PLP-dependent enzymes. A photochemical intermediate with absorption consistent with quinonoid was observed during nanosecond pump-probe experiments. Additional femtosecond pump-dump-probe experiments showed transiently dumping SB singlet excited state population reduces SB triplet yield. Repumping SB triplet facilitates intersystem crossing causing rapid filling of PLP-SB ground state. These data suggest incoherent optical control of an enzymatic reaction. Because of this, we are able to show dramatic increases in catalytic activity of the PLP-dependent enzyme aspartate aminotransferase (AAT) and K258A AAT, an inactive mutant) under exposure to 440-nm light.

# Photochemistry, Photophysics, and Structures of Functional Tryptophan Residues: Radical Intermediates and Protein Anchors

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The aromatic amino acid tryptophan is unique among the 20 natural amino acids; for example, tryptophan exhibits the largest accessible nonpolar surface area that is highly polarizable, has the greatest ionization potential, possesses an indole N-H moiety that is capable of hydrogen bond donation, and displays the greatest electrostatic potential for cation- $\pi$  interactions. These important chemical properties render tryptophan an important functional residue in diverse biological systems. Our group utilizes vibrational and electronic spectroscopy to probe the specific photophysical, photochemical, and structural properties of tryptophan in two broad themes in biology: electron transfer chemistry and membrane proteins. We will primarily focus on the topic of biological electron transfer reactions for the current presentation.

Tryptophan radicals play a significant role in mediating biological electron transfer and catalytic processes. Here, we report on the photo-induced reduction of the copper(II) center in azurin from the native tryptophan residue, and present evidence supporting a direct electron transfer mechanism between the two redox-active species. The electronic, magnetic, and vibrational spectra of this long-lived neutral tryptophan radical in a hydrophobic pocket are compared to those of a partially solvent-exposed radical to identify spectral characteristics of tryptophan radicals that are sensitive to the local environment. The optical absorption spectra show characteristic double-peak features that can be attributed to two different electronic states, and the absorption wavelength decreases by 25 nm in a hydrophobic environment. Electron paramagnetic resonance spectroscopy reveals an anisotropic signal with partially resolved coupling, and microwave saturation experiments support intramolecular electron transfer. The resonance Raman frequencies are downshifted by  $\sim 10\text{ cm}^{-1}$  for the hydrophobic radical and display different relative intensities. The comparison of electronic absorption, electron paramagnetic resonance, and resonance Raman spectra reveal the hydrophobicity, conformation, hydrogen bonding, and protonation state of a tryptophan radical within a protein. Additional studies in wild type azurin reveal a novel photo-induced charge-separation reaction over a distance of  $20\text{ \AA}$  that involves the copper center, and native tryptophan and tyrosine residues. Proposed electron and proton transfer pathways are discussed.



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