



January 28th –January 30th , 2004, Asilomar Conference Center, Pacific Grove, CA

Meeting Schedule

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

Wednesday, January 28th

- | | |
|-----------------|---|
| 3:00-6:00 p.m. | Registration in Main Lodge |
| 4:00-5:00 p.m. | Set up for Poster Session I in Merrill Hall |
| 5:00-6:00 p.m. | Poster Session I |
| 6:00-7:00 p.m. | Dinner |
| 7:30-9:00 p.m. | Registration Continues in Merrill Hall |
| 8:00-8:10 p.m. | Welcoming Remarks in Merrill Hall
Steve Leone (University of California, Berkeley)
WSA Program Chairman |
| 8:10-9:00 p.m. | Opening Lecture
Roger Miller (University of North Carolina, Chapel Hill)
“Spectroscopic studies of reactive intermediates formed in helium nanodroplets” |
| 9:00-11:00 p.m. | Poster Session I Continues in Merrill Hall |

Thursday, January 29th

- 7:30 a.m. Breakfast
- 8:30-9:00 a.m. Registration in continues in Merrill Hall
- 9:00-10:30 a.m. *Session A Lectures*
Chairperson: **Anne Myers Kelley (University of California, Merced)**
- 9:00-9:35 a.m. **Andrei Tokmakoff (Massachusetts Institute of Technology)**
“Ultrafast infrared spectroscopy of hydrogen-bond dynamics in water”
- 9:35 - 9:55 a.m. **John Asbury (Stanford University)**
“Hydrogen bond dynamics probed with vibrational echo correlation spectroscopy”
- 9:55-10:30 a.m. **Jin Zhang (University of California, Santa Cruz)**
“Novel properties and emerging applications of nanomaterials studied by optical spectroscopy”
- 10:30-10:50 a.m. Coffee Break
- 10:50-12:20 p.m. *Session B Lectures*
Chairperson: **Joe Cline (University of Nevada, Reno)**
- 10:50-11:25 a.m. **Jun Ye (JILA, National Institute of Standards and Technology, and the University of Colorado, Boulder)**
“Control of coherent light and its applications to atomic/molecular spectroscopy”
- 11:25 -11:45 a.m. **Annalise Van Wyngarden (University of California, Berkeley)**
“Dynamics of the O(¹D) + CO₂ oxygen isotope exchange reaction”
- 11:45-12:20 p.m. **John Hepburn (University of British Columbia)**
“Dynamics and spectroscopy of threshold ion-pair photodissociation of molecules and clusters”
- 12:20-1:30 p.m. Lunch

Thursday, January 29th

- 1:30-3:20 p.m. *Session C Lectures*
Chairperson: **Philip Reid (University of Washington)**
- 1:30-2:05 p.m. **Mark Ratner (Northwestern University)**
“Molecular electronics in 2004”
- 2:05 -2:25 p.m. **Travis Humble (University of Oregon)**
“Molecular state reconstruction by nonlinear wave packet interferometry”
- 2:25-3:00 p.m. **Carlos Bustamante (University of California, Berkeley)**
“Recent advancements in single molecule manipulation”
- 3:00-3:20 p.m. **Bjoern Reinhard (Technical University Kaiserslautern)**
“Coordination versus internal reaction in niobium-acetonitrile complexes probed by free electron laser IR multiphoton dissociation spectroscopy”
- 3:20-5:00 p.m. Break
- 3:45-4:45 p.m. Ecology / history walk with Asilomar State Beach park ranger. Meet on steps west of Main Lodge.
- 5:00-5:15 p.m. Set up for Poster Session II in Merrill Hall
- 5:15-6:30 p.m. Poster Session II
- 6:30-8:00 p.m. Banquet (Seascape)
- 8:00-9:00 p.m. Banquet Address in Merrill Hall:
Wilson Ho (University of California, Irvine)
“Spectroscopy at the spatial limit”
- 9:00-11:00 p.m. Poster Session II Continues in Merrill Hall

Friday, January 30th

7:30 a.m.	Breakfast
9:00-10:15 a.m.	<i>Session D Lectures</i> Chairperson: Craig Taatjes (Sandia National Laboratories)
9:00-9:20 a.m.	David McCamant (University of California, Berkeley) “Femtosecond simulated Raman spectroscopy: a new technique for high performance femtosecond time-resolved vibrational spectroscopy”
9:20-9:55 a.m.	Kim Prather (University of California, San Diego) “Real-time investigation of heterogeneous processes at the single particle level: Taking it down to the nanoscale”
9:55-10:15 a.m.	Arthur Bragg (University of California, Berkeley) “Intra- and interband relaxation dynamics of anionic mercury clusters studied with time-resolved photoelectron imaging (TRPEI)”
10:15-10:35 a.m.	Break
10:35-11:40 am	<i>Session E Lectures</i> Chairperson: Eileen Spain (Occidental College)
10:35-10:55 a.m.	Yonggang He (Oregon State University) “Photoionization spectroscopy of water complexes of para-amino benzoic acid: from gas phase to solutions”
10:55-11:30 a.m.	Vicki Colvin (Rice University) “The unusual terahertz absorption of nanowater and its implications for water’s dielectric behavior”
11:30-11:40 a.m.	Closing Comments
11:40 a.m.	Checkout
12:00 p.m.	Lunch

ABSTRACTS OF CONTRIBUTED AND INVITED TALKS

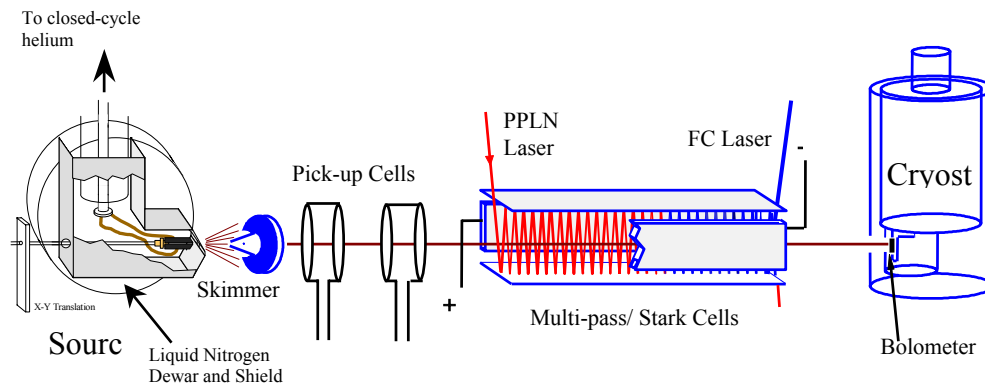
Mixing it up in helium nanodroplets: The spectroscopy of exotic clusters containing radicals, metals and biomolecules

R.E. Miller

*Department of Chemistry
University of North Carolina
Chapel Hill, N.C. 27599*

Infrared laser spectroscopy is being used to study molecules solvated in helium nanodroplets. This new spectroscopic medium has several important strengths that make it applicable to the study of a wide range of chemical and physical phenomena. Infrared laser spectroscopy has proven to be particularly useful in these studies, due to the fact that the resolution of the associated spectra is often very high. For these studies, helium turns out to be a nearly ideal matrix for isolating molecules. The number of atoms and/or molecules doped into the droplets can be varied at will by passing the droplets through a chamber maintained at an appropriate partial pressure of the species of interest.

Free radical clusters are being formed in helium nanodroplets and studied using high resolution infrared laser spectroscopy. The radicals of interest are formed by pyrolyzing a suitable precursor molecule, using a high temperature source. We currently have sources for I, Br, Cl, F and a range of organic radicals. Other approaches are being developed for N and O atoms and OH and CN radicals. Pick-up of the radicals is accomplished by passing the helium droplet beam close to the exit from the source. Complexes containing metals and biomolecules will also be discussed, along with new methods for obtaining the associated structures. In several cases, we clearly show that the rapid cooling of the growing species in the helium results in the stabilization of highly metastable species.



Ultrafast infrared spectroscopy of hydrogen-bond dynamics in water

C. J. Fecko, J. J. Loparo, J. D. Eaves,
P. L. Geissler* and **A. Tokmakoff**

*Department of Chemistry and G. R. Harrison Spectroscopy Lab
Massachusetts Institute of Technology
77 Massachusetts Ave., Cambridge, MA 02139*

**Department of Chemistry
University of California
Berkeley, CA 94720*

The hydrogen bond dynamics of water have been investigated using femtosecond nonlinear spectroscopy of the OH stretch of HOD in D₂O. We have used vibrational echo peak shift spectroscopy to characterize the ensemble-averaged time-scales for the OH frequency fluctuations. The OH frequency correlation function has a rapid 60 fs decay, a pronounced 170 fs oscillation, and a 1.2 ps long time decay. These fluctuations have been related to changes in hydrogen bonding configuration using a model that treats the intermolecular D₂O motions with classical molecular dynamics simulations. We show that the OH frequency shift arises from the molecular electric field on the OH coordinate, which has local and collective contributions. 2D IR spectroscopy is used to search for heterogeneous dynamics within the OH lineshape, which reflect different fast time dynamics for hydrogen bound and non-hydrogen bound species as well as the kinetics of hydrogen bond breaking and forming.

Hydrogen bond dynamics probed with vibrational echo correlation spectroscopy

John B. Asbury, Tobias Steinel and M. D. Fayer

Department of Chemistry
Stanford University
Stanford, CA 94305

Hydrogen bonded networks in water and alcohols are continually evolving in time. The hydroxyl stretch frequency is sensitive to the number and strength of hydrogen bonds. The hydroxyl stretch band displays inhomogeneous broadening, which prevents the linear spectrum from displaying the hydrogen bond dynamics. The inhomogeneous broadening can be decomposed and the underlying dynamics accessed using multidimensional vibrational echo correlation spectroscopy (VECS). Dynamics in the hydrogen bonded networks of HOD in H₂O and MeOD oligomers and CCl₄ are elucidated with exceptional detail using VECS, which displays the complicated dynamics in two frequency dimensions.

Hydrogen bond breaking dynamics are studied using the OD hydroxyl stretch of MeOD¹. The data indicate the strongest hydrogen bonds preferentially break following vibrational relaxation of the hydroxyl stretch. This surprising result is observed directly from the time evolution of the peaks in the data (see Fig.

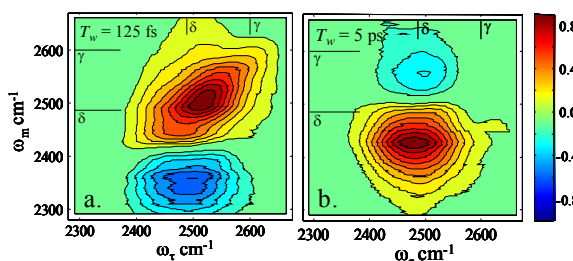


Fig. 1. Correlation spectra of MeOD **a.** before and **b.** after vibrational relaxation. The shift of the red peak indicates the Strongest H-bonds break.

1). Detailed model calculations corroborate the conclusion. The peak of the photoproduct that results from hydrogen bond breaking displays spectral diffusion dynamics in the correlation spectra, which indicates the MeOD

oligomers retain a detailed memory of the previously intact hydrogen bonded network.

The evolution of the strengths of hydrogen bonds in dilute HOD in H₂O is studied by monitoring the spectral diffusion dynamics displayed in the OD hydroxyl stretch. Two types of analyses of the correlation spectra reveal marked deviations of real water from its theoretical descriptions. First, the time correlation function (TCF) which is

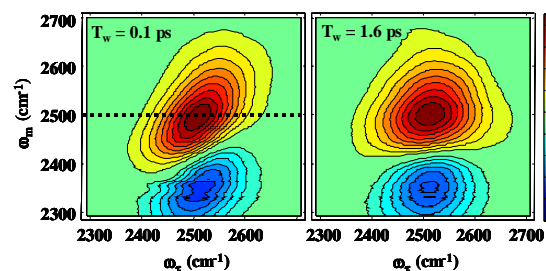


Fig. 2. Correlation spectra of HOD in H₂O. Changes in the width of the red peak along the horizontal axis (see the dashed line) report the spectral diffusion dynamics.

obtained by simulation of the correlation spectra (see Fig. 2) using full 3rd order diagrammatic perturbation theory is compared to the TCF's obtained by MD simulations of two models of water (TIP4P

and SPC/E). The comparison demonstrates the models significantly underestimate the time scale of the slowest fluctuations in water. Second, a frequency dependent analysis of the peaks in the correlation spectra indicates the hydrogen bond dynamics depend on the frequency of the hydroxyl stretch, indicating the dynamics in water are more complicated than previously assumed.

This work demonstrates VECS as a powerful new probe, capable of revealing hydrogen bond dynamics with exceptional clarity that has hitherto been unavailable from other spectroscopic probes.

¹ J.B. Asbury, T. Steinel, C. Stromberg, K.J. Gaffney, I.R. Piletic, A. Goun, and M.D. Fayer, *Chem. Phys. Lett.* (2003) **374**, 362-371.

Novel properties and emerging application of nanomaterials studied by optical spectroscopy

Jin Z. Zhang

*University of California Santa Cruz
1156 High Street
Santa Cruz, CA 95064*

As a consequence of spatial quantum confinement effect and exceedingly large surface area relative to volume, nanomaterials of both semiconductors and metals exhibit novel properties that make them promising for applications in areas such as nanophotonics and nanoelectronics including sensors, solar cells, and detectors. In this presentation, I will focus on a classic metal nanoparticle system, namely gold, that we have recently found several interesting new twists in its optical and structural properties. The particular gold nanoparticle aggregate (GNA) system studied turns out to have unique surface chemistry and optical properties useful for SERS (surface enhanced Raman Scattering) applications.

Spherical gold nanoparticles are known to have a characteristic surface plasmon absorption band near 520 nm. A new absorption band in the near IR appears for non-spherical geometries, such as nanorods, nanoshells, or aggregates. In 1994, it was first reported that the reaction between HAuCl_4 and Na_2S produced gold sulfide/gold core/shell nanostructures indicated by a strong near IR absorption. However, the core/shell structure has been challenging to reproduce. After extensive studies using a combination of experimental techniques, we found that the reported reaction produced mostly aggregates of gold nanoparticles, instead of core/shell structures.

In the interest to determine the electronic relaxation time in the GNA, we applied femtosecond transient absorption and observed a 1.5 relaxation time, which is similar to that of isolated gold nanoparticles or bulk gold. However, on longer time scales, we observed oscillations that were a surprise. Further study suggests that these oscillations are due to vibration of the GNA and that the broad near IR absorption is inhomogeneously broadened by the different size/shape of the GNAs. This conclusion is supported by a permanent hole-burning experiment, which suggests the interesting possibility of using light to narrow the size/shape distribution of GNAs. This is highly desired for SERS that is best served by uniformly distributed nanoparticles or aggregates.

We have demonstrated that these GNAs are indeed SERS active with enhancement factor on the order of 10^9 for ensemble-averaged samples of R6G. We have also observed SERS activity for single GNAs. There are two key factors for SERS to work: 1) resonance absorption of the incident light by the substrate, and 2) right surface chemistry for target molecules to adsorb on to the substrate surface. The GNAs we studied have strong near IR absorption that is desired for many chemical and biological applications and have undetermined sulfur species on the surface that facilitates adsorption of target molecules. These features make the GNAs a unique SERS substrate for developing chemical and biochemical sensors and imaging devices.

One final twist to this GNA system is that we have found very recently that the aged Na_2S solution works better for GNA generation. This leads to the suspicion that Na_2S may have been oxidized in the aging process. To test this, we have used $\text{Na}_2\text{S}_2\text{O}_3$ to replace Na_2S in the reduction of the gold salt. The product of the reaction turns out to be almost identical to that based on aged Na_2S . This suggests that the species responsible for the GNA production is most likely $\text{Na}_2\text{S}_2\text{O}_3$ generated from Na_2S during aging. The new reducing agent, $\text{Na}_2\text{S}_2\text{O}_3$, seems to generate more uniform and more reproducible GNAs.

Control of coherent light and its applications to atomic/molecular spectroscopy

Jun Ye

*JILA,
National Institute of Standards and Technology
University of Colorado,
Boulder, CO 80309-0440*

Recent progress in precision control of pulse repetition rate and carrier-envelope phase of ultrafast lasers has established a strong connection between optical frequency metrology and ultrafast science. A wide range of applications has ensued, including measurement of absolute optical frequencies, precision laser spectroscopy, optical atomic clocks, and optical frequency synthesis in the frequency-domain, along with pulse timing stabilization, coherent synthesis of optical pulses, and phase-sensitive extreme nonlinear optics in the time-domain. In this talk we will discuss the impact of the femtosecond optical frequency comb to molecular spectroscopy.

Understanding of molecular structure and dynamics often involves detailed spectral analysis over a broad wavelength range. Such a task can now be accomplished with a desired level of accuracy uniformly across all relevant spectral windows, allowing precise investigations of minute changes in the molecular structure over a large dynamic range. New technologies are being developed to prepare molecular samples in a well-controlled environment and in a well-defined internal state. On the other hand, time-domain analysis and experiments give us new possibilities for nonlinear optical spectroscopy and sensitive detections with real-time information. Stabilization of pulse timing and carrier-envelope phase at high precisions has been demonstrated, paving the groundwork for synthesizing electric fields with known amplitude and phase at optical frequencies. A fully developed capability of producing phase-coherent visible and IR pulses over broad spectral bandwidth, coupled with arbitrary control in amplitude and pulse shape, represents the ultimate instrumentation for coherent control of molecular systems. Simultaneous control of timing jitter and carrier-envelope phase can also be used to phase coherently superpose a collection of successive pulses from a mode-locked laser. Such a passive pulse “amplifier”, along with the synchronization technique we developed for pulse synthesis, has made a strong impact on the field of nonlinear-optics based spectroscopy and imaging of biomolecular systems, showing significant improvements in experimental sensitivity and spatial resolution. With the enhanced detection sensitivity comes the capability of tracking real time biological dynamics. In addition, we are exploring the use of pulse-cavity interactions to obtain a high sensitivity in intracavity spectroscopy (linear and non-linear) with a wide spectral coverage, as well as to enhance nonlinear interaction strengths for high efficiency nonlinear optical experiments.

Dynamics of the O(¹D) + CO₂ oxygen isotope exchange reaction

Annalise L. Van Wyngarden¹, Mark J. Perri¹, Kristie A. Boering², Jim Jr-Min Lin³, and Yuan T. Lee^{3,4}

¹*Department of Chemistry, University of California, Berkeley*

²*Departments of Chemistry and Earth and Planetary Science, University of California, Berkeley*

³*Institute of Atomic and Molecular Science, Academia Sinica, Taipei, Taiwan*

⁴*Department of Chemistry, National Taiwan University, Taipei, Taiwan*

Observations of both stratospheric O₃ and CO₂ have revealed unusual oxygen isotopic enrichments. The anomalous enrichment in CO₂ has the potential to be used as a tracer of integrated O₃ production and transport in the stratosphere while the corresponding anomalous depletion in O₂ can be used as a proxy for global photosynthesis on glacial/interglacial timescales. However, first the mechanisms for the production of these anomalous isotope enrichments must be understood. The anomalous enrichment in O₃ originates in the three-body O₃ formation reaction [Mauersberger et al. 1999, Gao et al. 2001]:



It has been proposed that the CO₂ isotopic enrichment arises from photochemical transfer of the anomaly from ozone via O(¹D) [Yung et al. 1991]:



However, the details of this transfer are still uncertain, and there is currently a debate whether anomalous fractionation must also occur in the O(¹D) electronic quenching step (Eq. 3). In order to help determine the role that the CO₃ intermediate plays in this exchange, we used crossed-molecular beam experiments to study the chemical dynamics of CO₂ + O(¹D).

A universal crossed molecular beam machine was used to determine the product angular and velocity distribution of the isotope exchange reaction between ¹⁸O(¹D) and ⁴⁴CO₂ at collision energies of 7.7 and 4.2 kcal/mol. An atomic beam of ¹⁸O(¹D) was prepared from 157nm photolysis of ³⁶O₂ and crossed with a molecular beam of ⁴⁴CO₂. Products that had undergone isotopic exchange (⁴⁶CO₂) were selected by a quadrupole mass filter and detected with a Daly detector coupled to a multi-channel scalar that records time of flight.

Two distinct isotope exchange channels were observed. One corresponds to the quenching reaction (3) and the other corresponds to isotope exchange that occurs without electronic quenching of the atomic oxygen product. This is the first evidence for isotope exchange on the singlet surface, since the electronic state of the product oxygen atoms has not been monitored in prior isotope exchange experiments. This non-quenching channel accounts for 33% and 17% of isotope exchange at 7.7 and 4.2 kcal/mol respectively. If this channel is still significant at stratospheric collision energies (1-2 kcal/mol) it may need to be considered in order to model isotope exchange between O₃ and CO₂.

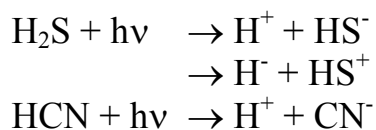
Dynamics and spectroscopy of threshold photoion-pair formation

Qichi Hu and **John Hepburn**

*Department of Chemistry
University of British Columbia
Vancouver, BC, Canada*

In this talk, recent results from high resolution studies of photoion-pair formation will be discussed. In our experiments, coherent vacuum ultraviolet light is used to excite molecules and clusters to Rydberg-like ion-pair states just below the ion-pair dissociation limit, with these “exotic-atom” states being subsequently detected by pulsed field ionization.¹

In recording a TIPP spectrum, one gathers information on which final state ion-pair channels are accessible from the neutral molecule. In H₂S and HCN, the rotational state distributions for the final diatomic ion fragment (HS⁺, HS⁻, and CN⁻) are very different, and show the differing dissociation dynamics in these three photodissociations:



The hydrogen bonded HF dimer cannot be photoionized to give (HF)₂⁺, one sees the very stable H₂F⁺ ion instead. We have carried out high resolution studies of the photoionization of the HF dimer, and have observed many sharp resonances from transient (HF)₂⁺ core Rydberg states, and pulsed field ionization signal from the H₂F⁺ + F⁻ ion-pair channel. This pulsed-field ionization signal provides information about highly vibrationally excited states of the H₂F⁺ ion, and probes the dynamics of the proton transfer reaction.

¹ J.D.D. Martin and J.W. Hepburn, *Phys. Rev. Lett.* **79**, 3154 (1997)

Molecular nanostructures: fabrication and transport aspects

Mark A. Ratner

*Department of Chemistry and Materials Research Center
Northwestern University
Evanston, Illinois 60208*

The characteristic internuclear potentials exhibited by molecules leads to unusual shapes of molecular nanostructures, shapes that challenge our ordinary understanding of how such structures are prepared as current-carrying components of molecular transport junctions.

The community has done pioneering research in both of these aspects, and this talk will focus on topics very close to its current interest. In the first part we will discuss the formation of micellar molecular aggregates in solution, and their dependence upon the properties of the individual molecular components. The second part will discuss some aspects of molecular charge transport in junctions, particularly the use of molecular dynamical stereochemistry as a gating mechanism.

Molecular state reconstruction by nonlinear wave packet interferometry

Travis S. Humble and Jeffrey A. Cina

*Department of Chemistry and Oregon Center for Optics
University of Oregon
Eugene, OR 97403*

The time and phase-resolved signals measured in a nonlinear wave packet interferometry (nl-WPI) experiment probe the overlaps between vibronic wave packets prepared by a pair of phase-locked pulse-pairs. Making use of the phase-control between pulse-pairs to measure and isolate the real and imaginary components to a molecular response which is linear in all four fields (i.e. a quadrilinear contribution) we consider the application of nl-WPI to isolated, gas phase species as a potential method for characterizing laser induced, photochemical reactions. In particular, we show that two-color nl-WPI can be used to reconstruct the probability amplitude of an optically prepared vibronic wave packet without prior detailed knowledge of the underlying potential energy surface. We analyze this form of vibronic state reconstruction in a model system excited by shaped laser pulses, and propose nl-WPI as a diagnostic tool for identifying optimized wave packets in adaptive coherent control experiments. Additionally, we demonstrate how knowledge of a propagating wave packet on an unknown surface gained using nl-WPI can be used to invert the Schrodinger equation, providing a potential method for mapping out multidimensional potential energy surfaces.

Recent advances in single molecules manipulation

Carlos Bustamante

*Howard Hughes Medical Institute
Departments of Physics and Molecular & Cell Biology,
University of California,
Berkeley, CA 94720*

Over the last ten years, a number of new approaches have emerged that have made it possible for scientists to mechanically manipulate individual molecules. These methods are proving themselves quite powerful to investigate the molecular mechanisms underlying many dynamic biochemical processes. Because molecules are studied one at a time, single molecule manipulation techniques avoid the ensemble average characteristic of bulk studies. This feature is particularly useful to follow complex dynamic processes in time where the presence of multiple species in solution blurs the dynamical description of the system. Moreover, many processes in the cell are known to be mechanical in nature and mechanical force is one of the “products” of the reaction. It follows that forces applied to the molecules undergoing these processes can be used to alter the extent and in some cases even the fate of the reactions, thus helping to reveal the molecular mechanisms by which force is generated in them. In this presentation, I will illustrate the use of optical tweezers with three different examples taken from my own research.

Coordination versus internal reaction in niobium-acetonitrile complexes probed by free electron laser IR multiphoton dissociation spectroscopy

Bjoern Reinhard

*Technical University Kaiserslautern
Fachbereich Chemie
Erwin-Schroedinger-Str. 52
Kaiserslautern, Germany 67663*

Experimental IR multiphoton dissociation spectra of cationic niobium-acetonitrile complexes with the formal stoichiometry $[\text{Nb},n\text{CH}_3\text{CN}]^+$, $n=4-5$, as provided by the Free Electron Laser at CLIO, Orsay, France, are compared to ab initio IR absorption spectra throughout the spectral “fingerprinting” range $780-2500\text{ cm}^{-1}$. For $n=4$ the vibrational spectra provide clear evidence for a square planar high spin quintet $[\text{Nb}^{\text{I}}(\text{NCCH}_3)_4]^+$ complex. For $n=5$, additional vibrational bands between $1300-1600\text{ cm}^{-1}$ are interpreted in terms of covalent C-C coupling in $[\text{Nb},5\text{CH}_3\text{CN}]^+$. Screening on the basis of ab initio calculations leads to an assignment of the recorded spectrum in terms of a metallacyclic species $[\text{Nb}^{\text{III}}(\text{NCCH}_3)_3(\text{N}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{N})]^+$ with an electronic triplet state. The observed processes upon fourfold and fivefold coordination of Nb^{I} with CH_3CN in the gas-phase are complexation only and reductive nitrile coupling, respectively. The minimum energy pathways of the reductive nitrile coupling reaction from $[\text{Nb}^{\text{I}}(\text{NCCH}_3)_n]^+$, $n=4-5$, investigated for singlet, triplet and quintet states ($S=0,1,2$) by density functional theory, account well for the observed (non-)reactivity. In ground state (triplet, $S=1$) $[\text{Nb}^{\text{I}}(\text{NCCH}_3)_5]^+$, the reaction is found to be exothermic and the activation barrier amounts to approximately 49 kJ mol^{-1} , whereas for ground state (quintet, $S=2$) $[\text{Nb}^{\text{I}}(\text{NCCH}_3)_4]^+$ the reaction is endothermic and requires activation of $\gg 116\text{ kJ mol}^{-1}$.

Spectroscopy at the spatial limit

Wilson Ho

*University of California, Irvine
Department of Physics & Astronomy
2162 Frederick Reines Hall
Irvine, CA 92697-4575*

Lasers have and continue to enable spectroscopic investigation of atoms, molecules, and liquid and solid matter with increasing precision largely through refinement of the energy and temporal resolutions. The diffraction limit of lasers, however, imposes a constraint on the spatial resolution. Since the invention of the scanning tunneling microscope (STM) in 1981, spectroscopy with sub-nanometer resolution has continuously been developed, and new capabilities have enabled seeing and probing matter at the atomic and molecular scales. The STM can also be used to manipulate individual atoms and molecules to create nanostructures not available by other means. In this talk, I will discuss the use of the STM to image, manipulate, and spectroscopically characterize individual atoms and molecules as well as artificially created nanostructures. We will see how elastic tunneling provides us with electronic and vibronic information, in contrast to inelastic tunneling which gives rise to vibrational spectroscopy and light emission. Spectroscopy can indeed be performed with sub-Ångstrom resolution with the STM, enabling a unique way for understanding chemical problems and revealing a number of interesting facets of single molecule chemistry.

Femtosecond Stimulated Raman Spectroscopy: A new technique for high-performance femtosecond time-resolved vibrational spectroscopy.

David W. McCamant, Philipp Kukura and Richard A. Mathies

*Department of Chemistry,
University of California
Berkeley, CA 94270*

We have developed the technique of femtosecond stimulated Raman spectroscopy (FSRS) which provides the unique ability to measure complete time-resolved vibrational spectra with <100-fs time resolution and 15-cm⁻¹ frequency resolution. The experiment utilizes three laser pulses: (1) a 40-fs visible pump pulse to initiate the photochemistry; (2) a narrow bandwidth ~1 ps pulse which pumps the stimulated Raman process, and (3) a 60-fs continuum to the red of the Raman pump which is amplified at the various Raman shifts. We have shown that FSRS spectra of standard solutions and solvents can be collected in seconds and that the stimulated Raman spectra can be obtained using just a single pump-probe pulse pair that illuminates the sample for only ~1 ps,¹ opening up new possibilities for real-time vibrational spectroscopy. Furthermore for highly fluorescent molecules, we demonstrated that the inherent fluorescence rejection of FSRS can decrease data-acquisition times by as much as 10⁷ relative to traditional spontaneous Raman spectroscopy.

We have exploited the intrinsic time resolution of FSRS to observe the intramolecular vibrational relaxation (IVR) processes in β -carotene's S₁ state following ultrafast internal conversion from S₂.² It was found that the C=C mode in S₁ is highly excited by internal conversion from S₂ and subsequently dissipates the excess energy into a localized subset of strongly anharmonically coupled modes in 200 fs. This bath of anharmonically-coupled modes relaxes by IVR throughout the remaining modes of the molecule in 450 fs. In further studies we have observed the vibrational spectrum of the ~100-fs lifetime S₂ states of diphenyloctatetraene³ and of β -carotene, both of which show no spectral shifting during their electronic lifetime, indication an absence of significant structural changes or vibrational relaxation on this time-scale. Comparing the vibrational spectra of the S₀, S₁, and S₂ states of these polyenes gives new experimental information about how molecular bonding changes upon $\pi \rightarrow \pi^*$ excitation. Work is currently underway to use FSRS to observe the excited state structural changes during the ultrafast primary events in rhodopsin and bacteriorhodopsin. Preliminary results from bacteriorhodopsin indicate that although the trans-cis isomerization of the chromophore is completed with a 500-fs time constant, the probed excited state population is structurally static throughout its lifetime. FSRS is a versatile spectroscopic tool that can be used to study Raman spectra of fluorescent molecules, ultrafast photochemistry and photophysics as well as chemical reaction dynamics and transition state structures.

- (1) McCamant, D.W.; Kukura,P; Mathies, R. A. *Appl. Spectrosc.* **2003**,57, 1217.
- (2) McCamant, D.W.; Kukura,P; Mathies, R. A. *J. Phys. Chem. A.* **2003**,107, 8208.
- (3) Kukura,P; McCamant, D.W.; Mathies, R. A. *Chem. Phys. Lett.* **2003**, submitted.

Real-time investigation of heterogeneous processes at the single particle level: Taking it down to the nanoscale

Kim Prather

*University of California, San Diego
9500 Gilman Dr.
La Jolla, CA 92093-0314*

Intra- and interband relaxation dynamics of anionic mercury clusters studied with time-resolved photoelectron imaging (TRPEI)

Arthur E. Bragg^a, Jan R. R. Verlet^a, Aster Kammrath^a, Ori Cheshnovsky^b,
and Daniel M. Neumark^a

^a Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720

^b School of Chemistry, The Sackler Faculty of Exact Sciences, Tel-Aviv University, 69978 Israel

Finite cluster studies present the opportunity to trace the evolution of material properties between molecular and bulk, changes arising generally from alteration of bonding-type with increasing size. Experiments and theory regarding clusters of divalent metals, such as $\text{Hg}_n/\text{Hg}_n^-$, have largely focused towards determining the size-regimes of transitions in bonding-type, which has been shown to progress from van der Waals to covalent¹ to metallic² as s - p band hybridization occurs. Additionally, above-threshold $6p \leftarrow 6s$ excitation of Hg_n^- was demonstrated to initiate competing charge-carrier thermalization and electron-hole recombination with Auger emission, processes previously unobserved in cluster species but common to bulk semiconductors.³

Towards understanding the bond-type size-dependence of these clusters we have applied time-resolved photoelectron imaging (TRPEI) to the study of intraband relaxation dynamics in Hg_n^- across the van der Waals-to-covalent transition ($n=6-20$). Cluster anions of divalent metals ($p^{2n}s^1$) present the opportunity to directly study electronic-vibrational interactions leading to single electron thermalization within rudimentary bands. In our studies the excess electron is pumped below threshold through a broad (>300 meV) $6p^* \leftarrow 6p$ band resonance with 100 fs pulses at near-IR and visible wavelengths. Excited clusters are probed via detachment with ~ 100 fs pulses at near-UV energies; photoelectrons are collected via velocity map imaging (VMI), permitting acquisition of both photoelectron velocity and angular distributions.

Observed Hg_n^- dynamics broadly exhibit fast initial relaxation (<1 ps) followed by slow thermalization (~ 10 -50 ps). Size-varying timescales and dynamical details, coupled to measured photofragmentation yields and photoelectron angular distributions, reflect evolution of bond-type across this size-range. Notably, small clusters, particularly $n=7$ and 8, exhibit $\tau \sim 800$ fs coherences, suggesting that vibrational relaxation is initially mediated by wavepacket motion along cluster breathing modes. These clusters and selected larger clusters have been studied in detail towards deciphering the nature of cohesive interactions and charge (de)localization in the van der Waals and covalent regimes. Contrasts are drawn to relaxation behavior of small transition metal clusters.

Towards understanding interband cluster relaxation dynamics we have applied TRPEI to clock electron-hole recombination and probe the effect of electron-electron interactions on intra- $6p$ -band thermalization, which may be compared to the 'pure' thermalization dynamics. Size-incremented studies are planned towards probing relative rates of thermalization and recombination, with the anticipation that thermalization will compete more effectively with recombination dynamics at increased size.

¹Garcia, Pastor, and Benneman, *Phys. Rev. Lett.* **67**, 1142 (1991).

²Busani, Folkers, and Chesnovsky, *Phys. Rev. Lett.* **81**, 3826 (1998).

³Busani *et al.*, *Phys. Rev. Lett.* **90**, 083401 (2003).

Photoionization spectroscopy of water complexes of para-amino benzoic acid: from gas phase to solutions

Yonggang He, Chengyin Wu, and Wei Kong

*Department of Chemistry,
Oregon State University,
Corvallis, Oregon 97331*

Water complexes of para-amino benzoic acid $\text{PABA}\cdot(\text{H}_2\text{O})_n$, prepared in a pulsed supersonic expansion, have been studied using resonantly enhanced multiphoton ionization (REMPI) and zero energy kinetic electron (ZEKE) spectroscopy. The vibrational energy levels of the S_1 state for complexes with $n = 0 - 6$ were characterized, and the geometry of the corresponding complex was analyzed. From the appearance energy of the cation and ZEKE spectroscopy, the ionization potential (IP) was measured for complexes with n up to 40. Aided by *ab initio* calculations, we present a detailed road map for the solvation process of PABA. Due to the strong hydrogen bonds between water molecules and water-COOH, solvation of PABA initiates at the acidic side of the ring and progressively engulfs the whole molecule when more than 20 water molecules are available. This mechanism can satisfactorily explain the changes in vibrational frequency and the gradual decrease of IP with increasing water content.

The unusual terahertz absorption of nanowater and its implications for water's dielectric behavior

Vicki Colvin

*Rice University
MS 60 Chemistry
6100 Main Street
Houston, TX 77005*

The behavior of water under nanoscale confinement is critical for diverse areas in science. Here we evaluate how geometrical confinement influences the dielectric properties of water. We focus on model systems of nanometer-sized water pools containing from 300 to 3000 molecules. In this mesoscopic size range prior studies have indicated that much of the local hydrogen bonded network of water is relatively unperturbed by the three dimensional confinement. However, many dynamical properties of bulk water are thought to involve collective molecular motion and thus may be changed substantially even in relatively big water pools. The timescales of these highly damped processes, which are proposed to underlie the the debye-like dielectric behavior, are on the order of 1 picosecond making terahertz spectroscopy an ideal probe of their behavior. We have systematically evaluated the evolution of the terahertz dielectric properties as a function of increasing water pool size. A strong Terahertz absorption is observed in water pools which contain structured water; this feature is absent in bulk water. An analysis of the size dependence of this absorption suggests that it arises from collective oscillations of nanoscale water droplets. This data predicts unusual dynamics in water clusters, and provides a model for evaluating nanoscopic water found in the controlled cavities of biological systems.