

**PHYS 101 [752720]: Minimizing photobleaching in experiments combining optical tweezers and single-molecule fluorescence**

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**Abstract**

To obtain high-resolution information on position or conformation of a biomolecule and at the same time apply forces to it, optical trapping can be combined with single-molecule fluorescence microscopy. We show that experiments like these are feasible even when the fluorophore is directly attached to the trapped particle. We found, however, that the photostability of the fluorophores we tested suffered from the presence of the additional laser light used for trapping. Our results indicate that the enhanced photobleaching is caused by the absorption of a visible photon followed by the excited-state absorption of a near-infrared photon. The higher excited singlet states generated in this way readily form non-fluorescent dye cations. We found that different dyes suffer to a different extent from enhanced photobleaching.

**PHYS 102 [767597]: The art of mechano-transduction: Deriving structural insights**

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**Abstract**

Gaining structural insights into how mechanical force can switch protein function is critical to learning how mechanical forces regulate cell function. The function of cells is tightly controlled by their interaction with the surrounding extracellular matrix to which they are coupled via the transmembrane integrins. Using experimental and computational techniques (steered molecular dynamics simulations), we studied how tension applied to extracellular matrix proteins affects the exposure of their molecular recognition sites. The adhesion protein fibronectin is a particularly attractive model protein to explore the underlying engineering principles how force-induced structural perturbations affect its multiple functions, since fibronectin contains multiple molecular recognition sites distributed over more than 50 modules, and it is coupled via transmembrane integrins to the contractile elements of the cytoskeleton. We will also provide new structural insights into how divalent ions stabilize the mechanical coupling of integrins to RGD-containing peptides and proteins and discuss potential down-stream effects on cell signaling.

**PHYS 103 [746631]: Promoter unwinding and promoter escape by RNA polymerase: Detection and control by single-molecule DNA nanomanipulation**

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## **Abstract**

By monitoring the end-to-end extension of a mechanically stretched, supercoiled, single DNA molecule, we have been able directly to observe the change in DNA extension associated with the unwinding of  $\approx 1$  turn of promoter DNA by RNA polymerase (RNAP). By performing parallel experiments with negatively and positively supercoiled DNA, we have been able to deconvolute the change in extension due to RNAP-dependent DNA unwinding (with  $\approx 1$  bp resolution) and the change in extension due to RNAP-dependent DNA compaction (with  $\approx 5$  nm resolution). We have used this approach to quantify the extent of unwinding and compaction, the kinetics of unwinding and compaction, and effects of temperature, supercoiling, promoter sequence, ppGpp, and nucleotides. We also have used the approach to detect promoter clearance and promoter recycling by successive RNAP molecules. We find that the rate of formation and the stability of the unwound complex depend profoundly on supercoiling and that supercoiling exerts its effects mechanically (through torque), and not structurally (through the number and position of supercoils). The approach should permit analysis of other nucleic-acid-processing factors that cause changes in DNA twist and/or DNA compaction.

## **PHYS 104 [749313]: Visualizing localized domain transformations of single molecules and cells through nano- and micro-technology**

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## **Abstract**

Understanding the dynamic response of single molecules and cells is essential in chemistry, engineering, physics, and biology. Through characterizing these interactions between molecular and cellular responses, we can begin to bridge the gap between these systems, which are inherently at different size scales. To link their behaviors though, we must develop and utilize novel technologies to understand their localized response under spatiotemporally controlled conditions. Here we present a method to stimulate and visualize individual molecules and cells at localized domains where diffusion limitations normally dictate the homogeneity of the environment. We use defined configurations of microscale fluidic channels that operate on the principal of low Reynolds number flow to maintain laminar nanoscale chemical delivery to local regions of cells and molecules. This allows us to investigate DNA deformation as well as visualize signal transduction in single cells at a domain level. This technology has applications that range from utilization for in vitro diagnostics to investigating polymer physics.

## **PHYS 105 [767514]: Mechanism of DNA compaction by Abf2p studied by atomic force microscopy and optical tweezers**

**Raymond W. Friddle**, Jennifer E. Klare, Shelley S. Martin, Michelle Corzett, Rod Balhorn, Enoch P. Baldwin, Yun Pei Chang, Ryan Case, Carlos Bustamante, Ronald J. Baskin, and Aleksandr Noy, Lawrence Livermore National Laboratory, Livermore, CA 94550, [friddle1@llnl.gov](mailto:friddle1@llnl.gov)

## **Abstract**

We used high resolution Atomic Force Microscopy (AFM) to image the compaction of linear

and circular DNA by the yeast mitochondrial protein Abf2p, which plays a major role in packaging mitochondrial DNA. AFM images show that protein binding induces drastic bends in the DNA backbone for both linear and circular DNA. At a high concentration of Abf2p DNA collapses into a tight globular structure. We quantified the compaction of linear DNA by measuring the end-to-end distance of the DNA molecule at increasing concentrations of Abf2p. We also derived a polymer statistical mechanics model that provides a quantitative description of compaction observed in our experiments. This model shows that sharp bends in the DNA backbone are often sufficient to cause DNA compaction. Comparison of our model with the experimental data showed excellent quantitative correlation and allowed us to determine binding characteristics for Abf2p. These studies indicate that Abf2p compacts DNA through a simple mechanism that involves bending of the DNA backbone. Optical tweezers force-extension experiments at high protein concentration reveal a higher complexity of organization that is unresolvable under normal imaging conditions. We discuss the implications of these phenomena on mitochondrial DNA maintenance and organization.

### **PHYS 106 [755452]: Reaction kinetics of atmospheric hydrogen oxide and halogen oxide radicals**

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#### **Abstract**

As new global measurement systems of atmospheric composition come on-line, chemical-transport models (CTM's) are continually challenged to reproduce the temporal and spatial variability of the observations, and assess the implications for climate change and air quality. We will present some recent laboratory results on processes that have significant effects on CTM predictions in the troposphere and stratosphere. These include the self- and cross-reactions of HO<sub>2</sub> and RO<sub>2</sub> radicals, the reaction of ClOOCl with radicals such as OH, and the recombination of OH with NO<sub>2</sub> to form HONO<sub>2</sub> and HOONO.

### **PHYS 107 [753396]: Search for possible stratospheric bromine reservoir species: Theoretical study of the photostability of mono-, tri-, and pentacoordinated bromine compounds**

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#### **Abstract**

Previous work has shown that pentacoordinated bromine compounds have their lowest excited electronic states shifted to the blue relative to monocoordinated bromine molecules, and that this

shift may be large enough to render them photostable in the lower stratosphere. Our earlier work has also shown that certain pentacoordinated bromine compounds are thermodynamically stable relative to their mono- or tricoordinated isomers, suggesting that if a bromine stratospheric reservoir species exists, then it is most likely a pentacoordinated compound. In this study we have examined the singlet excited electronic states of several bromine compounds in order to assess their photostability under stratospheric conditions and in order to shed some light on the nature of lowest excited states in mono-, tri-, and pentacoordinated bromine molecules. Due to the strong spin-orbit mixing in bromine, we have also examined the lowest triplet excited state.

**PHYS 108 [749826]: Reactions of open shell radicals:  $\text{OH} + \text{O} = \text{O}_2 + \text{H}$  and  $\text{OH} + \text{OH} (+\text{M}) = \text{H}_2\text{O}_2 (+\text{M})$**

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**Abstract**

Many reactions of atmospheric relevance involve radicals with open electronic shells. A detailed understanding of these processes poses considerable problems which are only partially solved today. There are several electronic states involved which at large reactant distances interact and which may influence the dynamics. In addition, the coupling of angular momenta from reactant rotation, orbiting motion, electronic angular momentum and spin have to be taken into account. Finally the potential energy surfaces have long-range electrostatic and short-range valence components with non-smooth transitions in between. This talk demonstrates the state-of-the-art of calculating rate constants for the reactions  $\text{OH} + \text{O} = \text{O}_2 + \text{H}$  and  $\text{OH} + \text{OH} (+\text{M}) = \text{H}_2\text{O}_2 (+\text{M})$ . Statistical adiabatic channel/classical trajectory calculations are performed employing ab initio potential energy surfaces.

**PHYS 109 [752951]: Theoretical studies of hydroxyl chemistry in the mesosphere**

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**Abstract**

In this talk we discuss several aspects of hydroxyl chemistry in the upper stratosphere and mesosphere. It has recently been suggested that the reaction between vibrationally excited molecular hydrogen with atomic oxygen may be an important source of OH in the upper mesosphere. Using quantum calculations on chemically accurate potential energy surfaces of the  $\text{O}+\text{H}_2$  system we show that the proposed mechanism is not an important source of OH in the mesosphere. Our calculations also reproduce the markedly different  $\text{OH}(v'=0)/\text{OH}(v'=1)$  branching in  $\text{O}+\text{H}_2(v=1)$  reaction observed in experiments that use different oxygen atom sources. We also present results of quantum calculations of the  $\text{H}+\text{O}_2$  reaction using a recently developed ab initio potential energy surface. Most previous studies of this system employed semi-empirical potential energy surfaces. We show that results are sensitive to details of the

potential energy surface and that theoretical understanding of this important atmospheric reaction is far from complete.

**PHYS 110 [754631]: Influence of CO<sub>2</sub>-O and NO-O vibrational energy transfer on the temperature and density structure of the upper atmosphere**

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**Abstract**

Collisions of O with the trace species CO<sub>2</sub> and NO provide significant cooling of the Earth's upper atmosphere between 70 and 200 km. The collisions efficiently populate the CO<sub>2</sub>( $\nu_2$ ) and NO( $\nu=1$ ) levels, respectively. These levels subsequently emit 15- $\mu\text{m}$  and 5.3- $\mu\text{m}$  photons into space, removing ambient kinetic energy from the atmosphere. We have performed laboratory measurements to better characterize the vibrational energy transfer (VET) efficiencies for the NO-O and CO<sub>2</sub>-O systems. Model predictions of upper atmospheric temperature and density are sensitive to the VET input parameters, including their temperature dependence. In particular, the large CO<sub>2</sub>-O VET efficiency and increasing global CO<sub>2</sub> concentrations suggest that the thermosphere may be cooling and contracting over time. This hypothesis is supported by recent analyses of satellite orbital motion, and provides an interesting connection between a molecular-level parameter, the CO<sub>2</sub>-O VET efficiency, and the macroscopic effects of atmospheric density and satellite longevity.

**PHYS 111 [755540]: Quasiclassical trajectory studies of mesospheric O + OH ( $\nu$ ) collisions**

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**Abstract**

In the terrestrial mesosphere, hydrogen atoms and ozone react to produce vibrationally excited OH radicals. For OH vibrational levels  $\nu > 4$ , inelastic collisions with O<sub>2</sub> and N<sub>2</sub> provide the primary route for quenching the OH vibrational coordinate. For vibrational levels  $1 \leq \nu \leq 4$ , however, quenching by O<sub>2</sub> and N<sub>2</sub> is inefficient and O + OH collisions are thought to provide the primary quenching mechanism. These collisions may remove vibrationally excited OH radicals through a variety of inelastic and reactive processes; however, the vibrational-state-specific rate constants for these processes are poorly known. Better estimates of these rate constants could improve our understanding of the chemistry and energy balance of the mesosphere. We present the results of classical trajectory simulations of O + OH ( $\nu$ ) collisions at typical mesospheric temperatures and examine the relationship between the reaction dynamics and the underlying potential surface.

**PHYS 112 [752242]: Reactions of O<sup>+</sup> with hydrocarbons at low-Earth orbit conditions**

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### **Abstract**

As part of a large collaboration to study “Materials Chemistry in the Space Environment” (a US AFOSR Multidisciplinary University Research Initiative), we have embarked on a program to study gas phase analogs of reactions of ions that occur at the surface of model space materials, specifically hydrocarbon self-assembled monolayers. In low-Earth orbit, at which altitudes the prevalent ambient ion is  $O^+$ , spacecraft move at typically 7.8 km/s, corresponding to ion – surface collisions in the hyperthermal energy range. We will present guided-ion beam measurements of the reactions of  $O^+$  with alkanes ( $C_nH_{2n+2}$ ,  $n=1,4$ ) which provide a good test for theoretical efforts that eventually will be applied to larger hydrocarbon systems. The results include absolute reaction cross section and product recoil velocity measurements for each channel observed as a function of kinetic energy from near-thermal to  $\sim 16$  eV.

### **PHYS 113 [752804]: Prediction of reaction rate constants and product branching ratios using ab initio potential energy surfaces in combination with RRKM and radiationless transition theories**

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### **Abstract**

Accurate ab initio calculations of potential energy surfaces combined with RRKM and radiationless transition theories are applied to predict reaction rate constants and product branching ratios in photodissociation of benzene and for the  $O(^1D) + CO_2$  reaction. For benzene, the ab initio/RRKM approach is employed to investigate its photodissociation mechanism at various wavelengths upon absorption of one or two UV photons followed by internal conversion into the ground electronic state. For  $O(^1D) + CO_2$ , we investigate the  $CO_3$  system in singlet and triplet electronic states. The rate constants are computed using RRKM theory and the theory of radiationless transitions for intersystem crossing rates, determined as a product of the overlap of electronic wavefunctions (spin-orbit coupling) and the overlap of vibrational wavefunctions (Franck-Condon factor). The branching ratios are calculated for the  $^{16}O(^1D) + ^{46}CO_2$  and  $^{16}O(^3P) + ^{46}CO_2$  products of the isotope-labeled  $^{18}O(^1D) + ^{44}CO_2$  reaction and are compared with experiment.

### **PHYS 114 [754173]: From pair correlation to reactive resonance in polyatomic reactions**

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## **Abstract**

A novel time-sliced velocity imaging technique has been developed and implemented in crossed-beam scattering experiments. Using this new approach, a number of atoms/radicals with methane, such as F, Cl, OH + CH<sub>4</sub> etc., and its isotopic variants were investigated. What revealed from these studies is the coincident information of the state-resolved pair-correlation of the two products. The correlated state distributions and differential cross sections show striking differences for various product pairs, which open a new way to unravel the complexity of a typical polyatomic reaction. In this talk, we will elucidate the concept of product pair correlation and highlight some of the major findings. In addition, we will show how such kind of measurements leads to the discovery of a reactive resonance in six-atom reactions of F + CH<sub>4</sub> and F + CHD<sub>3</sub>.

## **PHYS 115 [754910]: Molecular beam studies of the dissociation and isomerization of radical isomers**

**Laurie J. Butler**<sup>1</sup>, D. E. Szpunar<sup>1</sup>, J. L. Miller<sup>1</sup>, J. A. Mueller<sup>2</sup>, and J. Shu<sup>3</sup>. (1) The Department of Chemistry, The University of Chicago, The James Franck Institute, 5640 S. Ellis Ave, Chicago, IL 60637, Fax: 773-702-5863, LJB4@midway.uchicago.edu, (2) Santa Clara University, (3) Chemical Dynamics Beamline, Berkeley, CA

## **Abstract**

New molecular beam scattering experiments investigate the unimolecular dissociation and isomerization of radical isomers under collision-less conditions. We present results on three radical isomers important in combustion: allyl, 2-propenyl, and vinoxy radicals. The work first resolves the 15 kcal/mol discrepancy on the relative heights of the allyl → 2-propenyl isomerization barrier and the barrier to the unimolecular dissociation to H + allene. It then measures the differing onsets of and the change in branching ratio between the H + allene and the H + propyne product channels of the high-energy 2-propenyl isomer as a function of internal energy in the radical, providing a benchmark for electronic structure calculations on radicals. The unimolecular dissociation of rotationally-excited allyl radicals shows marked centrifugal effects. The measured change in product branching with internal energy compares favorably with the predictions of statistical transition state theories using a single potential energy surface. In contrast, the competing unimolecular dissociation channels of the vinoxy radical suggest that the electronic wavefunction cannot evolve as required along the adiabatic reaction coordinate, resulting in one product channel being dramatically suppressed. Prior studies of the competing H + ketene and CH<sub>3</sub> + CO dissociation, in experiments which excited the vinoxy radical to the *B* state, concluded that the reaction proceeds via internal conversion and got rough agreement with RRKM predictions. However, in planar geometries the dissociating vinoxy radical traverses a conical intersection en route to H + ketene. Thus we undertook to measure the branching between these two dissociation channels from ground state vinoxy radicals, expecting to see some reduction of the H + ketene product branching due to nonadiabatic recrossing of that transition state. The surprising results are presented in the talk.

## **PHYS 116 [752752]: Quantum dynamics of vibrationally activated OH-CO reactant complexes**

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### **Abstract**

We present six-dimensional quantum dynamics studies of the unimolecular decay of vibrationally activated OH-CO reactant channel complexes. We employ the ab initio based Lakin-Troya-Schatz-Harding (LTSH) potential energy surface for the A' and A'' states. We obtain good agreement with the experimental product distributions and lifetimes of Pond and Lester. We confirm that complexes with two vibrational quanta of excitation in OH and no vibrational excitation in CO ( $V_{OH} = 2$ ,  $V_{CO} = 0$ ) decay through two pathways. One pathway,  $V \rightarrow R$ , leads to products ( $V_{OH} = 1$ ,  $V_{CO} = 0$ ) with relatively high rotational energy. The other pathway,  $V \rightarrow V$ , results in ( $V_{OH} = 1$ ,  $V_{CO} = 1$ ) products and relatively low OH rotational energy. We propose an explanation for the experimental finding that there is a propensity for forming A'' products. We will also discuss quantum dynamics studies of the effect of the OH-CO reactant channel complex on the reaction probability for the OH + CO reaction.

### **PHYS 117 [754040]: DC slice imaging: A powerful probe of reaction dynamics**

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### **Abstract**

We present several applications of a new variation of the velocity map ion imaging method that allows the central section of the product ion cloud to be recorded exclusively. The relevant speed and angular distributions for a molecular photodissociation or scattering event may therefore be obtained without need to utilize reconstruction methods such as the inverse Abel transform. We have adapted this technique to measure the absolute speed-dependent angular momentum polarization anisotropy parameters in photodissociation. We will present the theoretical machinery for interpretation of a small set of sliced experimental images recorded under different laser polarization geometries and then demonstrate its application in the study of electronic orbital angular momentum alignment and orientation of excited oxygen atoms following UV photodissociation of ozone. We will also present applications of the technique for crossed-beam reactive scattering experiments as well as photochemistry.

### **PHYS 118 [754839]: Chemical reactions of highly vibrationally excited molecules**

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### **Abstract**

The role of state density in highly excited molecules as they undergo collisional relaxation and chemical reactions is investigated using high resolution transient IR absorption techniques. Highly vibrationally excited molecules are prepared with state density ranging between  $10^{13}$  and  $10^{19}$  states/cm<sup>-1</sup> using pulsed ns UV excitation. Collisional energy transfer from hot molecules to individual quantum states of neighboring bath molecules is probed with transient IR absorption, while reactive collisions are monitored by appearance of reaction products. Rotational and translational energy profiles following collisions form the basis of energy transfer probability

distribution functions and the results are compared with a predictive model based on Fermi's Golden Rule. This study explores the influence of energy, isomerization and electrostatic interactions.

**PHYS 119 [741292]: Ultrafast vibrational spectroscopy of shock compression at a solid-liquid interface**

**Dana D. Dlott**<sup>1</sup>, James Patterson<sup>2</sup>, Alexi Lagoutchev<sup>2</sup>, and Wentao Huang<sup>1</sup>. (1) School of Chemical Sciences, University of Illinois at Urbana-Champaign, 600 S. Mathews Ave, Urbana, IL 61801, [dlott@scs.uiuc.edu](mailto:dlott@scs.uiuc.edu), (2) School of Chemical Sciences, University of Illinois at Urbana Champaign

**Abstract**

This work is an experimental study of molecular dynamics at a metal-liquid interface under conditions of large amplitude motion. A laser-driven shock wave is used to push a metal layer into a viscous liquid at high velocity. Vibrational sum-frequency generation spectroscopy is used to monitor, in real time, the dynamics of a self-assembled monolayer of probe molecules covalently bound to the metal layer. Shock compression dynamically disorders the monolayer. The subsequent return to the ordered state can be discerned with picosecond time resolution and angstrom spatial resolution.

**PHYS 120 [742298]: Ultrafast dynamics of liquids in nanoporous glasses**

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**Abstract**

The study of the structure and dynamics of liquids at interfaces is made challenging by the relative paucity of interfacial molecules as compared to those in the bulk. Our group's approach to overcoming this difficulty has been to study liquids confined in materials with high surface areas. In this talk we will present some of the latest results of our ultrafast optical Kerr effect studies of liquids confined in nanoporous sol-gel glasses. This technique allows us to develop a molecular-level picture of how liquid structure and dynamics are influenced by the presence of curved interfaces. We will discuss the influence of molecular shape and surface curvature on the dynamics of weakly-wetting liquids and the role of surface interactions on the dynamics of wetting and networked liquids.

**PHYS 121 [747389]: Can fluid flow be used to drive surface-mounted altitudinal rotors?**

Dominik Horinek, Deborah L. Casher, Lukas Kobr, Thomas F. Magnera, Douglas Caskey, and **Josef Michl**, Department of Chemistry, University of Colorado, Boulder, CO 80309, [horinek@eefus.colorado.edu](mailto:horinek@eefus.colorado.edu), [michl@eefus.colorado.edu](mailto:michl@eefus.colorado.edu)

**Abstract**

Having demonstrated in the laboratory and by computer modeling that altitudinal surface-

mounted molecular rotors can be prepared and turned by outside electric field, we now ask whether they can be driven by a stream of liquid or gas. We shall describe the results of molecular dynamics simulations as well as progress towards finding an answer by experiment.

### **PHYS 122 [744472]: Solvation dynamics in confined and interfacial water**

**Branka M. Ladanyi**<sup>1</sup>, James Faeder<sup>2</sup>, Lucimara R. Martins<sup>3</sup>, and Munir S. Skaf<sup>3</sup>. (1)

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#### **Abstract**

In bulk liquids, solvation dynamics (SD) usually occurs primarily through reorientation of the surrounding solvent molecules. In heterogeneous environments, other solvation mechanisms, associated with changes in the location of the solute relative to the interface, are possible and can play an important role. In this talk, I will describe the results of our molecular dynamics computer simulation studies of SD in two different heterogeneous systems: the aqueous phase of reverse micelles and the water-zirconia interface. Our reverse micelle model is designed to represent microemulsions formed by Aerosol-OT (AOT), an anionic surfactant. Negatively charged chromophores are repelled by the AOT headgroups, while the positively charged ones are attracted to them. Because of this, the two types of chromophores reside in different environments within the reverse micelles. The impact of this fact as well as of the effects of confinement and of the size of the water pool on SD in reverse micelles will be discussed. In its ground electronic state, the coumarin 343 (C343) chromophore is adsorbed on the surface of zirconia nanoparticles in aqueous solution. In its electronically excited state, C343 becomes more attractive to water, which leads to its partial desorption. Our results on the contributions of this process to SD as well as for the structure and dynamics of water at the zirconia interface will be presented.

### **PHYS 123 [755725]: Exploiting polarization in nonlinear optical measurements of biological interfaces**

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#### **Abstract**

The unique nonlinear optical properties of chiral interfaces suggest a wealth of nascent structural information in studies of biological interfaces can be mined from polarization-dependent second harmonic and sum-frequency spectroscopic measurements. A key theme in our research is the development of novel and intuitive approaches for acquiring polarization measurements in SHG and SFG and for relating these macroscopic measurements back to molecular and surface structure. Using relatively simple measurements acquired with a novel ellipsometric polarization analysis method, we have demonstrated that chiroptical phenomena observed in SHG and SFG surface measurements can be interpreted using simple orientational models. These results suggest that nonlinear optical measurements can yield exquisite structural information in studies of biological interfaces. For example, by taking advantage of the symmetry properties present in biological surface films, the refractive index of the interfacial layer can be measured directly by SHG to four significant figures with no adjustable parameters, resolving a long-standing issue

regarding the appropriate choice of the interfacial optical constants in polarization analysis using SHG and SFG.

**PHYS 124 [766949]: Abiotic synthesis of homochiral oligopeptides via “symmetry breaking” processes at the air/liquid and solid/liquid interfaces**

**Meir Lahav**<sup>1</sup>, I. Rubinstein<sup>1</sup>, G. Jose-Nery<sup>1</sup>, G. Bolbach<sup>2</sup>, R. Eliash<sup>1</sup>, and I. Weissbuch<sup>1</sup>. (1)

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**Abstract**

The origin of chirality in the biological world is one of the yet unsolved problems in prebiotic chemistry and early evolution. The problem of symmetry breaking is usually tackled on the basis of two different research directions: the one deals with the origination of an initial enantiomeric excess (e.e.); the second focus on the amplification of this e.e. up to a theoretical degree of homochirality. Of particular interest is the pre-biotic formation of homochiral biopolymers, such as primordial polypeptides, and polynucleotides by amplification processes. Current theories suggest that such polymers had been formed at surfaces of minerals or within primitive amphiphilic self-assemblies in the form of vesicles or micelles that serve as pre-biotic proto-cells. Several routes of symmetry breaking had been elaborated. We shall present a plausible way for attaining spontaneous symmetry breaking by a two-step process comprising self-segregation of racemates into enantiomeric and racemic domains within 2-d and 3-d crystalline architectures, followed by lattice controlled chemical transformations. This methodology will be followed by description of experiments where racemic mixtures of oligopeptides of homochiral sequence were produced from monomers of activated amino-acids, either within monomolecular films at the air/water interface or via heterogeneous reactions at the solid/liquid interfaces of racemic 3-d crystals. Homochiral oligopeptides of single handedness have been generated by poly-condensation of non-racemic mixtures of monomers of low enantiomeric imbalance at the air/water interface and within a membrane-like environment in the form of uncompressed Langmuir phospho-lipid monolayers.

**PHYS 125 [750019]: Computational study of the dynamics and thermodynamics of room-temperature ionic liquids**

**Claudio J. Margulis**, Department of Chemistry, University of Iowa, Iowa City, IA 52242, claudio-margulis@uiowa.edu

**Abstract**

Green chemistry ionic liquids are interesting for three reasons. (1) They can dissolve a wide range of polar and nonpolar organic and inorganic molecules. (2) Although they are liquids at room temperature, their vapor pressure is negligible. (3) New chemical reactions are being discovered that can only be carried out in these solvents. We have recently studied structural and dynamical properties of 1-alkyl-3-methylimidazolium hexafluorophosphate (where alkyl=hexyl, octyl, decyl, dodecyl) using molecular dynamics. We find that the radial distribution functions that couple anions and cations are more structured when alkyl substituent chains are longer. We also find that diffusion constants for anions and their corresponding cations are highly correlated. We find that large cavities, if present in the liquid, can have very long lifetimes. At least two

different time scales for the decay of energy fluctuations in the liquid are observed after a neutral apolar diatomic probe molecule is photo-excited into a dipolar excited state. Fast sub-picosecond relaxation occurs after which correlations decay in approximately 0.1 ns.

### **PHYS 126 [752758]: Cluster-based approaches to extended systems**

**Mark S. Gordon**, Ames Lab/Iowa State University, 201 Spedding Hall, Ames, IA 50011, Fax: 515-294-5204, mark@si.fi.ameslab.gov

#### **Abstract**

Cluster and embedded cluster methods have attracted increasing attention as an efficient means for accurately addressing problems related to the condensed phase. Two such methods are the effective fragment potential (EFP) method, developed for exploring solvent effects and liquid behavior, and the SIMOMM (Surface Integrated Molecular Orbital Molecular Mechanics) method for treating surface science and heterogeneous catalysis. Each of these methods will be briefly introduced, followed by the presentation of interesting applications.

### **PHYS 127 [744820]: Structure and dynamics of magic number protonated water clusters**

**Kenneth D. Jordan**, Richard A. Christie, and Jun Cui, Dept. of Chemistry and Center for Molecular and Materials Simulations, University of Pittsburgh, Pittsburgh, PA 15260, jordan@pitt.edu

#### **Abstract**

Vibrational spectra have recently been measured for the  $H^+(H_2O)_n$ ,  $n = 6-29$ , clusters using predissociation. [J.-W. Shin, N.I. Hammer, E.G. Diken, M.A. Johnson, R.S. Walters, T.D. Jaeger, M.A. Duncan, R.A. Christie and K.D. Jordan, Science, in press]. The spectra in the free OH stretch region displays a change in character at the  $n = 21$  magic number cluster which has been interpreted in terms of a distorted  $(H_2O)_{20}$  dodecahedron with an encaged  $H_2O$  molecule and an Eigen-type  $H_3O^+$  ion on the surface. Surprisingly, the measured spectra do not show evidence of photodissociation near  $2500\text{ cm}^{-1}$  where the absorption due to the Eigen cation is expected to occur. This has led us to investigate theoretically the barriers for proton transfer and the pathways for  $H_2O$  evaporation. These results are combined with MD simulations to examine energy relaxation upon excitation of the various OH stretch modes of the  $n = 21$  cluster.

### **PHYS 128 [754747]: Quantum molecular dynamics with gaussians**

**Vladimir Mandelshtam** and Pavel Frantsuzov, Chemistry Department, University of California at Irvine, Irvine, CA 92697, Fax: 949-824-8571, mandelsh@uci.edu

#### **Abstract**

The Gaussian propagation method for computation of equilibrium density matrices for a quantum multi-particle system is developed. The density matrix is expressed in terms of Gaussian resolution, in which each Gaussian is propagated independently in imaginary time (inverse temperature) starting at the classical limit corresponding to a high temperature. For a N-particle system a Gaussian is represented by its center, the width matrix and the scale, all treated

as dynamical variables. The Monte Carlo method is used to generate the initial distribution of Gaussians at high temperature, where the density matrix is purely classical. At not-very-low-temperatures the method is surprisingly accurate for a range of model systems including the case of double-well potential. Ideally, a single Gaussian propagation requires numerical effort comparable to propagation of a single classical trajectory for a system with  $(N^2+3N+3)/2$  degrees of freedom. However, the success of the method depends on whether various Gaussian integrals needed for calculation of, e.g, the potential matrix elements or pair correlation functions could be evaluated efficiently. Techniques to accomplish these goals are presented. The method is applied to van der Waals clusters. In addition, it is demonstrated that the approximation using a direct product of single-particle Gaussians, rather than a fully coupled Gaussian, yields much less accurate results.

### **PHYS 129 [749239]: Coupled quantum-continuum mechanics methods for studying the mechanical response of materials**

**Emily A Carter**, Departments of Chemistry and Biochemistry and Materials Science and Engineering, University of California, Los Angeles, Box 951569, Los Angeles, CA 90095-1569, Fax: 310-267-0319, eac@chem.ucla.edu

#### **Abstract**

Development and applications of methods that couple first principles density functional theory to continuum solid mechanics will be presented. These multiscale algorithms include on-the-fly coupling of a linear scaling DFT to the local quasicontinuum method and informed continuum methods where the DFT input is calculated ahead of time due to the expense of the DFT that must be used to attain the required accuracy. We present two applications, one of nano-indentation of an aluminum alloy and shock-induced phase transformations in Fe that produce a complex microstructure. In the latter case, we are able to explain both an observed pressure hysteresis loop and the scatter in measured bcc to hcp transition pressures. The metastable microstructure formed accounts for the former, while the latter is proposed to be due to modest amounts of shear present in the experiments.

### **PHYS 130 [749088]: Quantum shuttles**

**Eric R Bittner**, Department of Chemistry, University of Houston, !36 Fleming Building, Houston, TX 77204, Fax: 713-743-2709, bittner@uh.edu

#### **Abstract**

There have been a number of recent experiments measuring the electronic transmission through single small molecules such as hydrogen. What is amazing in these experiments is the appearance of vibrational side bands in the current/voltage (IV) curves. In my talk I will discuss a simple 3 site model in which the center site is free to oscillate between the two terminal sites, which in turn are coupled to semiinfinite leads. Electronic transmission occurs by tunneling between from one site to the next. We will discuss both the coherent regime where the electron tunnels through the system via vibronic states in which the electronic part of the wavefunction is delocalized over all three sites (as in a superexchange mechanism) . We will then examine the incoherent regime where the electron first hops from the first to the center site, is shuttled over to the third site. Finally, we will compare an exact calculation with a simple mixed quantum/classical description of this system.

## PHYS 131 [755488]: Importance of interfacial chemistry in ultrathin ferroelectrics

Alexie M. Kolpak, Na Sai, and Andrew M. Rappe, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, PA 19104, kolpak@sas.upenn.edu

### Abstract

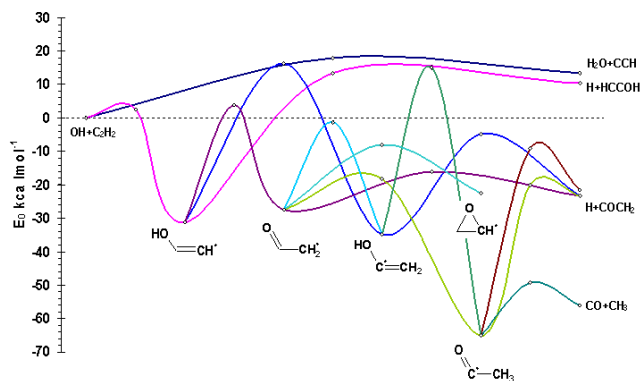
The properties of ferroelectric thin films have recently excited a great deal of interest as numerous potential applications in integrated microelectronics have been envisioned. However, with industrial demand driving the development of ever smaller devices, it has become important to understand how the desirable properties of such films behave as atomic scale dimensions are approached. Here we present an ab initio study of the ferroelectric properties of ultrathin PbTiO<sub>3</sub> and BaTiO<sub>3</sub> capacitors. We demonstrate the existence of a ferroelectric ground state in films of < 10 Å, and we show that, with the right choice of ferroelectric and electrode materials, the magnitude of the polarization can be equal to or greater than that of the bulk ferroelectric material. Our results also illustrate the importance of the different chemical interactions at the two ferroelectric/electrode interfaces in stabilizing ferroelectricity. Taking these interactions into account, we propose an electrostatic model to describe ferroelectricity in ultrathin films.

## PHYS 132 [752927]: A theoretical investigation of the reaction kinetics of acetylene with OH radicals

Juan P. Senosiain, James A. Miller, and Stephen J. Klippenstein, Combustion Research Facility, Sandia National Laboratories, PO Box 969, MS 9055, Livermore, CA 94551-0969, Fax: 925-294-2276, jpsenos@sandia.gov

### Abstract

The reaction of acetylene with hydroxyl radicals is important in combustion processes and in the chemistry of terrestrial and planetary atmospheres. The doublet potential energy surface of C<sub>2</sub>H<sub>2</sub> and OH was calculated with the RQCISD(T) method and extrapolated to the infinite basis set limit, and is shown in the Figure.



Previous theoretical and experimental studies have identified direct abstraction as the main pathway at high temperatures and low pressures, despite its substantial energy barrier and

endothermicity. At low temperatures and high pressures the reaction proceeds via a series of association, isomerisation and decomposition steps. To investigate the reaction kinetics on this complex potential energy surface we employ an RRKM/master equation approach, conserving both energy and angular momentum, and treating some transition states variationally. Rate coefficients for the different channels are calculated over a broad temperature and pressure range and compared to existing data.

### **PHYS 133 [750055]: Ab initio modeling of neutral and cationic Hg-arene complexes**

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#### **Abstract**

Neutral and cationic complexes of Hg with benzene, thiophene and furan are studied by means of *ab-initio* coupled cluster and second order perturbation theory calculations. Hg and benzene form a Mulliken outer  $\pi$  complex for which CCSD(T) calculations predict a binding energy of -0.15 eV. The (Hg-benzene)<sup>+</sup> complex has a minimum energy structure in the form of a  $\pi$  complex with a binding energy of -1.73 eV as predicted by MP2 calculations. (Hg-benzene)<sup>2+</sup> forms a  $\sigma$  complex with a binding energy of -6.54 eV. This complex may pass through a  $\pi$  complex transition state with an activation energy of only 0.25 eV; therefore it is predicted that the Hg<sup>2+</sup> cation may hop from C atom to C atom around the ring. Hg forms Mulliken outer  $\pi$  complexes with furan and thiophene, both with binding energies of -0.13 eV as predicted by CCSD(T). Interesting potential energy surfaces are presented for Hg-thiophene and Hg-furan cationic complexes.

### **PHYS 134 [755416]: Characterization of aqueous solutions of amphiphilic triblock copolymers: Micellar and hydrogel phases**

**Karen E. Steege**, Christian D. Grant, Tatiana A. Fadeeva, Michelle R. DeRitter, and Edward W. Castner Jr., Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, NJ 08854-8087, Fax: 732-445-5312, [ksteege@rutchem.rutgers.edu](mailto:ksteege@rutchem.rutgers.edu)

#### **Abstract**

Pluronic F88 is an amphiphilic A-B-A triblock copolymer that forms aqueous micelles and hydrogels. In aqueous solution, the hydrophobic cores are comprised of the B blocks of poly(propylene oxide) and the hydrophilic exteriors are formed by the two poly(ethylene oxide) A blocks. We present results on 5 and 25 w/v % aqueous solutions of F88 to probe the micellar and hydrogel phases, respectively. Different temperature responses are observed for the F88 hydrogels using experiments that probe microscopic versus macroscopic length scales. Pre-aggregation phenomena are observed at a temperature 15-20 degrees below T<sub>gel</sub>, using microscopic measurements including DLS and fluorescence. Specific probing of interior versus exterior environments is achieved using a series of coumarin fluorescence probes of varying hydrophobicity. Shear viscosity measures macroscopic gelation at higher temperatures. Interestingly, thermodynamic measurements by DSC show heat flow occurring predominantly at the pre-aggregation temperatures. Investigations of micelle temperature responses will also be reported.

### **PHYS 135 [752265]: Coarse-grain molecular dynamics simulations of hydraphile cation translocation across a lipid bilayer**

**Goundla Srinivas**, department of Chemistry, Center for Molecular Modeling, Department of Chemistry, University of Pennsylvania, 231S, 34th Street, Philadelphia, PA 19104, srini@cmm.upenn.edu, **Carlos F. Lopez**, Department of Chemistry, Center for Molecular Modeling, University of Pennsylvania, and **Michael L. Klein**, Department of Chemistry, University of Pennsylvania

#### **Abstract**

The mechanism of hydraphile assisted cation translocation across a lipid bilayer is investigated by means of coarse-grain molecular dynamics simulations. We find that hydraphiles with appropriate length adopt a channel-like conformation in agreement with recent experimental studies. In trans membrane conformation, hydraphiles assist ion-passage across the bilayer via a mechanism that is found to be rare but effective. The observed time for ion translocation is approximately 0.3 ns. Trajectory studies reveal that the translocating ion shows relatively less mobility in the vicinity of the hydraphile ring when compared to that in bulk water. The present coarse grain simulations confirmed that hydraphile molecules with a chain length matching the bilayer thickness can assist ion transport, whereas hydraphiles having a shorter or longer chain length fail to do so. In addition, the present simulation study underscores the necessity of a polar central relay for a molecule to act as a translocation facilitator.

### **PHYS 136 [755622]: Coarse-grain molecular dynamics study of nanotube insertion in lipid bilayers**

**Bernd Ensing**<sup>1</sup>, **Steve O. Nielsen**<sup>2</sup>, **Preston B. Moore**<sup>3</sup>, and **Michael L. Klein**<sup>2</sup>. (1) Department of Chemistry, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104, Fax: 215-573-6233, ensing@cmm.upenn.edu, (2) Department of Chemistry, Center for Molecular Modeling, University of Pennsylvania, (3) Department of Chemistry & Biochemistry, University of the Sciences in Philadelphia

#### **Abstract**

Synthetic peptide nanotubes were recently demonstrated to have strong anti-microbial properties. The mechanism for their anti-bacterial activity is still largely unknown. Nanotubes have been proposed to disrupt the lipid bilayer via a carpet-like mode of membrane permeation. Alternatively, nanotubes can form trans-membrane multimeric entities that form nanopores which conduct water, ions and small molecules. To simulate the slow process of insertion of nanotubes from the aqueous phase into the membrane and the aggregation into multimeric entities, we apply a coarse-grain model. This allows us to study the nanotube behavior as a function of generic properties, such as the size, shape and hydrophobic/hydrophilic matching.

### **PHYS 137 [755185]: Collisions of alcohols and D2O with molten NaOH/KOH**

**David J Castro**, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706, castro@chem.wisc.edu, and **Gilbert M. Nathanson**, Department of Chemistry, University of Wisconsin

## **Abstract**

Molecular beam and mass spectroscopy techniques have been used to explore the surface chemistry of molten NaOH/KOH at its eutectic composition of 51/49 mol %. We find that the fraction of gaseous  $\text{CH}_3(\text{CH}_2)_n\text{OD}$  molecules that thermalize, undergo proton exchange, and desorb at  $T_{\text{liq}} \sim 463$  K remains roughly constant for  $n = 1$  to 3. However, this D->H exchange reaction channel is absent for  $\text{CD}_3\text{OD}$  and  $\text{D}_2\text{O}$ . The experiments also show that lowering the incident energy of the gas molecules increases the fraction of thermalized molecules on the surface but does not alter the D->H exchange fraction. Preliminary sticking probability measurements for 1-propanol at high incident energy indicate that about half of the incident molecules undergo decomposition. Indirect evidence for decomposition into  $\text{H}_2\text{O}$  and carbonaceous species is found by the enhanced desorption of  $\text{H}_2\text{O}$  as the liquid is exposed to the alcohols. Finally, after alcohol scattering, a decrease in the intensity of inelastically scattered high energy argon atoms suggests that the surface roughness of the NaOH/KOH mixture increases with alcohol exposure. These preliminary results provide evidence that extremely basic liquids interact with incoming protic gases through multiple pathways, including immediate desorption, D->H exchange, and irreversible reactions that generate  $\text{H}_2\text{O}$  and decompose the alcohol.

## **PHYS 138 [753068]: Combining spectroscopic and computational studies to understand water structure at liquid/liquid interfaces**

**Dave S. Walker**, Cathryn L. McFearin, and Geraldine L. Richmond, Department of Chemistry, University of Oregon, 210 Willamette Hall, Eugene, OR 97403-1253, [dswalker@darkwing.uoregon.edu](mailto:dswalker@darkwing.uoregon.edu)

## **Abstract**

Vibrational sum-frequency spectroscopy (VSFS) has recently emerged as a very powerful tool for the study of interfaces. For many years, computational methods such as Monte Carlo (MC) or molecular dynamics (MD) have also been used to study the structure of interfacial water. The combination of VSFS experiments with MD simulations allows for a multifaceted approach in which the success of the simulations can be validated by comparing experimental and computational sum-frequency spectra, and elusive details behind experimental results can be further explored using molecular-scale knowledge of the condensed-phase environment provided by simulations. In this work we use this approach to create a description of interfacial water structure at liquid/liquid surfaces, and discuss recent results on how this structure is affected by the properties of the organic liquid phase.

## **PHYS 139 [751922]: Dissociation dynamics of vibrationally excited trans-perp HOONO**

**Ian M. Konen**, Ilana B. Pollack, Eunice X. J. Li, and Marsha I. Lester, Department of Chemistry, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104-6323, [ikonen@sas.upenn.edu](mailto:ikonen@sas.upenn.edu)

## **Abstract**

Peroxynitrous acid ( $\text{HOONO}$ ) is formed by the reaction of OH and  $\text{NO}_2$  in conjunction with the more stable isomer, nitric acid. Determination of the  $\text{HOONO}$  binding energy is essential for atmospheric models to correctly budget these two reactive species. We have used an infrared

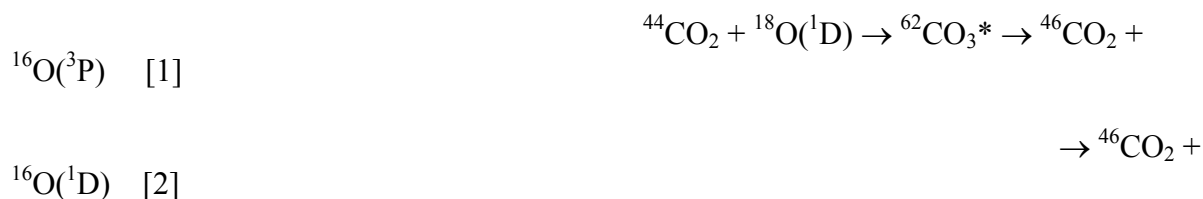
pump-ultraviolet probe technique to obtain an accurate measurement of the binding energy of the trans-perp (tp) conformer. The OH internal state distribution resulting from dissociation of tp-HOONO ( $2\nu_{\text{OH}}$ ) was measured by laser-induced fluorescence, and found to be consistent with a prior distribution. A dissociation energy of 16.2 kcal/mol was obtained from the best fit of the data, in good agreement with the value inferred from the highest observed channel. This information, combined with the best available *ab initio* value of 3.4 kcal/mol for the relative conformational stability, provides an estimate of 19.6 kcal/mol for the binding energy of the more stable cis-cis conformer.

### **PHYS 140 [746319]: Dynamics of CO<sub>2</sub> + O(<sup>1</sup>D) and implications for isotope exchange between O<sub>3</sub> and CO<sub>2</sub>**

**Annalise L. Van Wyngarden**<sup>1</sup>, Mark J. Perri<sup>1</sup>, Alexander M Mebel<sup>2</sup>, Jim J. Lin<sup>3</sup>, Yuan T. Lee<sup>4</sup>, and Kristie A. Boering<sup>5</sup>. (1) Department of Chemistry/Boering Group, University of California, Berkeley, CA 94720, Fax: 510-643-2156, vanwyn@uclink.berkeley.edu, (2) Department of Chemistry, Florida International University, (3) Institute of Atomic and Molecular Sciences, Academia Sinica, (4) President, Academia Sinica, (5) Departments of Chemistry and Earth and Planetary Science, University of California, Berkeley

#### **Abstract**

The dynamics of the isotope exchange reaction between CO<sub>2</sub> and <sup>18</sup>O(<sup>1</sup>D) have been investigated in crossed-molecular beam experiments, revealing that the exchange can proceed through two channels:



In addition, branching ratios (O(<sup>3</sup>P):O(<sup>1</sup>D)) and conventional mass-dependent isotope effects for the decomposition of <sup>62</sup>CO<sub>3</sub> via [1] and [2] as a function of collision energy have been calculated using high level *ab initio* and statistical theories. These new experimental and theoretical results are highlighted and included in a photochemical kinetics model to assess their impact on the transfer of the unusual heavy isotopic signature of ozone to CO<sub>2</sub> through O(<sup>1</sup>D) in laboratory experiments and the stratosphere.

### **PHYS 141 [753058]: Effects of surface charge and ionic strength on polarity at liquid surfaces**

**Carmen L. Beildeck**, William H. Steel, and Robert A. Walker, Department of Chemistry and Biochemistry, University of Maryland, College Park, Building 091, College Park, MD 20742, Fax: 301-314-9121, beildeck@wam.umd.edu

#### **Abstract**

Solvation at liquid-liquid interfaces plays a key role in interfacial solute concentration,

conformation and reactivity. Our research uses second harmonic generation (SHG) and unique surfactants dubbed "molecular rulers" to examine interfacial solvent polarity. Molecular rulers consist of a solvatochromic probe and a charged headgroup connected by an alkyl chain of variable length. The charged headgroup anchors the molecule to the aqueous phase while the alkyl spacer length controls the position of the chromophore within the interface. An SHG spectrum of the adsorbed ruler shows the excitation energy of the solvatochromic probe thus allowing us to profile polarity across the interface. Recent experiments show how surface charge and ionic strength affect interfacial polarity. We use both anionic and cationic molecular rulers adsorbed to liquid interfaces in the presence of inorganic salts to probe the extent to which electric fields penetrate into adjacent phase.

### **PHYS 142 [763916]: Formyl radical (HCO): Elementary reactions and the role in hydrocarbon combustion**

**Lev N. Krasnoperov**<sup>1</sup>, Evgeni N. Chesnokov<sup>1</sup>, Harald Stark<sup>2</sup>, and A. R. Ravishankara<sup>3</sup>. (1) Department of Chemistry and Environmental Science, New Jersey Institute of Technology, University Heights, Newark, NJ 07102, krasnoperov@adm.njit.edu, (2) NOAA, Aeronomy Laboratory and CIRES, University of Colorado, (3) Aeronomy Laboratory, NOAA

#### **Abstract**

The sensitivity of the hydrocarbon combustion parameters such as the flame propagation speed, the ignition delay, etc.) to the rate constants of several elementary reactions of formyl radical (HCO) has been analyzed. Two major mechanisms, characteristic for lean and rich mixtures, that have opposite impacts on the combustion parameters, were revealed. Several elementary reactions of formyl radical of combustion importance were studied using laser photolysis coupled to sensitive UV-Vis absorption spectroscopy:  $\text{HCO} \rightarrow \text{H} + \text{CO}$  (1),  $\text{HCO} + \text{HCO} \rightarrow$  products (2),  $\text{HCO} + \text{CH}_3 \rightarrow$  products (3). Reaction 1 was studied over the buffer gas (He) pressure range 0.8 – 100 bar and the temperature range 498 - 769 K. Reactions 2 and 3, as well as the UV absorption spectrum of HCO, were studied at 298 K and 591 K, and the buffer gas (He) pressure of 1 bar. New rate constants were obtained. The impact on the combustion modeling is discussed.

### **PHYS 143 [754292]: Ground state of small protonated water clusters**

**Massimo Mella**<sup>1</sup>, David C. Clary<sup>2</sup>, Michael L. Klein<sup>3</sup>, Jer Lai Kuo<sup>3</sup>, and Michael Taylor<sup>2</sup>. (1) Department of Chemistry, Cardiff University, P.O. Box 912 Main Building, Park Place, CF10 3TB Cardiff, United Kingdom, Fax: +44-29-2087-4030, MellaM@cf.ac.uk, (2) Physical and Theoretical Chemistry Laboratory - Department of Chemistry, University of Oxford, (3) Department of Chemistry, Center for Molecular Modeling, University of Pennsylvania

#### **Abstract**

Protonated water clusters  $(\text{H}_2\text{O})_n\text{H}^+$  ( $n=1-6$ ) have been studied employing the OSSn potentials and electronic structure theory.

Zero point energy has been calculated by means of the harmonic approximation and using the exact diffusion Monte Carlo (DMC) method. At 0 K, the anharmonicity decreases the total and binding energy by 1.5-5.5 mhartree (0.9-3.5 Kcal/mol) .

Despite the lower potential energy of the cage-like clusters, the inclusion of the anharmonic zero point energy reverses the stability ranking suggesting the branched species to be more stable. Transition state barriers between cyclic and branched clusters are found to be low (1-4 kcal/mol) and easily surmounted during the DMC simulations.

Mono-deuterated cluster energies indicates D to be preferentially located close to the charged moiety without belonging to it.

Classical interconversion rates between different linear and branched isomers are also computed using a novel and efficient molecular dynamics approach.

### **PHYS 144 [754288]: H-atom elimination of n-propyl and iso-propyl radicals: A photodissociation study**

Weidong Zhou, Yan Yuan, and **Jingsong Zhang**, Department of Chemistry and Air Pollution Research Center, University of California, Riverside, CA 92521-0403, weidongz@citrus.ucr.edu, jingsong.zhang@ucr.edu

#### **Abstract**

The H-atom elimination channels in the UV photodissociation of jet-cooled n-propyl and iso-propyl radicals are studied in the region of 237 nm using the high-n Rydberg-atom time-of-flight technique. Upon excitation to the 3p state by the UV photolysis radiation, n-propyl radical and iso-propyl radical dissociate into the H atom and propene products. The product center-of-mass translational energy release of both n-propyl and iso-propyl radicals have bimodal distributions. The H-atom product angular distribution in n-propyl is anisotropic (with  $\beta \sim 0.5$ ), and that in iso-propyl is isotropic. The overall average translational energy release is  $\sim 0.27E_{\text{avail}}$  for n-propyl and  $\sim 0.21E_{\text{avail}}$  for iso-propyl. The bimodal translational energy distributions indicate two dissociation pathways: (i) a unimolecular dissociation pathway from the ground-state propyl after internal conversion from the 3p state, and (ii) a repulsive pathway directly connected with the excited state of the propyl radical. Isotope labeling has also been carried out. The possible photodissociation mechanisms will be discussed.

### **PHYS 145 [755642]: Halide salts at the liquid water-air interface probed by second harmonic generation (SHG)**

**Poul B. Petersen**, Justin C. Johnson, Kelly P. Knutsen, and Richard J. Saykally, Department of Chemistry, University of California, Berkeley, CA 94720, Fax: 510-642-8566, poul@uclink.berkeley.edu

#### **Abstract**

The increased surface tension of salt solutions relative to pure water has resulted in the general conception that the water surface is completely void of ions, as interpreted through the Gibbs adsorption equation. However, a more detailed molecular picture presented by recent molecular dynamics simulations show that the upper-most molecular layers of the interface can exhibit preferential anion adsorption depending on the polarizability of the ion. We present direct experimental evidence of positive adsorption of iodide ions at the water-air interface, as well as an observed change in the water structure of aqueous solutions of the smaller halide salts, using the surface specific second harmonic generation (SHG) technique.

### **PHYS 146 [755221]: Heats of formation of acetyl and propanoyl radicals and ions with threshold photoelectron photoion coincidence**

**Hideya Koizumi**<sup>1</sup>, Elizabeth A. Fogleman<sup>2</sup>, James P Kercher<sup>1</sup>, Balint Sztaray<sup>3</sup>, and Tomas Baer<sup>3</sup>. (1) Department of Chemistry, University of North Carolina at Chapel Hill, CB#3290, Chapel Hill, NC 27599-3290, Fax: 919-843-6041, koizumi@email.unc.edu, (2) Chemistry, University of North Carolina, (3) Department of Chemistry, University of North Carolina

#### **Abstract**

Threshold photoelectron photoion coincidence (TPEPICO) was used to determine the 0 K onsets for dissociative photoionization of acetone, butane-dione, butanone and pentanone in order to experimentally measure the heats of formation of the acetyl and propanoyl radicals and ions to a precision of  $\pm 1$  kJ/mol. The analysis of the breakdown diagram (fractional abundance of energy selected ions) required modeling both the first dissociation as well as the second dissociation of butanone. The measured onsets for the reactions:  $C_2H_5COCH_3 + h\nu \rightarrow C_2H_5CO^+ + CH_3\cdot + e^-$  and  $C_2H_5COCH_3 + h\nu \rightarrow CH_3CO^+ + C_2H_5\cdot + e^-$  yield a new heat of formation of butanone, which is 8 kJ/mol lower than the literature value. *Ab initio* calculations support this lower value. This study has provided accurate heats of formation of the acetyl and propanoyl radical and ion heats of formation.

### **PHYS 147 [753583]: Ion-molecule reactions within mass selected clusters**

**James Garvey**, Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14260-3000, Fax: 716-645-6963, garvey@buffalo.edu

#### **Abstract**

Experiments utilizing a molecular beam/tandem quadrupole mass spectrometer apparatus will be presented which clearly indicate how solvation can effect the course of chemical reactivity in the course of ion-molecule reactions within gas phase clusters. We will first focus on ion clusters containing *p*-difluorobenzene and methanol. For this particular system, HF elimination is only observed when  $n > 2$  for cluster ions of the type  $(CH_3OH)_n C_6H_4F_2^+$ . However, for the first time, we observe that for  $n > 5$ , elimination of two HF's can also occur from the same *p*-difluorobenzene, generating the *p*-dimethoxybenzene cation. The fact that a new reaction channel can open up as a function of cluster size will be explained due to hydrogen bonding changes around the central *p*-difluorobenzene reagent cation. We will then discuss a wide range of ion-molecule chemistry with binary cluster ions containing either NO and  $CH_3OH$  or NO and  $H_2O$ . In both of these system, new chemical reactions are also observed and can be explained via consideration of the cluster ion structure and the hydrogen bonding around the central cation.

### **PHYS 148 [749464]: Kinetic and mechanistic studies of aqueous phase reactions of Cl atoms and $Cl_2^-$ radicals with organic sulfur compounds of atmospheric interest**

**Lei Zhu**, School of Earth & Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Dr, Atlanta, GA 30332-0340, Fax: 404-894-5638, lei.zhu@eas.gatech.edu, J. Michael Nicovich, School of Chemistry & Biochemistry, Georgia Institute of Technology, and Paul H. Wine, Schools of Chemistry & Biochemistry and Earth & Atmospheric Sciences, Georgia Institute of Technology

## Abstract

The kinetics of aqueous phase reactions of Cl and Cl<sub>2</sub><sup>-</sup> radicals with four organic sulfur species of atmospheric interest: CH<sub>3</sub>S(O)CH<sub>3</sub> (DMSO), CH<sub>3</sub>(O)S(O)CH<sub>3</sub> (DMSO<sub>2</sub>), CH<sub>3</sub>S(O)O<sup>-</sup> (MSI), and CH<sub>3</sub>(O)S(O)O<sup>-</sup> (MS) have been investigated at 295 K using a laser flash photolysis - long path UV-visible absorption technique. Except for the DMSO + Cl and DMSO + Cl<sub>2</sub><sup>-</sup> reactions, all measured rate coefficients are reported for the first time. Cl is found to be more reactive than Cl<sub>2</sub><sup>-</sup> with each sulfur compound, and the less oxidized species DMSO and MSI are found to be more reactive with both radicals than the more oxidized species DMSO<sub>2</sub> and MS. Reactions with chlorine radicals in cloud droplets can be a significant atmospheric degradation pathway for DMSO and MSI. The absorption spectrum of the DMSO-Cl adduct, produced from the DMSO + Cl<sub>2</sub><sup>-</sup> reaction, is reported; the peak extinction coefficient ( $\epsilon$ ) is found to be  $4.2 \times \epsilon(\text{SO}_4^-)$  at  $\lambda \approx 390$  nm.

## PHYS 149 [755331]: Photodissociation of CH<sub>3</sub>OCl and HNO<sub>3</sub> at 248 nm

**Maria J. Krisch**<sup>1</sup>, Laura R. McCunn<sup>1</sup>, Matthew Reid<sup>1</sup>, Kana Takematsu<sup>1</sup>, Laurie J. Butler<sup>1</sup>, Frances Blase<sup>2</sup>, and Jinian Shu<sup>3</sup>. (1) The Department of Chemistry, The University of Chicago, The James Franck Institute, 5640 S. Ellis Ave, Chicago, IL 60637, krisch@uchicago.edu, (2) Department of Chemistry, Haverford College, (3) Chemical Sciences Division, Ernest Orlando Lawrence Berkeley National Laboratory

## Abstract

We use photofragment translational spectroscopy in a crossed laser-molecular beam apparatus with tunable VUV photoionization detection to probe the 248 nm photodissociation of methyl hypochlorite (CH<sub>3</sub>OCl) and nitric acid (HNO<sub>3</sub>), two atmospheric compounds. The primary CH<sub>3</sub>OCl photodissociation channel is direct dissociation of the O-Cl bond to produce Cl atoms and CH<sub>3</sub>O radicals with a narrow range of internal energies. A model predicts from conservation of angular momentum that nearly all of the internal energy is in rotational excitation; accordingly, no secondary dissociation is observed. CH<sub>3</sub>OCl thus serves as a photolytic precursor of CH<sub>3</sub>O radicals with high and well-defined rotational and translational energies. Only one product channel was definitively observed in HNO<sub>3</sub>: cleavage to form OH + NO<sub>2</sub>, with an upper limit on the contribution from the O + HONO formation channel of 3%. These data contribute an independent measurement to a literature debate regarding the branching between these two channels.

## PHYS 150 [764677]: Pressure-dependent automated mechanism generation for high-conversion ethane pyrolysis

**David Matheu**, Physical and Chemical Properties Division, National Institute of Standards and Technology, 100 Bureau Dr. Stop 8380, Gaithersburg, MD 20899, david.matheu@nist.gov, Anthony M. Dean, Chemical Engineering Dept, Colorado School of Mines, and Jeffrey M. Grenda, Corporate Strategic Research, ExxonMobil Research and Engineering

## Abstract

Advancement in the design of such important gas-phase processes as hydrocarbon cracking, combustion, and partial oxidation hinges, in part, on the development of correct, detailed chemical kinetic models. But the complexity of the required chemical mechanisms can make them extremely difficult to construct by hand. Modelers turn to software algorithms that build

these large mechanisms automatically, but the current tools are too limited to treat many difficult systems. We describe an algorithm, called “XMG-PDep,” which overcomes these limitations with a comprehensive approach to pressure-dependent reactions, and a rational, flux-based criteria for truncating mechanism growth. Application to the challenging, high-conversion ethane pyrolysis system of Glasier and Pacey reveals a highly complex, interconnected kinetic model for the formation and destruction of possible soot precursors (such as acetylene, butadiene, and benzene). Proper treatment of the pressure-dependence is essential to the predictions of the soot precursor concentrations. We discuss rate-limiting steps for these precursors.

### **PHYS 151 [766951]: Simulations of solubilities in supercritical fluids**

**Zemin Su**, Department of Chemistry, Penn State University, 152 Davey Laboratory, University Park, PA 16802, Fax: 814-863-5319, [zus102@psu.edu](mailto:zus102@psu.edu), and **Mark Maroncelli**, Department of Chemistry, Pennsylvania State University

#### **Abstract**

We present calculations of solubilities (or solvation free energies) of a range of solutes in supercritical fluids (SCF) by all-atom Molecular Dynamics (MD) simulation. Comparison to measured solvation free energies of the solutes anthracene, iodoform, and iodine in SCF CO<sub>2</sub>, ethane and Xe shows that standard potential models do a reasonable job of reproducing experimental data. We also use these simulations to provide insight into the nature of solubilities in SCFs. We find that cavity formation energies are qualitatively similar to the predictions of hard-sphere theories. Using the hard-sphere system as a reference, we find that the solvation free energies controlling solubility are relatively unaffected by local density augmentation. This insensitivity results from cancellation of opposing effects on the enthalpy and entropy of solvation, both of which are quite sensitive to the local density in the vicinity of a solute.

### **PHYS 152 [766972]: Structure and dynamics of protein-water interfaces**

**Wolfgang Doster**, R. Gebhard, and A. Soper, Physics Department E 13, Technical University of Munich, James Franckstrasse, Garching D-85748, Germany, Fax: 49-89-289-12473, [wdoster@ph.tum.de](mailto:wdoster@ph.tum.de)

#### **Abstract**

The stability of protein structures depends crucially on interactions with interfacial water. But whether water is actually stabilizing or destabilizing, whether hydrophilic or hydrophobic forces dominate, is not yet clear. We use a combination of neutron diffraction and dynamic scattering experiments, to probe molecular motions and structure near protein-water interfaces. Effects of temperature and pressure on protein-water and water-water correlations are studied. We present a moment analysis of displacement distributions on a pico-second time scale as water changes from a glassy state at 180 K to liquid behaviour (figure). The transition involves an extended time region of anomalous diffusion due to partially localized states. Interfacial water has a plasticizing effect on protein residues, which leads to limited translational displacements. Using radial distribution functions we discuss changes of the myoglobin-water system in response to pressure. At the unfolding transition protein-water motions slow down, indicating stronger bonds in the denatured state. Pressure-induced shifts in the water structure and release of internal voids mainly destabilize the native state. Lit. W. Doster et al. Chem. Phys. 292 (2003) 383 W. Doster et al. Faraday Disc. 103 (1996) 269

## **PHYS 153 [755586]: Temperature-dependent feature sensitivity analysis for combustion modeling**

**Zhenwei Zhao**, Juan Li, Andrei Kazakov, and Frederick L. Dryer, Mechanical and Aerospace Engineering Department, Princeton University, Princeton, NJ 08540, Fax: 609-258-1939, [zzhao@princeton.edu](mailto:zzhao@princeton.edu)

### **Abstract**

Sensitivity analysis is widely used in kinetic modeling, typically with the relative importance of each reaction to a particular observable determined by perturbing only the A-factor for the individual reaction rate coefficients. This approach does not yield any information on individual reaction temperature dependent parameters. Many combustion processes, for example, premixed flames, involve large ranges of temperature, and the relative importance of individual reaction rates may vary considerably throughout.

An extension of conventional sensitivity analysis is developed and shown to provide a means of identifying the temperature windows of importance for the individual reaction rate coefficients and specific experimental conditions. The derived information is demonstrated to be of significance in optimizing complex reaction schemes against multiple experimental targets. The developed methodology is shown to apply more broadly to evaluating the effects of any temperature-dependent property on predicted observables, for example the relative importance of diffusive transport coefficients on flame speed.

## **PHYS 154 [753562]: Theoretical studies of the O<sub>2</sub> + methane, ethane and propane reactions**

**Diego Troya** and George C. Schatz, Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, Fax: 847-491-7713, [troya@chem.northwestern.edu](mailto:troya@chem.northwestern.edu)

### **Abstract**

The reactions of ground state molecular oxygen with short chain alkanes have been studied using electronic structure calculations and molecular dynamics simulations. The energy profiles of the  $O_2 + RH \rightarrow HO_2 + R$  (H abstraction) and  $O_2 + RH \rightarrow RO_2 + H$  (H elimination) reactions ( $R=CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ ) have been characterized using *ab initio* and density functional theory methods. Both reactions are strongly endothermic, and whereas H abstraction does not show any barrier other than the reaction energy, the lowest energy H elimination saddle point is reminiscent of that of an SN2 reaction. Direct dynamics calculations have been carried out using the classical trajectory method in conjunction with a high-quality semiempirical Hamiltonian. Excitation functions, products energy and angular distributions reveal the importance and dynamics characteristics of the different reaction channels as well as the microscopic mechanisms of reaction. Our calculations at hyperthermal collision energies provide additional insight into low Earth orbit (LEO) erosion of materials through collisions with  $O_2$  present in orbit and also reveal that the contribution to reaction of hyperthermal  $O_2$  contaminating hyperthermal atomic oxygen beams produced through laser detonation of  $O_2$  and used in experiments of LEO erosion is negligible compared to the reactivity of atomic oxygen. The dynamics features of inelastic events are compared to those of inelastic collisions of short chain alkanes with Ar and atomic oxygen to gain deeper insight into collisional energy transfer in hyperthermal energy regime.

**PHYS 155 [752925]: Use of near-IR spectroscopy in HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in evaluating photodissociation pathways relevant to atmospheric chemistry**

**Daniel K. Havey**, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Boulder, CO 80309, Fax: 303-492-5894, havey@colorado.edu, Karl J. Feierabend, Department of Chemistry, University of Colorado, Paul E Hintze, Kennedy Space Center, and Veronica Vaida, Department of Chemistry and Biochemistry, University of Colorado

**Abstract**

This work combines new observations in the vibrational spectra of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> with previous experimental work to assess the validity of the “local mode” approximation with regard to O-H stretching modes. New experimental values for vibrational anharmonicities have been extracted from the measurements made in this study and interesting trends are discussed. Vibrational overtone frequency and intensity trends are compiled and compared to other experimentally studied systems. In addition, the presence of high-energy mode coupling involving O-H stretches is examined in the context of vibrationally-mediated photodissociation. This work examines the usefulness of IR/NIR spectra in elucidating physical pictures for these processes. These extensions have a direct connection to the abundance of recent work on overtone-induced photodissociation of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> in the atmosphere.

**PHYS 156 [754038]: USEXAS studies of NiOETPP in solid and solvated forms**

**Ting Guo** and Fang Shan, Department of Chemistry, UC Davis, One Shields Ave., Davis, CA 95616, Fax: 530-752-8995, tguo@ucdavis.edu

**Abstract**

We have recently developed an ultrafast x-ray based spectroscopic method (USEXAS, or ultrafast selected energy x-ray absorption spectroscopy) with which we can study chemical dynamics of certain x-ray absorbing atoms, usually the relatively heavier elements in a compound. The pre-edge and near edge x-ray absorption spectra are used to determine the local structures of the absorbing elements. In this talk, we will discuss the immediate chemical environmental differences between Ni atoms in Ni octaethyl-tetraphenylporphyrin (NiOETPP) in its solid and solvated forms.

**PHYS 157 [755047]: UV dissociation of ethyl ethynyl ether and the production of the ketenyl radical (HCCO): A study by Time-Resolved FTIR Emission Spectroscopy**

**William McNavage**<sup>1</sup>, Michael Wilhelm<sup>1</sup>, Raymond Groller<sup>1</sup>, and Hai Lung Dai<sup>2</sup>. (1) Department of Chemistry, The University of Pennsylvania, 321 S. 34th Street, Philadelphia, PA 19104, Fax: 215-898-8926, mcnavage@sas.upenn.edu, (2) Department of Chemistry, University of Pennsylvania

**Abstract**

Excited electronic and vibrational states and their associated dynamics of ketenyl (HCCO), a radical that plays an important role in the oxidation of most C<sub>2</sub> hydrocarbons and a major

intermediate in the formation of CO and CO<sub>2</sub> in the troposphere, have been characterized. HCCO was generated through UV dissociation of Ethyl Ethynyl Ether (EEE), a precursor chosen for unity quantum yield in the production of HCCO. IR emission from photoproducts following the EEE dissociation was detected by sub-microsecond time-resolved Fourier transform emission spectroscopy. Two previously unknown vibrational modes, the  $\nu_1$  CH stretch and the symmetric  $\nu_3$  CCO stretch of HCCO have been identified. Nascent product distribution from the EEE photo-dissociation indicates that some of the HCCO produced are in the first excited quartet state, which then dissociates following collision assisted internal conversion.

**PHYS 158 [764673]: Vacuum-UV dissociative photoionization dynamics of perfluorocarbons by ion imaging with synchrotron radiation**

Ramsey Smith, Howard University, Washington, DC 20059, ramsmith@howard.edu

**Abstract**

Perfluorocarbons (PFCs) are of major interest in global warming due to their long atmospheric lifetimes and infrared cross sections in the absorption windows of CO<sub>2</sub> and H<sub>2</sub>O. The only plausible removal of PFCs from the Earth's atmosphere is by reactions with radicals or photochemical processes occurring in the mesosphere and ionosphere. One of the most important photochemical processes is vacuum ultraviolet dissociative ionization and it is the principle decay mechanism that follows the excitation of these molecules. The dissociative ionization of the perfluorocarbons c-C<sub>4</sub>F<sub>8</sub> and C<sub>2</sub>F<sub>6</sub> was studied using the photofragment-imaging technique coupled with a vacuum ultraviolet synchrotron radiation on beamline 9.0.2 at the Advanced Light Source Laboratory (ALS), Lawrence Berkeley National Laboratory (LBNL). The objective of this study is to understand the dissociative photodynamics of the perfluorocarbon and their ions. A direct inversion of the raw data will yield translational energy, speed and angular distributions for the products.

**PHYS 159 [747973]: Vibration-rotation distribution of the nascent NO resulting from the N(<sup>2</sup>D)+O<sub>2</sub>-->NO+O reaction**

James W. Duff<sup>1</sup>, Hoang Dothe<sup>1</sup>, and Ramesh D. Sharma<sup>2</sup>. (1) Spectral Sciences, Inc, 4 Fourth Avenue, Burlington, MA 01803, Fax: 781-270-1161, duff@spectral.com, (2) Space Vehicles Directorate/VSBYB, Air Force Research Laboratory, 29 Randolph road, Hanscom AFB, MA 01731-3010, Fax: 781-377-8900, ramesh.sharma@hanscom.af.mil

**Abstract**

The SABER (Sounding of the Atmosphere by Broad band Emission Radiometry) instrument aboard TIMED (Thermosphere, Ionosphere, Mesosphere, Energetics, and Dynamics) satellite has recorded 5.3 mm emission from NO during recent space-weather events that is 20-30 times enhanced over its ambient level in the 90-300 km tangent altitude range and over almost the entire globe. Nitric oxide is known to be produced during such events by the N(2D)+O<sub>2</sub>-->NO+O reaction. To model the emission observed by SABER, and the energy budget of the atmosphere, one must know not only the vibration-rotation distribution of the nascent NO produced by this reaction but also rate of relaxation of these vibration-rotation levels. We have calculated new PES at the CASSCF/MP2 (Complete Active Space Self Consistent Field followed by 2nd order Moller-Plesset perturbation) level using the quadruple z basis set of gaussian functions. Our new PES do not give barriers in the entrance channels of the lowest

lying doublet NO<sub>2</sub> surfaces, consistent with the low temperature measurements of the rate coefficients of the N(2D)+O<sub>2</sub> reaction. We report the vibration-rotation distribution of nascent NO obtained by performing the quasiclassical trajectory calculations over these surfaces.

**PHYS 160 [753990]: Vibrational spectroscopy of the OCCN radical through Time Resolved FTIR Emission Spectroscopy and 2-D Cross Spectra Correlation Analysis**

**William McNavage**<sup>1</sup>, Hai Lung Dai<sup>2</sup>, and William P. Dailey<sup>2</sup>. (1) Department of Chemistry, The University of Pennsylvania, Philadelphia, PA 19104, Fax: 215-898-8926, mcnavage@sas.upenn.edu, (2) Department of Chemistry, University of Pennsylvania

**Abstract**

The CN stretch ( $\nu_1$ ) and CO stretch ( $\nu_2$ ) of the cyanooxomethyl radical (OCCN), an important radical species in urban atmospheres, were observed for the first time at 2093 cm<sup>-1</sup> and 1774 cm<sup>-1</sup> respectively. The vibrational modes were detected by nanosecond Fourier-transform infrared emission spectroscopy of vibrationally excited radicals generated through 193 nm photodissociation of carbonyl cyanide, CO(CN)<sub>2</sub>, methyl cyanofornate CO(CN)(OCH<sub>3</sub>), and pivaloyl cyanide CO(CN)(CH<sub>3</sub>)<sub>3</sub>. Assignment of the vibrational modes was accomplished by using the two-dimensional cross-spectra correlation analysis and *ab initio* calculations.

**PHYS 161 [753954]: Probing gene expression in living *Sacchomyce cerevisiae* cells**

**Jialu Yin**, Ji Yu, Jie Xiao, and X. Sunney Xie, Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, MA 02138, Fax: 617-496-8709, jialuyin@fas.harvard.edu

**Abstract**

We demonstrated that the modified beta-galactosidase (beta-gal) reporter system can be applied to *Saccharomyce cerevisiae* to probe stochastic gene expression events. In this reporter system, short-lived beta-gal hydrolyzes a fluoregenic and membrane-permeable substrate and degrades inside a cell in a few minutes. Benefiting from the enzymatic amplification of the hydrolysis product, we were able to observe individual fluorescence bursts corresponding to stochastic expression in single *Sacchomyces cerevisiae* cells. This work demonstrated for the first time continuous realtime monitoring of gene expression in individual eukaryotic cells with extremely low-copy sensitivity for proteins, and provides a foundation for gene expression profiling as well as system-wide studies of eukaryotic gene regulation.

**PHYS 162 [746744]: In vitro and in vivo single molecule imaging and spectroscopy**

**Shimon Weiss**, Chemistry and Biochemistry, University of California Los Angeles, 607 Charles Young Drive East, Los Angeles, CA 90095, Fax: 310-267-4672, sweiss@chem.ucla.edu

**Abstract**

Advances in single molecule (SM) studies performed at UCLA by the Single Molecule

Biophysics group will be reviewed. These include SM studies of: (1) protein folding; (2) initiation of transcription by e-coli RNA polymerase; (3) analysis of macromolecular (protein-protein, protein-DNA) interactions; (4) accurate quantification of proteins and nucleic acids in complex solutions; (5) targeting and detection of individual proteins in live cells using peptide-coated quantum dots; and (6) their utilization to the study of lipid rafts in membranes and cellular trafficking.

### **PHYS 163 [767646]: Imaging information in DNA**

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#### **Abstract**

*Abstract text not available.*

### **PHYS 164 [752972]: Electron transfer dynamics at a single-molecule-single-nanoparticle junction**

Wanhee Goh, Jianchang Guo, and **Tianquan Lian**, Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, GA 30322, Fax: 404-727-6586, tlian@emory.edu, tlian@emory.edu

#### **Abstract**

Single molecule spectroscopy was used to study electron transfer(ET) dynamics of single rhodamin(donor)-bridge-nanoparticle (acceptor) complexes. Single molecule emission from donor molecule was confirmed by the observed blinking behavior, fluorescence spectrum, and excitation polarization dependence. The rate of forward electron transfer from molecule excited state to nanoparticles was measured by time-correlated single photon counting and the rate of back electron transfer was determined by the off-time correlation function of single molecule trajectories. Comparison of complexes with different methylene bridges reveals bridge length dependent ET rates. The dependences of these rates on particle size and bridge length are being fully investigated. In addition to static heterogeneity, dynamic heterogeneity will also be investigated in complexes with long bridges, which may serve as a model system for examining how conformation dynamics affect ET rate on the single molecule level.

### **PHYS 165 [747421]: Probe conformational dynamics of proteins by single molecule fluorescence and phosphorescence**

**Robin M. Hochstrasser**, Erwen Mei, Jianyong Tang, A. Sharonov, and Feng Gao, Chemistry Department, University of Pennsylvania, Philadelphia, PA 19104, hochstra@sas.upenn.edu

#### **Abstract**

Experiments of probing conformational dynamics of proteins by single molecule fluorescence and phosphorescence will be presented. A various methods developed to immobilize single proteins or dye molecules in nonperturbing environments will be discussed. Directly visualizing nano-structures of sample by single molecule imaging or tracking method will also be presented.

### **PHYS 166 [753140]: Single molecules as nanoscale probes of microenvironments**

**Edward S. Yeung**, Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, IA 50011, Fax: 515-294-0266, yeung@ameslab.gov

#### **Abstract**

Due to intense research in the past few years there are now many approaches to single molecule detection. The next step is to design experiments to answer specific molecular questions that cannot be addressed by many-molecule experiments. Single fluorescent molecules in free solution can be followed directly as they diffuse and photodecompose. We are able to monitor single chromatographic events at various liquid/solid interfaces. This represents direct verification of the statistical theory of chromatographic retention.

### **PHYS 167 [755240]: Single molecule detection and fluorescence characterization of 3-MI, a guanosine analog**

Jason E. Sanabia<sup>1</sup>, **Lori S. Goldner**<sup>1</sup>, Pierre Antoine Lacaze<sup>1</sup>, and Mary E. Hawkins<sup>2</sup>. (1) Physics Laboratory, National Institute of Standards and Technology, 100 Bureau Dr, Gaithersburg 20899, lori.goldner@nist.gov, (2) Pediatric Oncology Branch, National Cancer Institute

#### **Abstract**

Nucleic acid analogs offer advantages over linker-attached dyes in the study of DNA binding and dynamics. For single molecule studies, the use of analogs has been thwarted by their smaller absorption cross sections, absorption maxima in the UV, and photobleaching. We investigate the potential of 3-MI [3-Methyl-8-(2-deoxy- $\beta$ -D-ribofuranosyl)isoxanthopterin], in the study of single DNA molecules. 3-MI is a pteridine-based fluorescent guanosine analog with quantum yield 0.88 (monomer), absorbance maximum at 350 nm, emission maximum at 430 nm and a reputation for being chemically robust and photostable. We use fluorescence correlation spectroscopy to characterize the fluorescence properties of 3-MI monomer. For one-photon excitation, single-molecule detection of 3-MI monomer is possible with signal-to-background ratio of 5, a count rate per molecule above 4 kHz, and a quantum yield of photobleaching of 0.0025. Upon incorporation into DNA, a dark state becomes evident and count rate is reduced but individual molecules are still detectable.

### **PHYS 168 [755193]: Single particle mass spectrometry of aerosol particles using vacuum ultra violet lasers**

**Tomas Baer** and Roger E. Miller, Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, Fax: 919 962 2388, baer@unc.edu

#### **Abstract**

The detection and identification of organic species in aerosol particles remain difficult problems primarily because most ionization methods result in significant fragmentation of the organic ions. This problem is particularly severe when dealing with complex mixtures of organic species, which are often found in atmospheric aerosols. Photoionization with a low photon energy but high intensity source is an ideal method for gently ionizing organic species. When combined with complete vaporization of the aerosol particle prior to vuv photoionization, it is possible to

detect organic species quantitatively. Detection efficiencies of various species in aerosol particles will be reviewed and the approach will be applied to various kinds of aerosol particles.

**PHYS 169 [753302]: Interfacial vibrational spectroscopic studies of acids, oleic to sulfuric: Application to atmospheric aerosol chemistry**

**Heather C. Allen**, Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, OH 43210, Fax: 614-292-1685, allen@chemistry.ohio-state.edu

**Abstract**

Air-liquid interfaces were investigated using broad bandwidth and scanning sum frequency generation spectroscopies. Several organics and acids were investigated at the air-liquid interface. Studies of the air-aqueous oleic acid interface during reaction with gas-phase ozone will be presented in addition to studies of several aqueous ammonium and sulfuric acid air-liquid interfaces.

**PHYS 170 [764210]: Real-time broadband sum frequency studies of the heterogeneous interaction of partially oxidized alkenes with ozone**

**Andrea B. Voges** and **Franz M. Geiger**, Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, geigerf@chem.northwestern.edu, geigerf@chem.northwestern.edu

**Abstract**

Biogenic emissions are composed of volatile organic compounds (VOCs) that can react with atmospheric OH and ozone. These gas phase reactions produce partially oxidized organic species that are often surface active. Using the surface-selective nonlinear optical spectroscopy sum frequency generation (SFG) in broadband mode, we studied the heterogeneous interaction of ozone with a partially oxidized VOC, namely limonene, adsorbed to silica surfaces. The experiments are carried out in situ, at 1 atm, and at room temperature. Molecular reorientation during interaction of limonene with ozone is monitored by recording the methyl- and methylene infrared transitions in real time. The interaction of limonene with ozone at high concentrations reaches a steady state within minutes, whereas steady state is achieved only after several hours when using small ozone concentrations.

**PHYS 171 [748268]: Photodissociation action spectroscopy at organic aerosol particle-air interfaces**

**Sergey Nizkorodov**, Anthony Gomez, Ao Lin, David Whitt, and Ahmad Alshawa, Department of Chemistry, University of California at Irvine, 516 Rowland Hall, Irvine, CA 92697, Fax: 949-824-8571, nizkorod@uci.edu

**Abstract**

Photodissociation action spectra of organic solid-air and liquid-air interfaces representative of atmospheric aerosol particles are studied. The approach is to excite laboratory-generated aerosol particles (or suitable polycrystalline samples) with a radiation source and detect the escaping gas-phase photochemical products as a function of the excitation frequency. The resulting action spectrum carries information on the chemical identities of the absorbers and photochemical

products, thus providing insights into the reaction mechanism. The research is focused on aerosol particles consisting of an organic surfactant on an inorganic substrate such as sub-monolayers of partially oxidized unsaturated fatty acids on sea-salt aerosol particles.

### **PHYS 172 [763955]: Atmospheric aerosol chemical and microphysical properties as measured by an aerosol mass spectrometer**

**Douglas R. Worsnop**<sup>1</sup>, John T. Jayne<sup>2</sup>, Manjula Canagaratna<sup>1</sup>, Leah R. Williams<sup>1</sup>, Jay G. Slowik<sup>3</sup>, E. Spencer<sup>3</sup>, Paul Davidovits<sup>3</sup>, P. Decarlo<sup>4</sup>, A. Huffman<sup>5</sup>, and Jose L. Jimenez<sup>6</sup>. (1) Center for Aerosol and Cloud Chemistry, Aerodyne Research, Inc, Billerica, MA 01821, Fax: 978-663-4918, [worsnop@aerodyne.com](mailto:worsnop@aerodyne.com), (2) Center for Aerosol and Cloud Chemistry, Aerodyne Research, Inc, (3) Department of Chemistry, Boston College, (4) Chemistry and Biochemistry, University of Colorado at Boulder, (5) Department of Chemistry & Biochemistry, University of Colorado, (6) Dept. of Chemistry & Biochemistry, University of Colorado

#### **Abstract**

Assessment of atmospheric aerosol impacts on global climate change and health effects requires detailed study of aerosol chemical and microphysical properties, including size dependent chemistry and morphology. A recently developed Aerosol Mass Spectrometer (AMS) measures size and compositionally resolved mass loadings of ambient aerosol. Sub-micron particles are aerodynamically focused into high vacuum. Aerodynamic diameter is determined via particle time-of-flight measurement. Flash vaporization followed by 70 eV electron impact ionization mass spectrometry provides universal and quantitative determination of mass loading for the non-refractory components (that vaporize at 600-900C). Mass spectra clearly separate inorganic (sulfate, nitrate, ammonium, chloride) and organic components. Additional beam width and light scattering probes measure shape and optical properties. These measurements provide correlation of sub-micron particle size, shape and chemical composition. Combining physical mobility diameter (measured via SMPS) provides detailed information of particle morphology and density. A detailed study of fractal soot particles demonstrates these capabilities, which can be directly applied to ambient atmospheric observations.

### **PHYS 173 [752662]: Oxidation of size-selected soot nanoparticles**

**Amanda Nienow**, Jeffrey T. Roberts, and Henry Ajo, Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455, Fax: 612-626-7541, [nienow@chem.umn.edu](mailto:nienow@chem.umn.edu)

#### **Abstract**

The kinetics of reaction between soot nanoparticles and simple oxidants, including molecular oxygen, were studied by tandem differential mobility analysis. The particles were extracted from a laminar diffusion flame fueled by ethene and air. Reactions were studied at atmospheric pressure over broad ranges of temperature (room temperature - 1100 °C), initial particle size (30 nm mobility diameter), and oxygen partial pressure (0 -1 atm). Measurements as a function of oxygen partial pressure establish that the oxidation kinetics are not first-order in oxygen pressure ( $P_{O_2}$ ). Rather, the oxidation rate increases rapidly and linearly with  $P_{O_2}$  between 0 and 0.05 atm, and then more slowly with  $P_{O_2}$  between 0.05 and 1 atm. Temperature dependent measurements suggest that the origin of this behavior is associated either with a surface saturation effect or with a mechanism involving the rapid interconversion of two distinct oxidation sites.

### **PHYS 174 [764680]: Oxidation of PAHs at the air-aqueous interface**

B.T. Mmereki, Susannah Handley, and **D. James Donaldson**, Department of Chemistry, University of Toronto, 80 St. George St., Toronto, ON M5S 3H6, Canada, mmereki@chem.utoronto.ca, jdonalds@chem.utoronto.ca

#### **Abstract**

Many atmospherically important chemical processes are believed to occur at the interface between the air and aqueous phases. We have developed a laser-induced fluorescence method to study chemistry involving polycyclic aromatic hydrocarbons (PAHs) at the air-aqueous interface. Adsorptive uptake of several PAHs as well as the kinetics of their oxidation reactions with gas phase oxidants have been measured at the pure water surface, and the surfaces of water coated with an organic film, and ice. These results will be presented; the oxidation kinetics suggest that aqueous surface oxidation of PAHs by ozone could be as important as the gas phase oxidation by OH.

### **PHYS 175 [752079]: Infrared spectroscopy of large molecular aggregates in helium droplets**

**Andrey F. Vilesov**, Department of Chemistry, University of Southern California, Los Angeles, CA 90089, Fax: 213-740-3972, vilesov@usc.edu

#### **Abstract**

In this talk experiments on spectroscopy of large molecular clusters ( $N = 100 - 1000$ ) in helium droplets will be presented. Recent developments of experimental techniques at USC, including the use of pulsed infrared lasers will be introduced.

### **PHYS 176 [748858]: Superfluid solvation in helium and parahydrogen clusters**

**Francesco Paesani**, Robert Zillich, Yongkyung Kwon, and K. Birgitta Whaley, Department of Chemistry and Pitzer Center for Theoretical Chemistry, University of California, Berkeley, CA 94720-1460

#### **Abstract**

We present a detailed study of quantum and superfluid solvation for five different linear molecules inside  $^4\text{He}$ , parahydrogen ( $p\text{H}_2$ ), and mixed  $^4\text{He}/p\text{H}_2$  clusters, using zero and finite temperature quantum Monte Carlo methods. Ground state properties (energetics and structures) of clusters containing a single molecule with variable numbers of  $^4\text{He}$  and  $p\text{H}_2$  species are calculated using the diffusion Monte Carlo method. Excited rotational states are calculated with the POITSE approach, which evaluates a zero temperature imaginary time correlation function by Monte Carlo and subsequently inverts this to obtain energetics. Fitting to sets of rotational energy levels allows the effective rotational and distortion constants of the embedded molecules to be extracted as a function of the cluster size. We focus on clusters containing between  $N=1$  and  $N\approx 20$   $^4\text{He}$  or  $p\text{H}_2$  species, i.e., up to a full solvation shell, around the dopant molecule. The size evolution of the spectroscopic constants is discussed with reference to related path integral Monte Carlo calculations that reveal the onset of exchange permutations. We show that at small  $N$  these quantum clusters correspond to van der Waals complexes and that as  $N$  increases a transition to a quantum solvated molecule occurs which is characterized by the onset of superfluidity in the solvating species both  $^4\text{He}$  and  $p\text{H}_2$ . Vibrational shifts of the embedded

molecule will also be presented as a function of  $N$  and discussed in terms of the structural properties of the clusters.

### **PHYS 177 [751009]: Infrared spectroscopy of small helium clusters**

**A. Robert McKellar**, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, ON K1A 0R6, Canada, Fax: 613-991-2648, robert.mckellar@nrc.ca

#### **Abstract**

Direct infrared absorption spectroscopy is used to probe small He droplets (2 to 20 atoms) doped with a single chromophore molecule (CO, CO<sub>2</sub>, OCS, N<sub>2</sub>O). The clusters are generated in a pulsed supersonic jet expansion and probed with a tunable IR diode laser. A slit-shaped jet nozzle gives sharper spectral lines and higher effective cluster temperatures (>0.5 K), while a pinhole nozzle gives more clustering and lower temperatures (>0.1 K). The results are relevant to studies of larger He nanodroplets and to the nature of superfluidity in small systems. For example, with CO<sub>2</sub> as the chromophore, the cluster rotational moment of inertia increases from 1 to 5 added He atoms as expected for a semirigid body. However, addition of atoms 6 to 10 results in a paradoxical decrease in the moment of inertia, indicating a decoupling of the helium atoms from the CO<sub>2</sub> rotation. Analogous results have also been obtained for hydrogen clusters.

### **PHYS 178 [752123]: Liquid helium droplets: 0.4 Kelvin nanoscale test tubes**

**C. Michael Lindsay**, Paul Stiles, Jeremy M. Merritt, William K. Lewis, Gary E. Doublerly, and Roger E. Miller, Department of Chemistry, University of North Carolina at Chapel Hill, B5 Venable Hall, CB#3290, Chapel Hill, NC 27599, Fax: 919-843-6041, cmlindsa@alumni.uchicago.edu

#### **Abstract**

Over the past decade, liquid helium droplets have emerged as a powerful tool in which to conduct chemistry at ultra-low temperatures. The large heat capacity of the droplets coupled with their high thermal conductivity effectively freezes out the internal and translational degrees of freedom of the reactants, before they undergo a reaction. The corresponding chemistry in these cases is often unusual; in helium solvated reactions, the long-range dipolar and van der Waals forces guide the reactant's approach trajectory along the reaction surface, and due to the low initial kinetic energy, frequently trap the products in metastable states. Recent experiments in our lab have encompassed a wide range of systems including metal clusters, free radical pre-reactive complexes, metastable van der Waals polymers, salt nanocrystals, amino acid-water complexes, and semiconductor clusters. The extraordinary pace at which this work is expanding into other fields is due to the generality of the technique as well as the droplet's ability to act as both a powerful synthetic tool and a characterization technique.

### **PHYS 179 [747986]: Theoretical studies of cold open-shell molecular complexes**

Gerrit C. Groenenboom, Guillaume Dhont, Jacek A. Klos, Wilfried Zeimen, and **Ad van der Avoird**, Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld 1, Nijmegen 6525 ED, Netherlands, Fax: +31 24 3653041, avda@theochem.kun.nl

#### **Abstract**

A main interest of our group is the *ab initio* study of (spin-dependent) interactions in open-shell

Van der Waals clusters and of the effects of non-adiabatic coupling between multiple asymptotically degenerate potential surfaces. With the use of these *ab initio* data we computed the bound levels of chemical reaction precursors such as Cl(<sup>2</sup>P)-HCl and F(<sup>2</sup>P)-HF that can be studied spectroscopically in cold helium clusters. In view of the interest in the open-shell species NH(<sup>3</sup>Σ) as a candidate ultracold molecule--it has a large dipole moment, so it can be decelerated and trapped electrostatically and it is paramagnetic, so it can be caught in a magnetic trap--we studied the NH-He complex and we are currently computing accurate intermolecular potential surfaces for the quintet, triplet, and singlet states of the NH-NH dimer. Elastic collisions with He are employed in buffer gas cooling of the NH molecules, spin-changing inelastic collisions determine the magnetic trap loss. The relevant rate constants have been obtained from scattering calculations by Krems et al. The NH-NH interactions are important when the temperature has dropped sufficiently, the He atoms are pumped off, and the temperature must be further reduced by evaporative cooling. The spin-dependent interactions between the two triplet NH molecules determine the efficiency of cooling versus trap loss. We plan to compute the relevant cross sections and rate constants by means of low-energy scattering calculations and we hope to be able to report the results at the meeting.

**PHYS 180 [754637]: Product distribution of the CH<sub>3</sub> + OH reaction using repetitive time-of-flight mass spectrometry**

**Christopher Fockenberg**, Chemistry Department 555A, Brookhaven National Laboratory, Upton, NY 11973, Fax: 631-344-5815

**Abstract**

Although the kinetics of the reaction between methyl and hydroxyl radicals has been studied numerous times, a complete understanding of the product distribution has not yet emerged. In particular, questions about the role of CH<sub>2</sub>O isomers as products remain open. The energies of almost all transition states involved in this reaction lie within a few kcal/mol of the entrance channel making a number of product channels accessible (most likely: CH<sub>3</sub>OH, <sup>1</sup>CH<sub>2</sub> + H<sub>2</sub>O, and HCOH + H<sub>2</sub>) leading to a product distribution that is sensitive to pressure and temperature. In this talk, experimental data acquired using our time-of-flight mass spectrometry apparatus, with which multiple species can be observed simultaneously, will be presented. The study focused on determining product yields for the CH<sub>2</sub>O isomers at low pressures and temperatures around 300 K and 650 K. The chemistry was analyzed *via* simulation calculations, using an iterative fitting routine based on a combination of genetic and simplex algorithms, which is capable of fitting many and diverse parameters such as rate constants, their temperature dependences, initial concentrations and signal-to-concentration conversion factors.

**PHYS 181 [752964]: Kinetics and products of radical-radical reactions of hydrocarbon-based radicals**

**Vadim D. Knyazev**, Irene R. Slagle, Stanislav I. Stoliarov, Eugene V. Shafir, and Mikhail G. Bryukov, Department of Chemistry, The Catholic University of America, 620 Michigan Ave., N.E, Washington, DC 20064, Fax: 202-319-5381, knyazev@cua.edu

**Abstract**

Radical-radical reactions are among the very important elementary processes occurring in the oxidation and pyrolysis of hydrocarbons and substituted hydrocarbons. However, experimental

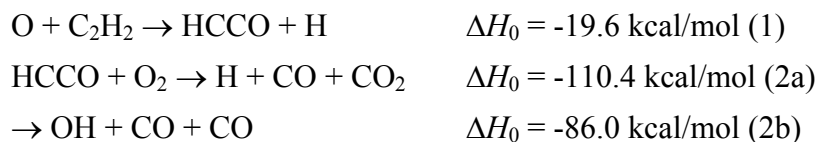
information on them is rather sparse and, in many cases, controversial. This lack of data is primarily due to the difficulties encountered in experimental studies of reactions between radicals. This presentation will focus on our experimental studies of the kinetics and products of a series of radical-radical reactions performed using the Laser Photolysis / Photoionization Mass Spectrometry technique. In all cases, rate constants were obtained as functions of temperature in direct real-time experiments over wide temperature ranges. The reactions studied include self reactions of C<sub>2</sub>H<sub>5</sub> and C<sub>3</sub>H<sub>3</sub> (propargyl) and cross-radical reactions of CH<sub>3</sub> with C<sub>2</sub>H<sub>3</sub>, C<sub>3</sub>H<sub>3</sub> (propargyl), C<sub>3</sub>H<sub>5</sub> (allyl), C<sub>2</sub>H<sub>5</sub>, n-C<sub>3</sub>H<sub>7</sub>, n-C<sub>4</sub>H<sub>9</sub>, and CCl<sub>3</sub> radicals. Product branching fractions of several reactions of this class were obtained as functions of temperature and pressure.

### **PHYS 182 [751119]: On the mechanism of the HCCO + O<sub>2</sub> reaction: Probing multiple pathways to a single product channel**

**David L. Osborn** and Peng Zou, Combustion Chemistry Department, Sandia National Laboratories, MS 9055, PO Box 969, Livermore, CA 94551-0969, Fax: 925-294-2276, dlosbor@sandia.gov

#### **Abstract**

The combustion of acetylene under lean conditions produces “prompt” CO<sub>2</sub>, meaning that CO<sub>2</sub> is formed with the same time constant as CO. A reaction sequence that could explain this observation is:



Product channel (2a) would produce prompt CO<sub>2</sub>, while channel (2b) would not. Using time-resolved Fourier transform infrared spectroscopy, we show that H + CO + CO<sub>2</sub> accounts for at least 90% of the reaction products at 298K, evidence that (2a) is the primary pathway for prompt CO<sub>2</sub> production in acetylene combustion.

However, the calculated potential energy surface for this reaction reveals several energetically allowed pathways through 3- and 4-membered ring intermediates that all lead to channel (2a). Utilizing isotopic labeling and state-specific product detection, we determine the relative flux through these different paths on the potential energy surface leading to H + CO + CO<sub>2</sub>.

These results call into question the common assumption that each observed product channel in a reaction arises from a single pathway on the potential energy surface.

This research is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences of the U.S. Department of Energy.

### **PHYS 183 [752273]: The reactions between NCO and simple alkyl radicals: Rate constants and products**

**Robert G. Macdonald**, Chemistry Division, Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60565, Fax: 630-252-9292, rgmacdonald@anl.gov

#### **Abstract**

The NCO radical is an important intermediate in the generation of NOX in combustion processes; however, there is a considerable lack of detailed information on the reactions of NCO with simple organic molecules, in particular open shell species. At a fundamental level, there are important issues to be addressed as to the influence of multiple electronic surfaces on the dynamics of radical-radical reactions. The reactions between NCO and simple alkyl radicals: H, CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> will be described. The radicals were produced by the 248 nm photolysis of CINCO and subsequent reaction of Cl atoms with RH to give the alkyl radical, R, and HCl. The temporal dependences of multiple species were followed by infrared-time-resolved absorption spectroscopy. The determination of rate constants and identification of possible product channels will be presented.

### **PHYS 184 [750964]: Theoretical kinetics studies of reactions related to the formation of the first aromatic ring**

**Stephen J. Klippenstein**<sup>1</sup>, James A. Miller<sup>1</sup>, Yuri Georgievskii<sup>1</sup>, and Lawrence B. Harding<sup>2</sup>. (1) Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551-0969, Fax: 925-294-2276, sjklipp@sandia.gov, (2) Chemistry Division, Argonne National Laboratory

#### **Abstract**

The results of a number of our recent theoretical studies related to the formation of the first aromatic ring will be discussed. These theoretical studies are based on high level ab initio determinations of the properties of the reaction path, sophisticated RRKM analyses of the microcanonical rates, and multiple-well multiple-channel master equation modeling of the temperature and pressure dependent rate coefficients. The focus will be on reactions of propargyl radical and of n-C<sub>4</sub>H<sub>3</sub>. We will discuss the formation of phenyl and benzene from these species as well as the formation of C<sub>3</sub>H<sub>3</sub> and n-C<sub>4</sub>H<sub>3</sub> from bimolecular reactants. The theoretical predictions indicate a dominant role for propargyl radical with at most a minor role for n-C<sub>4</sub>H<sub>3</sub>. Thus, we will also consider reactions that remove propargyl radical from the combustion environment. Finally, the formation of rings from allyl radical, from i-C<sub>5</sub>H<sub>3</sub>, and from i-C<sub>4</sub>H<sub>3</sub> will be briefly considered.

### **PHYS 185 [750091]: Pyrolysis of aromatic ions**

**Jürgen Troe**<sup>1</sup>, Abel Fernandez<sup>2</sup>, Vladimir G. Ushakov<sup>3</sup>, and Albert A. Viggiano<sup>2</sup>. (1) Institut für Physikalische Chemie, Universität Göttingen, Tammannstrasse 6, Göttingen D-37077, Germany, Fax: +49-551-393150, (2) Space Vehicles Directorate, Air Force Research Laboratory, (3) Institute of Problems of Chemical Physics, Russian Academy of Sciences

#### **Abstract**

A new method for studying the thermal dissociation of polyatomic molecular ions was developed. A turbulent ion flow tube has been built that can reach temperatures up to 900 K at

bath gas pressures from 15 to 700 Torr. Neutral aromatic molecules in this flow are transformed into aromatic radical cations by charge transfer in collisions with O<sub>2</sub><sup>+</sup>. The charge transfer produces chemically activated ions some of which dissociate and others are collisionally stabilized. After thermalization, the stabilized ions dissociate on a much slower time scale. The progress of the reaction is followed mass spectrometrically. The primary charge transfer kinetics, including stabilization of the excited intermediate by the buffer gas, and the pyrolysis are separated by varying both the neutral reagent concentration and the reaction time. The thermal dissociation rate constants are analyzed by unimolecular rate theory and compared with specific rate constants of energy-selected molecular ions and with results from an analysis of the chemical activation system.

### **PHYS 186 [743964]: Creating beakers without walls: Formation of deeply-supercooled binary liquid solutions from nanoscale amorphous solid films**

**Bruce D. Kay**<sup>1</sup>, Patrick Ayotte<sup>2</sup>, R. Scott Smith<sup>1</sup>, Glenn R. Teeter<sup>1</sup>, and Greg A. Kimmel<sup>1</sup>. (1) Fundamental Science Directorate, Pacific Northwest National Laboratory, K8-88, PO Box 999, Richland, WA 99352, Fax: 509-376-6066, bruce.kay@pnl.gov, (2) Département de Chimie, Université de Sherbrooke

#### **Abstract**

Supercooled liquids are metastable and their lifetimes are dictated by the kinetics for crystallization. Traditional experimental studies have used a variety of methods to suppress crystallization while cooling from the liquid phase. An alternate approach is to heat an amorphous solid above its glass transition temperature, T<sub>g</sub>, whereupon it transforms into a deeply-supercooled liquid prior to crystallization. We employ molecular beams, programmed desorption (both TPD and isothermal) and FTIR vibrational spectroscopy to synthesize and characterize compositionally tailored nanoscale films of glassy methanol and ethanol. We demonstrate that these films exhibit complete diffusive intermixing and suppressed crystallization when heated above T<sub>g</sub>. Furthermore, the resulting container-less liquids evaporate as continuously mixed ideal binary solutions while retaining their solid-like macroscopic shapes. This approach provides a new method for preparing deeply-supercooled liquid solutions in metastable regions of their phase diagram and for studying the kinetics of their phase separation and crystallization as they approach thermodynamic equilibrium. The applicability of this technique for studying aqueous liquid solutions will also be presented and discussed.

### **PHYS 187 [744380]: Dynamics of polar molecules in confined systems: Ultrafast laser spectroscopy and neutron scattering studies**

**Nancy E Levinger**, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872, Fax: 970-491-1801, levinger@lamar.colostate.edu

#### **Abstract**

Liquid interfaces are present in a wide range of systems of great importance to science. Ultrafast laser spectroscopy and quasielastic neutron scattering studies of liquids, primarily water, confined in a range of reverse micellar media and in sol-gel glasses have increased our understanding of the dynamics occurring in these systems. In particular, the impact of the interface on the dynamics will be discussed.

## **PHYS 188 [767568]: Behavior of arenes and trapped electrons in the nanosized cavities of polar-solvated zeolites**

**Eric H. Ellison**, Department of Chemistry and Biochemistry, The University of Mississippi, Room 322 Coulter Hall, University, MS 38677, Fax: (662) 915-7300, [eellison@olemiss.edu](mailto:eellison@olemiss.edu)

### **Abstract**

This report will comment on the behavior of arene molecules, such as pyrene and naphthalene, included in the polar-solvated, intracavity domains of the zeolites X and Y. Until now, most studies of arene behavior in zeolites have focused on either solvent-free zeolites, dehydrated zeolites bathed in non-polar solvents, or zeolites containing less-than-cage-filling amounts of polar solvent. This study examines arene behavior in zeolites completely submerged in polar solvents, such as methanol or acetonitrile – a medium for arenes which has not been examined before. One of the most fascinating discoveries from this study involves the entrapment of arene molecules as small as naphthalene in polar-solvated zeolites (PSZ). Essentially, molecules migrate into the internal cavity domains or supercages of the zeolites X and Y from non-polar solvents, but cannot be extracted from the cavities with polar solvents in which they are soluble. This is quite unlike what is typically observed for mesoporous solids such as silica gel, in which complete extraction occurs. This presentation will show how various factors influence the extraction of arenes from PSZ. These factors include Si/Al of the zeolite, the type of exchangeable cation of the zeolite, molecular size, solvent properties, temperature, and sample handling. The origin of the trapping effect will be discussed. The nature of the solvated, internal cavity domains will also be described in terms of photophysical studies which probe 1) the behavior of excited states; 2) photoinduced electron transfer; and 3) electron trapping by solvent and ion clusters.

## **PHYS 189 [770188]: Interfacial phase transitions in surfactant/alkane/water systems**

**Colin D. Bain**, Department of Chemistry, University of Oxford, Chemistry Research Laboratory, Mansfield Road, Oxford OX1 3TA, United Kingdom, [colin.bain@chem.ox.ac.uk](mailto:colin.bain@chem.ox.ac.uk)

### **Abstract**

Droplets of medium-chain alkanes on surfactant solutions show intriguing two-dimensional phase behaviour as a function of surfactant concentration and temperature. As the surfactant concentration increases, there is a first-order wetting transition from partial wetting to pseudo-partial wetting. The pseudo-partial wetting state can be viewed as a mixed monolayer of surfactant and alkane, and can exist either in a solid or liquid state depending on the temperature. The thermal phase transition between these two states is first-order. The low temperature phase has different characteristics depending on the relative chain lengths of the surfactant and alkane. A first-order thermal phase transition can also be observed at the bulk alkane-aqueous surfactant interface. The low-temperature phase is analogous to the surface phase observed at the alkane-air interface, and the phase transition at the liquid-liquid interface can be viewed as surfactant-induced surface freezing.

## **PHYS 190 [749395]: Diffuse X-ray scattering studies of the liquid-vapor interfaces of metals and alloys**

**Stuart A. Rice**, The James Franck Institute, University of Chicago, 5640 S. Ellis Avenue, Chicago, IL 60637, s-rice@uchicago.edu

### **Abstract**

The results of studies of diffuse x-ray scattering from the liquid-vapor interfaces of pure Ga and of a dilute alloy of Pb in Ga will be described and interpreted. The results for pure Ga show that the diffuse scattering is sensitive to the stratified density distribution along the normal to the liquid-vapor interface and to the asymptotic form of the effective ion core-ion core interaction. The latter is not probed by other measurements, so diffuse x-ray scattering can be a tool for testing models of the effective ion core-ion core interaction. The results for the dilute alloy of Pb in Ga reveal that the monolayer of Pb segregated in the liquid-vapor interface affects the diffuse scattering; in particular, there is a component of that scattering that is proportional the reciprocal of the in-plane scattering vector. This extra scattering is quantitatively duplicated by a Monte Carlo simulation of the height-height correlation function of a model of the alloy interface. However, at the time this abstract is submitted the physical origin of the extra scattering is not clear. The effect of phase transitions in the liquid-vapor interface, e.g. melting of a crystalline layer, on the diffuse x-ray scattering will also be discussed.

### **PHYS 191 [753079]: State-resolved scattering dynamics of CO<sub>2</sub> with liquids**

**Bradford G. Perkins Jr.**, Department of Chemistry and Biochemistry, JILA, University of Colorado, Box 440, Boulder, CO 80309, Fax: 303-492-5235, perkinbg@colorado.edu, and David J. Nesbitt, JILA/Department of Chemistry and Biochemistry, JILA/NIST and University of Colorado

### **Abstract**

Nascent quantum states of CO<sub>2</sub> colliding with liquid squalane in vacuum are probed via direct infrared absorption of the  $\nu_3$  asymmetric stretch with a Pb-salt diode laser. The high spectral resolution ( $\sim 10$  MHz) of the diode laser permits the dynamics of energy transfer between gas and liquid to be probed in both rotational and translational degrees of freedom. Incident CO<sub>2</sub> molecules are collimated in a skimmed supersonic expansion ( $T_{\text{rot}} \sim 15$  K) before colliding upon a liquid squalane surface. Measured rotational distributions indicate the CO<sub>2</sub> inelastically scatters from the liquid surface in a Boltzmann distribution characterized by the temperature of the liquid,  $T_s$ , independent of incident center of mass collision energy from 3.0 to 7.6 kcal/mol. However, high resolution Doppler analysis of rovibrational line shapes reveal a distribution of velocities parallel to the surface significantly warmer than  $T_s$  at high J states. Implications of the energy transfer dynamics will be discussed.

### **PHYS 192 [760882]: Mixed quantum mechanics/molecular mechanics (QM/MM) modeling of protein active site chemistry**

**Richard A. Friesner**, Department of Chemistry and Center for Biomolecular Simulation, Columbia University, New York, NY 10027, Fax: 212-854-7454, rich@chem.columbia.edu

### **Abstract**

We will discuss the use of DFT based mixed QM/MM methods to model a variety of enzymatic reactions. Systems to be discussed include methane monooxygenase, cytochrome P450, triose phosphate isomerase, beta-lactamase, and myoglobin. Our efforts combine quantum chemical

optimization with protein structure prediction methods to enable large scale reorganization of the protein (treated at the MM level) to be investigated effectively. The overall focus will be on quantitative structural and energetic comparison with experimental data.

### **PHYS 193 [749301]: Pushing the limit of QM/MM methods for studying complex biomolecular systems**

**Qiang Cui**, Demian Riccardi, and Patricia S. Schaefer, Department of Chemistry, University of Wisconsin, Madison, 1101 University Avenue, Madison, WI 53706, Fax: 608-262-4782, cui@chem.wisc.edu

#### **Abstract**

Recent developments in the area of QM/MM methods from our group will be discussed. First, a generalized solvent boundary potential method was implemented in the QM/MM framework for an approximate density functional QM method (SCC-DFTB). This development is an important step towards correctly describing electrostatics in QM/MM calculations, which is crucial for the robust simulation of chemical reactions in biological systems; the method is particularly promising for studying chemical events in supermolecular assemblies such as protein-DNA complexes and membrane-bound enzymes. Second, free energy perturbation (FEP) calculations with QM/MM potential will be discussed in the context of redox potential and pKa predictions; the QM/MM-FEP approach is more robust compared to traditional methods based on potential energy and continuum electrostatics. Finally, a constrained DFT approach for constructing diabatic states in electron transfer reactions will be briefly discussed, which is promising for exploring free energies of electron transfers in the condensed phase.

### **PHYS 194 [755677]: New development and application of the pseudobond ab initio QM/MM approach to studying enzyme reactions**

**Yingkai Zhang**, Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003, Fax: 212-260-7905, yingkai.zhang@nyu.edu

#### **Abstract**

The pseudobond approach offers a smooth connection at the QM/MM interface which passes through covalent bonds. It replaces the boundary atom of the environment part with a one-free-valence atom to form a pseudobond with the boundary atom of the active part. The pseudobond ab initio QM/MM approach has been successfully applied to investigate several enzymes, including enolase, acetylcholinesterase and 4-oxalocrotonate tautomerase. However, up to now, only the C(SP3)-C(SP3) pseudobond has been developed, thus in the case of proteins, it can only be used to cut the protein side chains. Here we employ a new formulation to construct this one-free-valence atom, and have developed and tested the pseudobonds not only for the cutting of protein side chains but also for the backbones. In addition, some new applications will be presented, including the study of mononuclear non-heme iron(II) enzymes.

### **PHYS 195 [752626]: DFT based QM-MM approach designed for the treatment of large molecular systems: Application to chorismate mutase**

Alejandro Crespo, Chemistry, University of Buenos Aires, Ciudad Universitaria, Pab. 2, Buenos Aires C1428EHA, Argentina, Dario A. Estrin, Department of Chemistry, University of Buenos

Aires, and **Adrian E Roitberg**, Department of Chemistry, University of Florida, Quantum Theory Project, Gainesville, FL 32611

### **Abstract**

We present a density functional theory (DFT) hybrid quantum mechanical/molecular mechanical (QM-MM) implementation developed for simulations of reactions in complex environments. It is particularly suited to study enzyme active sites or solutes in condensed phases. The method combines a QM description of the solute with a MM treatment of the environment. The QM fragment is treated using DFT as implemented in the computationally efficient program SIESTA, while the environment is treated using the Wang et al. Amber force field parametrization. We applied our new QM-MM scheme to study the conversion of chorismate to prephenate by computing the reaction energy profile in vacuo, aqueous solution and in the active site of the B. subtilis chorismate mutase enzyme. We have performed calculations for two different choices of the QM subsystem in the enzyme simulations: including only the substrate moiety and the substrate plus the charged side chains glu78 and arg90, respectively. In both cases, our results are in good agreement with experiment. The catalytic activity achieved by chorismate mutase relative to the uncatalyzed reaction in solution is due to both a minor destabilization of the substrate molecule by compression and a major electrostatic stabilization of the transition state, which reduce the activation energy of the reaction.

### **PHYS 196 [753463]: Toward a linear scaling algorithm for use in ab initio molecular dynamics and QM/MM simulations**

Radu Iftimie<sup>1</sup>, Jordan W. Thomas<sup>2</sup>, and **Mark E. Tuckerman**<sup>1</sup>. (1) Department of Chemistry, New York University, 100 Washington Square East, New York, NY 10003, Fax: (212) 260-7903, ri286@nyu.edu, mark.tuckerman@nyu.edu, (2) Department of Physics, Harvard University

### **Abstract**

In ab initio molecular dynamics and QM/MM calculations employing a density functional description of the electronic structure, the latter is the main computational bottleneck, as it scales as  $N^2M$ , where  $N$  is the number of explicitly treated electronic states, and  $M$  is the number of basis functions used to represent these states. Achieving linear scaling, therefore, requires not only reducing the scaling of the electronic structure but maintaining the favorable scaling as the dynamical simulation proceeds. Ab initio molecular dynamics and QM/MM dynamics calculations are often employed using the Car-Parrinello algorithm, in which a fictitious adiabatic dynamics for the electronic states is used to propagate the electronic structure from one minimized configuration to the next as the simulation evolves in time. In this talk, it will be shown that the Car-Parrinello method can be mapped onto a non-abelian gauge field theory. This mapping can then be exploited, via gauge fixing techniques, to yield a new dynamics that ensures the electronic orbitals are maximally spatially localized. By combining this scheme with a new localized real-space localized basis set, linear scaling can be achieved. We will also explore the possibility of dynamically generating maximally delocalized orbitals and combining these with the standard plane-wave basis set, which will also be shown to yield a linear scaling approach for certain classes of systems treated with periodic boundary conditions and dual grid algorithms.

**PHYS 197 [752201]: Protein pKa predictions: From QM/MM/LPBE and QM/LPBE methods to an empirical method**

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**Abstract**

QM/MM/LPBE and QM/LPBE methods have been developed and applied to predict and interpret protein pKa's. Using a QM/MM/LPBE method, the pKa of Lys55 in turkey ovomucoid third domain (OMTKY3) was predicted to be 11.0, in good agreement to experimental value 11.1. Routine application of this QM/MM/LPBE method to proteins was made available recently. Using a combined QM/PCM method, the pKa values of the five carboxyl residues in OMTKY3 were predicted within 0.5 units to experimental values, with an rmsd of 0.3 units. The determinants of the pKa shifts were analyzed with variously sized models of the pKa sites. Based on these studies, empirical relationships between pKa shifts and the microenvironments of the pKa sites were established and programmed for protein pKa predictions. This empirical method uses only geometrical parameters of the proximate atoms to determine the pKa shifts, thus is probably the fastest method currently available.

**PHYS 198 [781651]: Genetically targeted probes of dynamic intracellular signals**

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**Abstract**

Genetically encoded tags and indicators are molecular spies that reveal specific gene products and biochemical processes in living cells and organisms. The best known examples are fluorescent proteins originally from jellyfish and corals, which have been bred to cover the entire visible spectrum and to eliminate multimerization, facilitating their widespread use to track cells and fusion proteins. With further engineering, fluorescent proteins can report local dynamic signals such as redox potential, kinase/phosphatase activities, protein-protein interactions, and ion and neurotransmitter (e.g. glutamate) concentrations. Such indicators are beginning to provide high-resolution monitors of activity in neuronal networks. Short tetracysteine motifs are complementary tags, which can be labeled in live cells with membrane-permeant biarsenical dyes. Unique applications include green vs. red pulse-chase labeling of old vs. new copies of the same protein, electron-microscopic localization, and chromophore-assisted light inactivation of a chosen protein without the problems of antibody penetration.

**PHYS 199 [752294]: Probing gene expression in living cells one molecule at a time**

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## **Abstract**

We demonstrate for the first time continuous realtime monitoring of gene expression in individual living cells with single-copy sensitivity for a protein. Our approach is based on modified reporter proteins, which hydrolyzes fluoregenic and membrane-permeable substrates and degrade inside a cell in a few minutes. The enzymatic amplification of the hydrolysis products allowed us to observe fluorescence bursts corresponding to stochastic expression of the reporter protein in single E. Coli and S. cerevisiae cells . Each burst is triggered by a dissociation of repressor from its DNA binding site on the chromosome. Moreover, the time traces of the fluorescence bursts exhibit quantized levels corresponding to beta-gal molecules generated and degraded one at a time. The implication of this work to gene expression profiling as well as system-wide studies of gene regulation will be discussed.

## **PHYS 200 [754965]: NIH programs in single molecule biophysics, cellular imaging and nanoscience**

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## **Abstract**

A number of new programs and initiatives have been established at the NIH to support basic research in single molecule biophysics, cellular imaging and nanoscience. An overview of these programs will be presented. Specific information on funding opportunities, timelines, and program priorities will be discussed. NIH Roadmap initiatives related to these topics, as well as future directions, will be outlined. Examples of currently active or funded programs are:

[Single Molecule Detection and Manipulation](http://grants.nih.gov/grants/guide/pa-files/PA-01-049.html) <http://grants.nih.gov/grants/guide/pa-files/PA-01-049.html>

[Development of High Resolution Probes for Cellular Imaging](http://grants1.nih.gov/grants/guide/rfa-files/RFA-RM-04-001.html)  
<http://grants1.nih.gov/grants/guide/rfa-files/RFA-RM-04-001.html>

[Nanoscience and Nanotechnology in Biology and Medicine](http://grants.nih.gov/grants/guide/pa-files/PAR-03-045.html)  
<http://grants.nih.gov/grants/guide/pa-files/PAR-03-045.html>

[Bioengineering Research Partnerships](http://grants.nih.gov/grants/guide/pa-files/PAR-04-023.html) <http://grants.nih.gov/grants/guide/pa-files/PAR-04-023.html>

[Exploratory/Developmental \(R21\) Bioengineering Research Grants](http://grants.nih.gov/grants/guide/pa-files/PA-03-058.html)  
<http://grants.nih.gov/grants/guide/pa-files/PA-03-058.html>