APS March Meeting 2015
San Antonio, Texas
http://www.aps.org/meetings/march/index.cfm
Monday, March 2, 2015 8:00AM - 11:00AM –
Session A19 DCOMP DCMP DCP: Invited Session: Fifty Years of Molecular Dynamics Simulations I: Past, Present and Future  Mission Room 103B - Rajiv Kalia, University of Southern California

— No abstract available.

8:00AM A19.00001 Recent advances in Ab initio Molecular Dynamics ROBERTO CAR, Princeton University

8:36AM A19.00002 Combining Molecular Dynamics and Density Functional Theory, EFTTHIMOS KAXIRAS1, Harvard University — The time evolution of a system consisting of electrons and ions is often treated in the Born-Oppenheimer approximation, with electrons in their instantaneous ground state. This approach cannot capture many interesting processes that involved excitation of electrons and its effects on the coupled electron-ion dynamics. The time scale needed to accurately resolve the evolution of electron-ion dynamics is atto-seconds. This poses a challenge to the simulation of important chemical processes that typically take place on time scales of pico-seconds and beyond, such as reactions at surfaces and charge transport in macromolecules. We will present a methodology based on time-dependent density functional theory for electrons, and classical (Ehrenfest) dynamics for the ions, that successfully captures such processes. We will give a review of key features of the method and several applications. These illustrate how the atomic and electronic structure evolution unravels the elementary steps that constitute a chemical reaction.

1in collaboration with: G. Kolesov, D. Vinichenko, G. Tritis, C.M. Friend, Departments of Physics and of Chemistry and Chemical Biology

9:12AM A19.00003 Material Discovery and Design with Dynamic Charge Reactive Potentials SUSAN SINNOTT, University of Florida — Atomic scale computational simulations of multi-phase systems is increasingly important as our ability to simulate nanometer-sized systems becomes routine. The recently developed charge optimized many body potential (COMB) potentials have significantly enhanced our ability to carry out atomic-scale simulations of heterogeneous material systems. The formalism of this potential combines variable charge electrostatic interactions with a classical analytical bond-order potential. It therefore has the capacity to adaptively model metallic, covalent, ionic, and van der Waals bonding within the same simulation cell and dynamically determine the charges on individual atoms according to the local environment. The utility of the COMB potentials is illustrated for materials design and discovery by exploring the structure, stability, mechanical properties, and thermal properties of intermetallic systems and oxide-metal interfaces. They are also used to address key questions associated with corrosion, thin film growth, and heterogeneous catalysis.

9:48AM A19.00004 Massively Parallel Reactive and Quantum Molecular Dynamics Simulations PRIYA VASHISHTA, Collaboratory for Advanced Computing & Simulations, University of Southern California — In this talk I will discuss two simulations: Cavitation bubbles readily occur in fluids subjected to rapid changes in pressure. We use billion-atom reactive molecular dynamics simulations on a 163,840-processor BlueGene/P supercomputer to investigate chemical and mechanical damages caused by shock-induced collapse of nanobubbles in water near silica surface. Collapse of an empty nanobubble generates high-speed nanojet, resulting in the formation of a pit on the surface. The gas-filled bubbles undergo partial collapse and consequently the damage on the silica surface is mitigated. Quantum molecular dynamics (QMD) simulations are performed on 786,432-processor Blue Gene/Q to study on-demand production of hydrogen gas from water using Al nanoclusters. QMD simulations reveal rapid hydrogen production from water by an Al nanocluster. We find a low activation-barrier mechanism, in which a pair of Lewis acid and base sites on the Al, surface preferentially catalyzes hydrogen production. I will also discuss on-demand production of hydrogen gas from water using and LiAl alloy particles. Research reported in this lecture was carried in collaboration with Rajiv Kalia, Aichihiro Nakano and Ken-ichi Nomura from the University of Southern California, and Fuyuki Shimojo and Kohei Shimamura from Kumamoto University, Japan.

10:24AM A19.00005 Small is Different: Nanoscale Computational Microscopy, UZI LANDMAN, School of Physics, Georgia Institute of technology — Finite materials systems of reduced sizes exhibit discrete quantized energy level spectra and specific structures and morphologies, which are manifested in unique, non scalability, size-dependent physical and chemical properties. Indeed, when the scale of materials structures is reduced to the nanoscale, emergent phenomena often occurs. that is not commonly expected, or deduced, from knowledge learned at larger sizes. Characterization and understanding of the size-dependent evolution of the properties of materials aggregates are among the major challenges of modern materials science. Computer-based classical and quantum computations and simulations are tools of discovery of nanoscale emergent behavior [1]. We highlight such behavior in diverse systems, including: (i) Atomic simulations of nanoscale liquid jets and bridges and the stochastic hydrodynamic description of their properties [2]; (ii) Metal nanoclusters and their self-assembled superlattices exhibiting stabilities and properties originating from superatomic electronic shell-closing, atom packing, and interactions between protecting ligands [3]; (iii) Electric-field-induced shape-transitions and electrocrystallization of liquid droplets [4]; and (iv) Symmetry-breaking and formation of highly-correlated Wigner molecules between electrons in 2D quantum dots and bosons in traps [5].


Monday, March 2, 2015 8:00AM - 10:36AM –
Session A26 DCP: Focus Session: Non-Adiabatic Dynamics: New Insights from Experiment and Theory I  204A - Richard Dawes, Missouri University of Science and Technology

8:00AM A26.00001 Representing Adiabatic Potential Energy Surfaces Coupled by Conical Intersections in their Full Dimensionality Using Coupled Quasi-Diabatic States, DAVID YARKONY, Johns Hopkins University — The construction of fit single state potential energy surfaces (PESs), analytic representations of ab initio electronic energies and energy gradients, is now well established. These single state PESs, which are essential for accurate quantum dynamics and have found wide application in more approximate quasi-clasical treatments, have revolutionized adiabatic dynamics. The situation for nonadiabatic processes involving dissociative and large amplitude motion is less sanguine. In these cases, compared to single electronic state dynamics, both the electronic structure data and the representation are more challenging to determine. We describe the recent development and applications of algorithms that enable description of multiple adiabatic electronic potential energy surfaces coupled by conical intersections in their full dimensionality using coupled quasi-diabatic states. These representations are demonstrably quasi-diabatic, provide accurate representations of conical intersection seams and can smooth out the discontinuities in electronic structure energies due to changing active orbital spaces that routinely afflict global multistate representations.

8:48AM A26.00003 Non-adiabatic dynamics of reactions of O(1D) with Xe, CO, NO2, and CO2 from crossed atomic and molecular beam experiments. KRISTIE BOERING, University of California, Berkeley — Reactions of the first excited state of atomic oxygen, O(1D), with small molecules such as CO, NO2, and CO2 continue to be of interest in aeronomy and atmospheric chemistry, thus providing additional motivation to understand the dynamics of these reactions and how well they are predicted by theory. In collaboration with Prof. Jim Lin of the Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan, we have studied the dynamics of quenching and non-quenching reactions between O(1D) and various small molecules using a universal crossed atomic and molecular beam apparatus. New experimental results for the dynamics of quenching of O(1D) by Xe and CO will be presented and compared with previous results for NO2 (K.A. Mar, A.L. Van Wyngarden, C.-W. Liang, Y.T. Lee, J.J. Lin, K.A. Boering, J. Chem. Phys., 137, 044302, doi: 10.1063/1.4736567, 2012) and CO2 (M.J. Perri, A.L. Van Wyngarden, K.A. Boering, J.J. Lin, and Y.T. Lee, J. Chem. Phys., 119(16), 8213-8216, 2003; M.J. Perri, A.L. Van Wyngarden, J.J. Lin, Y.T. Lee, and K.A. Boering, J. Phys. Chem. A, 108(39), 7995-8001, doi: 10.1021/jp045884s, 2004). Among the most intriguing of the new results are for quenching of O(1D) by Xe, for which marked oscillations in the differential cross sections were observed for the O(1P) and Xe products. The shape and relative phase of the oscillatory structure depended strongly on collision energy. This behavior is likely due to the quantum nature of the collision dynamics, caused by interference among curves crossing pathways accessible during electronic quenching, known as Stueckelberg oscillations.

9:24AM A26.00004 Light, Molecules, Action: Broadband UV-visible transient absorption studies of excited state dynamics in photoactive molecules. ROSEANNE SENSION, Departments of Chemistry and Physics, Univ of Michigan - Ann Arbor — Broadband UV-visible transient absorption spectroscopy provides a powerful tool for the investigation of the dynamics of electronically excited molecules in the condensed phase. It is now possible to obtain transient spectra on a routine basis spanning the range from <300 nm to >800 nm with femtosecond time resolution. We have used this method to study the excited state dynamics and internal conversion of a range of molecular systems with potential application as optically powered molecular devices. The cyclohexadiene ring-opening reaction is the basis of a class of important optical switches and of the biological synthesis of vitamin D3. The ring-opening reaction is ultrafast, occurring on a picosecond to subpicosecond timescale depending on the substituents around the ring. These have a significant influence on the dynamics and electronic structure of the electronically excited molecule. The results of a series of transient absorption studies as a function of chromophore substitution and environment will be presented. The cis-trans isomerization of polynye molecules, especially substituted stilbenes, provides another important class of functional molecular transformations. Again the excited state dynamics can be ultrafast with photochemistry controlled by details of the curve crossings and conical intersections. Finally the photochemistry of the even more complex system of cobalamin chromophores with a photoactivle C-Co bond has been proposed as a tool for spatio-temporal control of molecule delivery including drug delivery. Broadband transient absorption spectroscopy has been used to investigate the ultrafast electronic dynamics of a range of cobalamin compounds with comparison to detailed theoretical calculations. The results of these studies will be presented.

10:00AM A26.00005 Long-lived complexes in the F + H2O and F + CH3OH Hydrogen Abstraction Reactions. ROBERT CONTINETTI, Univ of California - San Diego — Extending our recent study of the benchmark four-atom F · H2O system [1], we have now studied the dissociative photodetachment (DPD) of the seven-atom F+ (CH3OH) cluster as well. The energetics of this system dictate that DPD only occurs to the HF + OCH3+ e− product channel on the neutral potential energy surface resulting in diagonal banding in the photoelectron-fragmentation coincidence spectrum consistent with resolved HF vibrational excitation in the products. Evidence for photodetachment to long-lived (µs) van der Waals complexes (FH·OCH3) was also observed, as in the F-H2O system. The metastable states involved in F-H2O are best described as vibrational Feshbach resonances, and the energetics and dynamics of the metastable complexes in the two systems will be examined. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-FG03-98ER14679. [1] Otto, R., Ma, J.; Ray, A. W.; Daluz, J. S.; Li, J.; Guo, H.; Continettilt, R. E., Science 343 (2014) 396.

10:12AM A26.00006 Non-adiabatic dynamics in the detachment continuum of radical anions. JAN VERLET, Durham University — Using photoelectron (PE) spectroscopy at a range of photon energies above the detachment threshold of a radical anion, the dynamics of resonances can be identified by the appearance of various channels. These include: (i) direct and prompt autodetachment, which appears in the PE spectrum at the ionization potential of which is shifted to lower kinetic energy and typically does not shift with photon energy; and (ii) thermonic emission from the radical anion ground state which appears as an exponential decay at low very low kinetic energy. Using time-resolved PE spectroscopy, the non-adiabatic dynamics leading to the formation of the ground state anion can be monitored in real time. In some cases, these dynamics occur on timescales that vastly out-compete autodetachment, even at energies of 3 eV above the neutral. The methodology has been applied to a number of quinone-related molecules and provides insights into how electron capture can lead to stable anions, which is of relevance in electron transfer reactions and astrophysics.

10:24AM A26.00007 Photofragment vector correlations and rotational distributions from ozone dissociation at 266 and 248 nm. MICHELLE WARTER, WEI WEI, SIMON NORTH, Texas A&M University — Ozone photolysis is very important in the atmosphere and has been studied by many people, but there are still mysteries involved in O2 SEUngung experiments on O3 dissociation at 266 and 248 nm have been performed to reveal these mysteries. The even odd population alternations of the O2 rotational distribution and the vector correlations have been studied to determine if there is a dynamical effect on the odd state depletion.

Monday, March 2, 2015 8:00AM - 10:48AM
Session A27 DCP: Focus Session: Emerging Ultrafast Technologies I

2048 - Andrei Tokmakoff, University of Chicago
8:00AM A27.00001 Recent Progress in the Study of Single Molecule Chemistry at the Nanometer Length Scale and Picosecond Time Scale, RICHARD VAN DUYNE, Departments of Chemistry, Biomedical Engineering, and The Applied Physics Program, Northwestern University — During the last few years, there has been an explosion of interest and activity in the field of plasmonics. The goal of plasmonics is to control and manipulate light on the nanometer length scale using the properties of the collective electronic excitations in noble metal films or nanoparticles, known as surface plasmons. An improved understanding of the interactions between adsorbed molecules and plasmonic nanostructures (i.e., molecular plasmonics) is having a significant impact in a number of research areas including electrochemistry, surface science, catalysis for energy conversion and storage, the materials science of nanoparticles, biomedical diagnostics, art conservation science, and nano lithography. In the first part of this lecture, I will provide some background on the basic physical concepts underlying molecular plasmonics with an emphasis on surface-enhanced Raman spectroscopy (SERS), localized surface plasmon resonance (LSPR) spectroscopy, and tip-enhanced Raman spectroscopy (TERS). In the second part of this lecture, I will focus on three recent advances in TERS which illustrate the power of this nanoscale vibrational spectroscopy. First, new insights into the nature of the relative intensity fluctuations in single molecule tip-enhanced Raman spectroscopy (SMTERS) will be discussed. Second, our current understanding of the adsorbate surface interactions involved in the low temperature (LT), ultrahigh vacuum (UHV) TERS of the Ag tip/Rhodamine 6G (R6G) /Ag(111) system will be described. Finally, an update on our new results in coupling ultrafast lasers with TERS. This last topic illuminates a path forward toward the goal of understanding chemistry at the space-time limit.

8:36AM A27.00002 Coherent two-dimensional infrared microscopy, CARLOS BAIZ, DENISE SCHACH, ANDREI TOKMAKOFF, Univ of Chicago — We developed ultrafast 2D IR spectral microscopy, a new technique to measure spatially-resolved 2D infrared spectra and vibrational dynamics with diffraction-limited spatial resolution and femtosecond time resolution. The key enabling development consists of a new geometry where all three IR pulses propagate fully collinearly through an all-reflective IR microscope. A combination of polarization, chopping, and phase-cycling isolate the 2D IR signal by removing all unwanted signal and interference contributions. The single-beam collinear geometry enables us to implement 2D IR microscopy in three configurations: transmission, reflectance, and ATR. In terms of sensitivity, the 6 micron focus size produces an 8-fold enhancement of the signal compared to focusing with standard parabolic mirrors. These methods open up new possibilities for imaging proteins in cells, lipid membranes, or vesicles, as well as performing surface-sensitive studies on biological systems.

8:48AM A27.00003 Mapping the nanoscale energetic landscape in conductive polymer films with spatially super-resolved exciton dynamics, NAOMI GINSBERG, Univ of California - Berkeley — The migration of Frenkel excitons, tightly-bound electron-hole pairs, in polymeric organic semiconducting films is critical to the efficiency of bulk heterojunction solar cells. While these materials exhibit a high degree of structural heterogeneity on the nanoscale, traditional measurements of exciton diffusion lengths are performed on bulk samples. Since both the characteristic length scales of structural heterogeneity and the reported bulk diffusion lengths are smaller than the optical diffraction limit, we adopt far-field super-resolution fluorescence imaging to uncover the correlations between the structural and energetic landscapes that the excitons explore.

9:24AM A27.00004 Ultrafast electron microscopy and diffraction with laser-driven field emitters, CLAUS ROPERS, University of Goettingen — Ultrafast nanoscale dynamics in solids and nanostructures can be investigated by an increasing number of sophisticated electron and x-ray diffraction techniques. Electromagnetically excited field emitters are particularly suited for this purpose, exhibiting high scattering cross-sections and allowing for beam control by versatile electrostatic or magnetic lens systems. The capabilities of time-resolved electron imaging techniques critically depend on the employed source of laser-driven ultrashort electron pulses. Nanoscopic sources offer exceptional possibilities for the generation of electron probe pulses with very short durations and high spatial beam coherence. In this talk, I will discuss recent progress in the development of ultrafast electron microscopy and diffraction based on nanoscopic photocathodes. In particular, we implemented ultrafast low-energy electron diffraction (ULEED) and ultrafast transmission electron microscopy (UTEM) driven by nonlinear photoemission from field emission tips. ULEED enables the study of structural changes with high temporal resolution and ultimate surface sensitivity, at sub-keV electron energies. As a first application of this technique, we studied the structural phase transition in a stripe-like polymer superstructure on freestanding monolayer graphene. An advanced UTEM instrument was realized by custom modifications of a standard transmission electron microscope, leading to electron focal spot sizes in the microscope’s sample plane of about 10 nm and electron pulse durations of less than 700 fs. Utilizing these features, we investigate the quantum-coherent interaction between the ultrashort electron pulse and the optical near-field of an illuminated nanostructure. Finally, further applications and prospects of ultrafast electron imaging, diffraction and spectroscopy using nanoscale field emitters will be discussed.

10:00AM A27.00005 Time Resolved Imaging at 10GHz and Beyond Using the SSRL Scanning Transmission X-ray Microscope, HENDRIK OHLDAG, SLAC National Accelerator Laboratory, STEFANO BONETTI, Stockholm University, ROOPALI KUKREJA, UC San Diego, ZHAO CHEN, Stanford University, JOSEPH FRISCH, HERMANN DÜRR, JOACHIM STÖHR, SLAC National Accelerator Laboratory — Understanding magnetic properties at ultrafast timescales is crucial for the development of new magnetic devices. Such devices will e.g. employ the spin torque or spin Hall effect, whose manifestation at the nanoscale is not yet sufficiently understood. Hence, addressing these effects is of great fundamental significance. X-ray microscopy at the nanoscale is an excellent tool for the study of complex magnetic devices but it is crucial to push the time resolution and sensitivity well beyond the current capabilities. For this reason we developed a microprobe microscope with a single photon counting electronics that effectively allows us to achieve a double lock-in detection at 476MHz (the x-ray pulse frequency) and 1.28MHz (the synchrotron revelation frequency). The sample excitation is fully synchronized with the detection as well. This setup allows us to achieve a signal to noise ratio of better than 10000, enabling us to detect miniscule variations of the x-ray absorption cross section with tens of ps of time resolution. In this talk I will describe our setup and present first results. We successfully achieved the first direct observation of so called traveling spin waves and the detection of a spin polarized current in Cu injected from an adjacent Co layer.

10:12AM A27.00006 Seeing with the nano-eye: accessing structure, function, and dynamics of matter on its natural length and time scales, MARKUS RASCHKE, University of Colorado — To understand and ultimately control the properties of most functional materials, from molecular soft-matter to quantum materials, requires access to the structure, coupling, and dynamics on the elementary time and length scales that define the microscopic interactions in these materials. To gain the desired nanometer spatial resolution with simultaneous spectroscopic specificity we combine scanning probe microscopy with different optical, including coherent, nonlinear, and ultrafast spectroscopies. The underlying near-field interaction mediated by the atomic-force or scanning tunneling microscope tip provides the desired deep-sub wavelength nano-focusing enabling few-nm spatial resolution. I will introduce our generalization of the approach in terms of the near-field impedance matching to a quantum system based on special optical antenna-tip designs. The resulting enhanced and qualitatively new forms of light-matter interaction enable measurements of quantum dynamics in an interacting environment or to image the electromagnetic local density of states of thermal radiation. Other applications include the interference and dynamics in soft-matter hetero-structures, surface plasmon interferometry as a probe of electronic structure and dynamics in graphene, and quantum phase transitions in correlated electron materials. These examples highlight the general applicability of the new near-field microscopy approach, complementing emerging x-ray and electron imaging tools, aiming towards the ultimate goal of probing matter on its most elementary spatio-temporal level.
11:15AM B26.00001 Multistate trajectory and statistical theories of spin-forbidden kinetics. AHREN JASPER, Sandia National Laboratory — Rate coefficients for several spin-forbidden reactions relevant to combustion are calculated using multistate trajectory and statistical theories. The two approaches are compared, and the appropriateness of treating singlet/triplet crossing seams as “nonadiabatic transition states” for spin-forbidden reactions is discussed. We show that the spin-forbidden reaction coordinate is coupled to the remaining nuclear degrees of freedom, leading to multidimensional effects not typically included in statistical treatments. We identify: static multidimensional effects due to the geometry-dependence of the shape of the crossing seam and spin-orbit coupling, dynamical multidimensional effects where the electronic transition probability depends on the distribution of the total internal energy of the system, and nonlocal multidimensional effects due to the instantaneous value of the electronic phase at multiple seam crossings. A semiclassical model based on short-time full-dimensional trajectories that includes all three multidimensional effects as well as a model for electronic decoherence is presented. The results of this new multidimensional nonadiabatic statistical theory are compared with the results of one-dimensional Landau-Zener and weak coupling models for several reactions.

11:51AM B26.00002 Evidence for quantum effects in laser driven photodissociation of methyllumines. ILANA BAR, MICHAEL EPShteIN, ALEXANDER PORTNOV, Ben-Gurion University of the Negev — Non-adiabatic dynamics at conical intersections (CI) extensively affects the photostability of biomolecules by efficiently photoinducing decay routes that dissipate harmful excess ultraviolet energy. Here the photodissociation of the model test molecules, methylamine (CH₃NH₂) and its partially deuterated isotopologue (CD₃NH₂), excited to different specific vibrational modes in the electronically excited state has been investigated by H(D) photofragments detection with two-color reduced-Doppler ion imaging [1]. The H products, resulting from N-H bond cleavage via two dissociation pathways, showed anomalous distributions for some of the vibronic states, as indicated by dynamic resonances in the product branching ratio and in the anisotropy parameters. This vibronic-specific control is attributed to distinctive dynamical interferences of the initially prepared wavepackets, affecting the passage efficiency through the S₁/S₀ CIs. It is suggested that the H product distributions are extremely sensitive to the positions and energies of the CIs in the two electronic states, rather than to the unique initial nuclear motion that promotes the coupling between the two electronic states. These observations reveal uniquely detailed insights into the dynamics of state-specific control of internal conversion.

12:03PM B26.00003 ABSTRACT MOVED TO Q48.00005 —

12:15PM B26.00004 Real-Time Subsystem TD-DFT and its Ehrenfest Dynamics: Applications to solvation and exciton transfer. MICHELE PAVANELLO, Rutgers Univ - Newark — The subsystem formulation of DFT known as Frozen Density Embedding (FDE) provides a divide-and-conquer approach to Kohn-Sham DFT for a collection of weakly bound subsystems. We present theory and computer code development of the time-dependent extension of FDE. The code is now part of the Quantum–ESPRESSO suite of softwares. We also present the associated Ehrenfest dynamics, in which nuclei and electrons of selected subsystems are propagated simultaneously. Application of the code to exciton transfer phenomena as well as to solvatochromic shifts are discussed.

Landau-Zener and weak coupling models for several reactions.

12:27PM B26.00005 Ultrafast dynamics in DNA base pairs following ultraviolet excitation. ANDREW ORR-EWING, University of Bristol — Photo-protective mechanisms in DNA are essential to maintain the integrity of the genetic code by preventing damage from absorption of solar ultraviolet (UV) radiation. We have used time-resolved infra-red (TRIR) spectroscopy to observe the dynamics of Watson-Crick nucleobase pairs following absorption of femtosecond UV laser pulses. The base pairs are prepared as nucleosides in solution, and photo-induced dynamics are probed in the carbonyl and N-H bond stretching regions using broadband IR pulses with picosecond time resolution. Results will be presented for the guanine-cytosine (G-C) base pair, contrasting the rapid recovery of ground-state products (the photo-protection pathway) with formation of other photoproducts which might represent photo-damage mechanisms. This work is a collaboration with the group of Prof F. Temps (Christian-Albrechts-Universität zu Kiel).

3M.P. acknowledges funding by the ACS Petroleum Research Fund

1This research is supported by ERC Advanced Grant 290966 CAPRI

1:03PM B26.00006 Femtosecond Heterodyne Transient Grating Studies of Nonradiative Decay in β-Carotene and Peridinin: Contributions of Dark Intermediates and Double Quantum Coherences, SOUMEN GHOSH, JEROME ROSCIOLI, Michigan State Univ, HARRY FRANK, University of Connecticut, WARREN BECK, Michigan State Univ — Femtosecond transient grating spectroscopy with optical heterodyne detection was employed to characterize the ultrafast events in the nonradiative decay of β-carotene and peridinin in solution from the S₂ state. The contribution of double-quantum coherences to the time evolution of the third order signal was probed by scanning the interpulse delay between the first two pulses in the transient grating or stimulated photon-echo sequence. The results show that the double-quantum coherence pathways contribute significantly to the transient grating signal only at negative population delays, which is consistent with the requirements determined from double-sided Feynman diagrams when the third order signal is detected in the −k₁ + k₂ + k₃ direction. Response function calculations support the conclusion that the ultrafast (<20 fs) decay that contributes to the third order signal at positive population delays arises from a kinetic intermediate, which has been previously assigned to the S₅ state. We suggest that this intermediate arises not from a discrete electronic state but rather from a twisted conformation of the conjugated polyyne. This proposal has significant implications with respect to the energy transfer function of carotenoids in photosynthesis.

1:15PM B26.00007 Vibrational Conical Intersections: Implications for Ultrafast Vibrational Dynamics, MAHESH DAWADI, BISHNU PRASAD THAPALIYA, Department of Chemistry, The University of Akron, RAM BHATTA, Department of Polymer Science, The University of Akron, DAVID PERRY, Department of Chemistry, The University of Akron — The presence of conical intersections (CIs) between electronic potential energy surfaces is known to play a key role in ultrafast electronic relaxation in diverse circumstances. Recent reports have documented the existence of vibrational CIs connecting vibrationally adiabatic surfaces. Just as electronic CIs are now appreciated to be ubiquitous, controlling the rates of many photochemical processes, the present work on methanol and methyl mercaptan suggests that vibrational CIs may also be widespread, possibly controlling the outcome of some high-energy processes where vibrationally excited species are present. Other examples of vibrational CIs include the vibrational Jahn-Teller effect in C₂O₃ organic molecules and transition metal complexes. While the present work addresses only the couplings within bound molecules, the concept of vibrational CIs providing pathways for ultrafast relaxation also applies to molecular collisions.

1This work is supported by DOE (DEFG02-90ER14151).
reactions: photooxidation and photoaquation. Iron K-edge absorption spectra were obtained along with iron emission spectra. Our data support the presence of \[\text{Fe(II)(CN)}\_6^{2-}\] in an aqueous solution after excitation with 355 nm and 266 nm laser light. The system undergoes two wavelength dependent femtosecond time resolved resonant X-ray scattering at LCLS to derive how ultrafast spin-crossover and ligation determines the pathways of ligand exchange of \(\text{Fe(CO)}\_5\) in solution, ALEXANDER FÖHLISCH, Helmholtz-Zentrum Berlin für Materialien und Energie, Potsdam University — Tracking the charge and spin dynamics of electronic excited states in inorganic complexes, KELLY GAFFNEY, Stanford Synchrotron Radiation Lightsource and PULSE Institute at SLAC National Accelerator Laboratory and Stanford University — Inorganic complexes have many advantageous properties for solar energy applications, including strong visible absorption and photocatalytic activity. Whether used as a photocatalyst or a photosensitizer, the lifetime of electronic excited states of inorganic complexes represent a key property for solar energy applications. These dual needs have undermined the usefulness of many coordination compounds. Isocyanate iron and ruthenium based complexes represent a clear example. Ru-polypyridyl based molecules have been the workhorse of solar energy research and dye sensitized solar cells for decades, but the replacement of low abundance Ru with Fe leads to million-fold reductions in metal to ligand charge transfer (MLCT) excited state lifetimes. Understanding the origin of this million-fold reduction in lifetime and how to control excited state relaxation in 3d-metal complexes motivates the work I will discuss. We have used the spin sensitivity of hard x-ray fluorescence spectroscopy and the intense femtosecond duration pulses generated by the LCLS x-ray laser to probe the spin dynamics in a series of electronically excited \[\text{Fe(n)}\text{(CN)}\_6^{2-}\text{(2,2'-bipyridine)}\] complexes, with \(N = 1-3\). These femtosecond resolution measurements demonstrate that modification of the solvent and ligand environment can lengthen the MLCT excited state lifetime by more than two orders of magnitude. They also verify the role of triplet ligand field excited states in the spin crossover dynamics from singlet to quintet spin configurations.

1 Work supported by the AMOS program within the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences, Office of Science, U. S. Department of Energy.

11:51AM B27.00002 Time-resolved X-Ray Absorption Spectroscopy of a Cobalt-Based Hydrogen Evolution System for Artificial Photosynthesis, DOOSHAYE MOONSHIRAM, Argonne National Laboratory, CAROLINA GIMBERT, Inst. d’Investigació Química, CARL LEHMANN, STEPHEN SOUTHWORTH, Argonne National Laboratory, ANTONI LLORET, Inst. Català d’Investigació Química, ARGONNE NATIONAL LABORATORY TEAM, INSTITUT CATALÀ D’INVESTIGACIÓ QUIMICA COLLABORATION — Production of cost-effective hydrogen gas through solar power is an important challenge of the Department of Energy among other global industry initiatives. In natural photosynthesis, the oxygen evolving complex (OEC) can carry out four-electron water splitting with an efficiency of around 60%. Although, much progress has been carried out in determining mechanistic pathways of the OEC, biomimetic approaches have not duplicated Nature’s efficiency in function. Over the past years, we have witnessed progress in developments of light harvesting modules, so called chromophore/catalytic assemblies. In spite of reported high catalytic activity of these systems, quantum yields of hydrogen production are below 40% when using monochromatic light. Proper understanding of the mechanisms and bond making/breaking steps has to be achieved to improve efficiency of hydrogen evolution systems. This project shows the timing implementation of ultrafast x-ray absorption spectroscopy to visualize in “real time” the photo-induced kinetics accompanying a sequence of redox reactions in a cobalt-based molecular photocatalytic system. Formation of a Co(I) species followed by a Co(III) hydride species all the way towards hydrogen evolution is shown through time-resolved XANES.

12:03PM B27.00003 Spatiotemporal Imaging of Chemical Reactions: Making Molecular Movies with Femtosecond X-Ray Scattering, J.M. BUDARZ, Brown Univ, SLAC National Accelerator Laboratory, M.P. MINITTI, SLAC National Accelerator Laboratory, A. KIRKLAND, Univ. of Johannesburg, E. HASTINGS, SLAC National Accelerator Laboratory, P.M. WEBER, Brown Univ. — The study of ultrafast reaction dynamics of molecular systems has benefited from the rapid development of spectroscopic and imaging techniques that follow their temporal evolution on a sub-picosecond time scale. More complete understanding of molecular behavior, however, is expected to arise from a full observation of electronic and nuclear motions during reactions. Our recent experiments at the Linac Coherent Light Source (LCLS) have allowed us to develop and implement a method wherein the ultrafast reaction dynamics of molecules in dilute gases (4 Torr) are captured by time-resolved X-ray scattering. Using a pump-probe scheme with 267 nm excitation laser and 8.3 keV X-ray probe pulses, we performed a series of measurements on the interatomic positions at variable delay times to produce a ‘movie’ of the reaction. In our experiments, 1,3-cyclohexadiene (CHD) is prepared on an excited state surface, causing the molecule to accelerate down several potential energy surfaces coupled by conical intersections, to open into 1,3,5-hexatriene within 80 fs. The resulting ‘movie’ has been supplemented with molecular trajectory calculations to separate the multiple pathways the excited molecule takes toward the open ring. In this talk, the experimental methods and designs that made these experiments possible will be presented together with the first results describing the photochemical reaction dynamics of CHD.

12:15PM B27.00004 The orbital-based view on reaction dynamics: ligand exchange of \(\text{Fe(CO)}\_5\) in solution, ALEXANDER FÖHLISCH, Helmholtz-Zentrum Berlin für Materialien und Energie, Potsdam University — Time resolved soft X-ray spectroscopy has proven recently, that it can beat the complexity of dynamics in materials and chemical processes by its high selectivity towards elemental, chemical, and magnetic properties. Changes in chemical bonding, in particular bond breaking and bond creation seem conceptually simple, but as a result of coherent wave packet motion it is difficult to catch the dynamic pathways in a multidimensional potential energy landscape. In this contribution we exploit the unique approach of femtosecond time resolved resonant inelastic X-ray scattering at LCLS to derive how ultrafast spin-crossover and ligation determines the pathways of ligand exchange of ironpentacarbonyl \(\text{Fe(CO)}\_5\) in solution. As an outlook, it will be discussed, how non-linear X-ray processes can push time resolved soft X-ray spectroscopy in a new phase. In particular, stimulated Raman scattering and amplified spontaneous emission can overcome the weak scattering of molecular components represent a key property for solar energy applications. These dual needs have undermined the usefulness of many coordination compounds. Isocyanate iron and ruthenium based complexes represent a clear example. Ru-polypyridyl based molecules have been the workhorse of solar energy research and dye sensitized solar cells for decades, but the replacement of low abundance Ru with Fe leads to million-fold reductions in metal to ligand charge transfer (MLCT) excited state lifetimes. Understanding the origin of this million-fold reduction in lifetime and how to control excited state relaxation in 3d-metal complexes motivates the work I will discuss. We have used the spin sensitivity of hard x-ray fluorescence spectroscopy and the intense femtosecond duration pulses generated by the LCLS x-ray laser to probe the spin dynamics in a series of electronically excited \[\text{Fe(n)}\text{(CN)}\_6^{2-}\text{(2,2'-bipyridine)}\] complexes, with \(N = 1-3\). These femtosecond resolution measurements demonstrate that modification of the solvent and ligand environment can lengthen the MLCT excited state lifetime by more than two orders of magnitude. They also verify the role of triplet ligand field excited states in the spin crossover dynamics from singlet to quintet spin configurations.

1 The work was supported by the U.S. Department of Energy, Office of Science, Chemical Sciences, Geosciences, and Biosciences Division.
1:03PM B27.00006 Ultrafast Coherent Photoelectron Spectroscopy of Electronic States on a Cu (111) Surface , ADRA CARR, CONG CHEN, ZHENSHENG TAO, MARGARET MURNANE, HENRY KAPTEYN, PIOTR MATYBA, JILA/NIST, SEBASTIAN EMERICH, MARTIN AESCHLIMANN, University of Kaiserslautern, Germany, ULRICH HOEFER, University of Marburg, Germany — We use laser-assisted high-harmonic time- and angle-resolved photoemission to directly observe coherent photoemission from a Cu(111) metal surface and the interferences between the emitted photoelectron wavepackets. A comb of high harmonics in combination with interferometrically timed infrared pulses enable a powerful combination of attosecond time resolution and high energy resolution, making it possible to extract true information about the emitted photoelectron wavepackets and the distinct electronic states from which they emerge. By comparing photoemission from the well-known Shockley surface state to the sp and d bulk bands of Cu(111), we can observe non-negligible phase shifts in the emitted wavepackets, which cannot be attributed to time delays resulting from classical electron transport to the surface. Rather, we interpret these phase shifts as due to an intrinsic photoemission phase that is different for the sp and d band wavefunctions, thus providing a physical interpretation of temporal delays observed in photoemission from surfaces.

1:15PM B27.00007 Circularly polarized attosecond pulses for molecular atto-magnetism , ANDRE D. BANDRAUK¹, University of Sherbrooke — Circularly polarized molecular high order harmonic generation, MHOHG, is modelled from numerical solutions of the time-dependent Schroedinger equation, TDSE, for the one-electron H₂⁺ in the nonlinear nonperturbative regime of laser-molecule interaction. It is shown that molecules due to their nonspherical symmetry are the preferred medium for producing circularly polarized harmonics by few cycle intense IR (800,400nm) circularly polarized laser pulses. An intense Terahertz (4um) pulse is combined to force recollisions of the ionized electron with the parent ion thus enhancing the efficiency of the circularly polarized MHOHG process through single recollisions [1]. Superposition of these harmonics allows for the synthesis of single circularly polarized attosecond (10⁻¹⁸s) pulses such new ultrashort pulses allow for controlling electrons on their natural time scale [2]. In particular the TDSE simulations illustrate the generation with such new pulses coherent quantum electronic currents inside molecules for the creation of attosecond magnetic field pulses of intensity >10 Teslas [3].

1 Canada Research Chair-Computational Chemistry and Molecular Photonics


1:27PM B27.00008 Coherent Chemistry with THz Pulses: TDDFT-Ehrenfest Simulations of Field-Induced LiNC Isomerization¹, LENSON PELLOUCHOUD, EVAN REED, Stanford Univ — The ability to coherently rearrange molecular structures is among the grand challenges of physical chemistry. Some of the primary obstacles are non-adiabatic increases in energy, such as intramolecular vibrational relaxation (IVR) and electronic excitations. Motivated by recent advances in the generation and control of strong terahertz (THz) pulses, we have investigated their potential to circumvent these obstacles. THz pulses are promising because their spectral content is well separated from electronic excitation frequencies, yet they may be fast enough to add and remove energy from the ionic system without allowing IVR to take place. In this work, we utilize simulations to discover that LiNC can be isomerized to two distinct metastable conformations with very low residual heating and ionization rates, pointing out a new route towards THz coherent control of chemical bonds and materials. We use time-dependent DFT (TDDFT)-based Ehrenfest molecular dynamics simulations to test a variety of strong time-varying THz pulses applied to the molecule. We find the limits of how quickly an activation barrier can be surmounted before the driving pulse becomes strong enough to ionize the molecule, and how well the target must be aligned in order for the final configuration to be stable.

1Supported in part by NASA Space Technology Research Fellowship (NSTRF)

1:39PM B27.00009 Ultrafast high harmonics for probing the fastest spin and charge dynamics in magnetic materials, PATRICK GRYCHTOL, JILA, University of Colorado, Boulder, CO 80309, USA — Ultrafast light based on the high-harmonic up-conversion of femtosecond laser pulses has been successfully employed to access resonantly enhanced magnetic contrast at the Mₐbsorption edges of the 3d ferromagnets Fe, Co and Ni in a table-top setup. Thus, it has been possible to study element-specific dynamics in magnetic materials at femtosecond time scales in a laboratory environment, providing a wealth of opportunities for a greater fundamental understanding of correlated phenomena in solid-state materials. However, these investigations have so far been limited to linear polarized harmonics, since most techniques by which circular soft x-rays can be generated are highly inefficient reducing the photon flux to a level unfit for scientific applications. Besides presenting key findings of our ultrafast studies on charge and spin dynamics, we introduce a simple setup which allows for the efficient generation of circular harmonics bright enough for XMCD experiments. Our work thus represents a critical advance that enables element-specific imaging and spectroscopy of multiple elements simultaneously in magnetic and other chiral materials with very high spatial and temporal resolution on the tabletop.

In collaboration with Ronny Knut, Emrah Turgut, Dmitriy Zuzin, Christian Gentry, Henry Kapteyn, Margaret Murnane, JILA, University of Colorado, Boulder, Justin Shaw, Hans Nembach, Tom Silva, Electromagnetics Division, NIST, Boulder, CO; and Ofer Kfir, Avner Fleischer, Oren Cohen, Extreme Nonlinear Optics Group, Solid State Institute, Technion, Israel.

Monday, March 2, 2015 2:30PM - 5:18PM — Session D26 DCP: Focus Session: Water and Liquid Dynamics 204A - David Chandler, Sandia National Laboratories

2:30PM D26.00001 ABSTRACT WITHDRAWN

2:42PM D26.00002 New insights into the femtosecond-to-picosecond dynamics of liquid water from temperature dependence using terahertz spectroscopy studies and molecular dynamics simulations, CHOLA REGMI, DEEPU GEORGE, SHENGFENG CHENG, NGUYEN VINH, Virginia Polytechnic Institute and State University — Water plays an active and complex role in sustaining life. The hydrogen bonds between the water molecules exhibit the unique physical properties that distinguish water from other molecular liquids. Nevertheless, there is little agreement regarding the femtosecond to picosecond relaxation dynamics of water. In response, we have used the state-of-the-art terahertz spectroscopy (frequency-domain and time-domain) and molecular dynamics simulation techniques to study the molecular relaxation of water at different temperatures in the femtosecond to picosecond time scale. We show that the two-Debye model is insufficient to explain the observed relaxation dynamics of water and our results on the terahertz dielectric relaxation of water are best described as the sum of three-Debye processes. We compute the time autocorrelation function of the dipole moment of water molecules at different temperatures with molecular dynamics simulations and compare the calculations with the experimental data.
2:54PM D26.00003 Exploring the nonlocal dielectric susceptibility of liquid water in the terahertz regime - propagating modes, Debye relaxation and screening¹, DANIEL ELTON, MARIVI FERNANDEZ-SERRA, Stony Brook University — There is great interest in the dielectric and infrared spectra of water between 1-1000 cm⁻¹ (0.3-30 THz). To gain insight into this region we study the nonlocal (wavelength dependent) dielectric susceptibility. A curious feature of water is the presence of a propagating mode in the librational region. For the first time we study the temperature dependence of this mode and its range of propagation. We show that the librational band has two components - non-dispersive and dispersive. Previously this mode was suggested to be analogous to an optical phonon propagating along the H-bond network. We suggest a possible alternative - that it is the dipolaron mode predicted for dipolar systems. Next we study the region of 1.1-10 THz which is relevant to understanding the coupling between proteins and water. We show that in addition to H-bond vibrations, intramolecular inertial relaxations also contribute. We find that the Debye peak is dispersive, confirming its long range cooperativity. We report the first temperature dependent study of the static nonlocal susceptibility, which exhibits a negative region, a phenomena known as screening. We compare a rigid model (TIP4P/ε), a flexible model (TIP4P/2005f) and a polarizable model (TTM3-F).

¹This work was partially supported by DOE Award No. DE-FG02-09ER16052 (D.C.E.) and by DOE Early Career Award No. DE-SC0003871 (M.-V.F.-S.).


3:06PM D26.00004 A Dataset of First-Principles Molecular Dynamics Simulations of Water¹, FRANCOIS GYGI, WILLIAM DAWSON, Univ of California - Davis — We present a dataset of first-principles molecular dynamics simulations [1] of water performed using Density Functional Theory. A set of 32 independent 64-molecule samples was used in separate, parallel simulations for a duration of 58 ps. An analysis of atomic trajectories is given focusing on correlations of the Kohn-Sham energy, ionic kinetic energy, pair correlation functions, diffusion coefficient, and vibrational spectrum. The availability of 32 independent simulations allows for an estimation of the variance of averaged quantities, both within MD runs and between samples. The variability of oxygen pair correlation functions across samples provides a measure of the uncertainty associated with that quantity. We observe several instances of large fluctuations in the oxygen pair correlation functions that can be associated with increases in the local structure index (LSI) proposed by Shiratani and Sasai [2] supporting the hypothesis that water undergoes frequent changes to locally highly structured configurations. Complete atomic trajectories and simulation output files are available online[3].


¹Supported by DOE/BES grant DE-SC0008938

3:18PM D26.00005 Mutual Exclusion of Urea and Trimethylamine N-oxide from Amino Acids in Mixed Solvent Environment , PRITAM GANGULY, Univ of California - Santa Barbara, TIMIR HAJARI, TU Darmstadt, Germany, JOAN-EMMA SHEA, Univ of California - Santa Barbara, NICO F. A. VAN DER VEGT, TU Darmstadt, Germany — We study the salvation thermodynamics of individual amino acids in mixed urea and trimethylamine N-oxide (TMAO) solutions using molecular dynamics simulations and the Kirkwood-Buff theory. Our results on the preferential interactions between the amino acids and the cosolvents (urea and TMAO) show a mutual exclusion of both the cosolvents from the amino acid surface in the mixed cosolvent condition which is followed by an increase in the cosolvent-cosolvent aggregation away from the amino acid surface. The effects of the mixed cosolvents on the association of the amino acids and the preferential solvation of the amino acids by water are found to be highly non-linear in terms of the effects of the individual cosolvents. A similar result has been found for the association of the protein backbone, mimicked by triglycine. Our results have been confirmed by different TMAO force-fields and the mutual exclusions of the cosolvents from the amino acids are found to be independent of the choice of the strength of the TMAO-water interactions. Based on our data, a general mechanism can potentially be proposed for the effects of the mixed cosolvents on the preferential solvation of the solutes including the case of cononsolvency.

3:30PM D26.00006 ABSTRACT WITHDRAWN —

3:42PM D26.00007 Experiments on Tracer Diffusion in Water and Aqueous Mixtures¹, DAN SPIEGEL, Trinity University — We have used forced Rayleigh scattering to measure tracer diffusion coefficients in water and other liquids. The tracer molecule is the azobenzene deriviative methyl red (MR). In one set of experiments diffusion was measured at different temperatures to test the Cohen-Turnbull (CT) free volume diffusion theory. It was found that eight solvents were in reasonable agreement with CT, but the relevant energy in water was smaller by an order of magnitude. We believe this is due to the “zero-point” free volume that water would possess, due to its H-bonds, even at the glass transition temperature, and to the ability of MR to diffuse along its plane. In a second set of experiments we studied diffusion in aqueous and non-aqueous mixtures. The non-aqueous mixtures are in good agreement with free volume theory, but the aqueous mixtures show large disagreement. We suggest this is caused by the formation of two solvent shells in the aqueous mixtures, driven by the hydrophobicity of MR and water-amphiphile hydrogen bonding.

¹NSF Research at Undergraduate Institutions

3:54PM D26.00008 Spectroscopic studies on di-porphyrin rotor as micro-viscosity sensor , H. DOAN, S. RAUT, J. KIMBAL, Z. GRYCZYNSKI, S. DZYUBA, TCU, M. BALAZ, UW — In typical biological systems the fluid compartment makes up more than 70% of the system weight. A variety of mass and signal transportation as well as intermolecular interactions are often governed by viscosity. It is important to be able to measure/estimate viscosity and detect the changes in viscosity upon various stimulations. Understanding the influence of changes in viscosity is crucial and development of the molecular systems that sensitive to micro-viscosity is a goal of many researches. Molecular rotors have been considered the potential target since they present enhanced sensitivity to local viscosity that can strongly restrict molecular rotation. To understand the mechanics of rotor interaction with the environment we have been studied conjugated pophyrin-dimer rotor (DP) that emit in the near IR. Our goal is to investigate the photo physical properties such as absorption, transition moment orientation, emission and excitation, polarization anisotropy and fluorescence lifetime in various mediums of different viscosities from ethanol to poly vinyl alcohol (PVA) matrices. The results imply the influences of the medium’s viscosity on the two distinct confirmations: planar and twisted conformation of DP. Linear dichroism from polarized absorption in PVA matrices shows various orientations of transition moments. Excitation anisotropy shows similar transition splitting between two confirmations. Time resolved intensity decay at two different observations confirms the two different emission states and furthermore the communication between the two states in the form of energy transfer upon excitation.
4:06PM D26.00009 High pressure Raman spectroscopy of H2O-CH3OH mixtures, WEN-PIN HSIEH, YU-HSIANG CHIEN, Academia Sinica — Complex intra-molecular interactions and the hydrogen-bonding network in H2O-volatile mixtures play critical roles in many dynamics processes in physical chemistry, biology, and Earth and planeretary sciences. We used high pressure Raman spectroscopy to study the pressure evolution of vibrational frequencies and bonding behavior in H2O-CH3OH mixtures. We found that the presence of low CH3OH content in H2O increases the transition pressure where water crystallizes to ice VI, but does not significantly change the pressure where ice VI transforms to ice VII. Furthermore, the stiffening rates of C-H stretching frequencies dω/dP in CH3OH significantly decrease upon the crystallization of water, and the softening rates of the O-H stretching frequencies of ice VII are suppressed over a narrow pressure range, after which the frequencies of these modes shift with pressure in ways similar to pure CH3OH and ice VII, respectively. Such complex pressure evolution of Raman frequencies along with pronounced variations in Raman intensities of CH3 sample, and the hysteresis of the water-ice VI phase transition suggest pressure-induced segregation of low content CH3OH from ice VII.

4:18PM D26.00010 Discovery of Water Structural Transitions near Interfaces of Polarizable Solutes1, MOHAMMADHASAN DINPAJOOH, DMITRY MATYUSHOV, Arizona State Univ — The standard harmonic approximation describing polarization around the solute is expected to break down with increasing solute polarizability. The focus of this study is to investigate the structure of water around dipolar-polarizable solutes by Monte Carlo (MC) simulations in the non-harmonic regime. We observe a structural transition in the water hydration shell and its condensation, which are driven by increasing the solute polarizability. There is also a crossover in the orientational structure near the point of breakdown of the harmonic approximation. At lower polarizabilities, waters in the hydration shell point their hydrogens toward the solute. The dipoles flip their orientations at the transition to the non-harmonic regime. Both the hydration shell compressibility and the electric field susceptibility display maxima in the transition region. Using the water electric field at the center of the polarizable solute as the order parameter, a Landau-type model is formulated. Its predictions are in reasonable agreement with MC simulations performed for hard sphere and Lennard-Jones polarizable solutes in a TIP3P water model. The observed structural transition suggests a general crossover phenomenon driven by the stabilization energy required to polarize the solute.

1This research was supported by the National Science Foundation (CHE-1213288). CPU time was provided by the National Science Foundation through XSEDE resources (TG-MCB080116N).

4:30PM D26.00011 Ionic liquid and water molecules diluted in hydrophobic solvent matrix investigated by infrared absorption spectroscopy, DOSEOK KIM, WONGMO SUNG, JONGGWAN LEE, Department of Physics, Sogang University — Pure ionic liquids ([BMIM]: 1-butyl-3-methylimidazolium, X: Cl and I) and their aqueous solutions were loaded on top of non-polar solvent CCl4, and the infrared spectra of CCl4 phase were taken as a function of time for in-situ probing of the transfer of the ionic liquid and water molecules. We observed clear vibrational bands of methyl and methylene groups of the cations similar to that of bulk ionic liquids. On the other hand, normally strong infrared absorption from C(2)-H and C(4,5)-H vibrations was hardly observable. As these bands work as indicators of specific interaction between the imidazolium core and the halide anions, we concluded that ion pairs are fully dissociated and [BMIM] cations exist as monomers in CCl4. For 1 M of [BMIM]Cl and [BMIM]I aqueous solutions, water molecules transferred into CCl4 also exist mostly as monomers, with a possible existence of anion-bound water molecules inferred from the new band at 3421 cm\(^{-1}\) for [BMIM]Cl, and at 3452 cm\(^{-1}\) for [BMIM]I. Both transfer rate and saturation amount of ionic liquid molecules are larger for [BMIM]I than for [BMIM]Cl. For this, we propose that this difference in transfer rate originates from excess ionic liquid molecules at the interface between hydrophobic (aqueous solution) and hydrophobic (CCl4) medium.

4:42PM D26.00012 Electrical Conduction in Pure Water – Trapping and Scattering of Positive Protons and Negative Proton Holes, BINBIN JIE, CHIHTANG SAH, Professors of Physics, Xiamen University, China — Water has been characterized by hydronium (H\(_3\)O\(^{+}\)) and hydroxide (HO\(^{-}\)) ions, which fail to explain the electrical conductivity of even pure water. Experimental formulas of pure water versus temperature (0-100\(^\circ\)C) have employed 39 empirical parameters to fit 3 measured properties: ion concentration, and electrical conductance of pure water and (H\(_3\)O\(^{+}\)) ion. We have shown (4 invited talks, 3 articles in 14 months) that electrical conduction in pure water can be represented by 5 quasi-particles in the many-body water lattice: the mobile positively charged protons p\(^{+}\) and negatively charged proton holes p\(^{-}\), and the 3 charge states of the immobile water molecule as amphoteric protonic trap, V\(^{+}\) = (H\(_3\)O)\(^{+}\), V\(^{0}\) = (H\(_3\)O)\(^0\), and V\(^{-}\) = (HO\(^{-}\))\(^{-}\); and as few as 6 physics parameters: 3 binding energies, 1 protonic density of state, and 2 Coulombic scattering strengths. Protons in water are strongly coupled to the protonic-phonons, oxygen-phonons and protonic-local modes. Impurities and affinitons may be present in the hexagonal tunnels of the water lattices.

5:06PM D26.00014 Coupling of Solute Vibrational Modes with a Fabry-Perot Optical Cavity Mode, ADAM DUNKELBERGER1, RYAN COMPTON2, KENAN FEARS, BRYAN SPANN1, JAMES LONG, BLAKE SIMPKINS, JEFFREY OWRTUSKY, Naval Research Laboratory — Electronic transitions of systems confined in optical microcavities can strongly couple to cavity modes, giving rise to new, mixed-character modes. Recent studies have demonstrated coherent coupling between the vibrational modes of a thin polymer film and a Fabry-Perot optical cavity mode. This coupling manifests experimentally as a splitting of the transmissive cavity mode into two dispersive branches separated by the vacuum Rabi splitting. Here we present recent experimental results for the coupling of solution-phase compounds with an optical cavity. Solutions of W(CO)\(_6\), Mo(CO)\(_6\), and NCS\(^{-}\) contained in cavities show strong coupling between the solute chromophores in the mid-infrared and cavity modes. We show that the methodology established with polymer-filled cavities is generally applicable to liquids but that the fluidity of the sample complicates the cavity construction. Varied cavity thicknesses can give rise to spatial gradients in coupling strength and difficulty in targeting a specific cavity-mode order. We also compare the transmission of the mixed vibrational-cavity modes in cavities constructed from either metallic or dielectric reflectors which impacts the cavity resonance line width.

5:44PM D26.00013 Surface-enhanced Raman mapping of chemical hot spots, DMITRI VORONIN, Texas A&M University — Surface-enhanced Raman spectroscopy (SERS) and atomic force microscopy (AFM) are used for simultaneous chemical-topographic mapping of Raman hot spots on dielectric, semiconductor and metal surfaces. Raman signals enhanced by electromagnetic and chemical mechanisms are separated. Several approaches of nanoscale surface analysis are compared. Future experimental advances for spatiotemporal imaging of surface dynamics using ultrafast lasers and multiple tips are discussed.

Monday, March 2, 2015 2:30PM - 5:30PM – Session D27 DCP: Focus Session: Chemical Physics of Clusters: Bridging from Angstrom-scale Clusters to Micron-scale Aerosol Particles I
2:30PM D27.00001 From Clusters to Atmospheric Aerosol Particles: Nucleation in the CLOUD Experiment at CERN. Urs Baltensperger, Paul Scherrer Institute — Globally, a significant source of cloud condensation nuclei for cloud formation is thought to originate from new particle formation (aerosol nucleation). Despite extensive research, many questions remain about the dominant nucleation mechanisms. Specifically, a quantitative understanding of the dependence of the nucleation rate on the concentration of the nucleating substances such as gaseous sulfuric acid, ammonia, water vapor and others has not been reached. This is of relevance for climate as the atmospheric concentrations of sulfuric acid, ammonia and other nucleating agents are strongly influenced by anthropogenic emissions. By providing extremely well controlled and essentially contaminant free conditions in the CLOUD chamber, we were able to show that indeed sulfuric acid is an important component for such new particle formation, however, for the typical temperatures encountered in the planetary boundary layer the concentrations of sulfuric acid are not high enough to explain the atmospheric observations. Moreover, the effect of ammonia [1], amines [2] and oxidized organic molecules [3] on the nucleation rate of sulfuric acid has been investigated in CLOUD so far. Recent developments in instrument technology such as the Atmospheric Pressure interface-Time Of Flight (API-TOF) mass spectrometer have allowed us to investigate the chemical composition of charged [4] as well as neutral [5] clusters during such nucleation experiments. References [1] Kirkby, J. et al., Nature, 476, 42-433, 2011 [2] Almeida, J. et al., Nature, 502, 359-363, 2013. [3] Riccobono et al., Science, 344, 717-721, 2014. [4] Schobesberger S. et al., Proc. Nat. Acad. Sci., 110, 17223-17228, 2013. [5] Kürten, A. et al., Proc. Nat. Acad. Sci., 111, 15019–15024, 2014.

1The CLOUD (Cosmics Leaving OUtdoor Droplets) collaboration consists of 20 institutions from Europe and the United States and is funded by national funding institutions as well as the EU training network CLOUD-TRAIN (http://www.cloud-train.eu/)

3:06PM D27.00002 Aerosol Particle Interfacial Thermodynamics and Phase Partitioning Measurements Using Biphasic Microfluidics, Cari Dutcher, Andrew Metcalf, University of Minnesota, Twin Cities — Secondary organic aerosol particles are nearly ubiquitous in the atmosphere and yet there remain large uncertainties in their formation processes and ambient properties. These particles are complex microenvironments, which can contain multiple interfaces due to internal aqueous-organic phase partitioning and to the external liquid–vapor surface. Interfacial properties affect the ambient aerosol morphology, or internal structure of the particle, which in turn can affect the way a particle interacts with an environment of condensable clusters and organic vapors. To improve our ability to accurately predict ambient aerosol morphology, we must improve our knowledge of aerosol interfaces and their interactions with the ambient environment. Unfortunately, many techniques employed to measure interfacial properties do so in bulk solutions or in the presence of a ternary (e.g. solid) phase. In this talk, a novel method using biphasic microscale flows will be introduced for generating, trapping, and perturbing complex interfaces at atmospherically relevant conditions. These microfluidic experiments utilize high-speed imaging to monitor interfacial phenomena at the microscale and are performed with phase contrast and fluorescence microscopy on a temperature-controlled inverted microscope stage. From these experiments, interfacial thermodynamic properties such as surface or interfacial tension, rheological properties such as interfacial moduli, and kinetic properties such as mass transfer coefficients can be measured or inferred.

3:18PM D27.00003 Formation of Cluster Complexes by Cluster-Cluster-Collisions, Masaiko Ichihashi, Toyota Technological Institute, Hideho Oda, Genesis Research Institute, Inc. — Multi-element clusters are interesting in their chemical and physical properties, and it is expected that they are utilized as catalysts, for example. Their properties critically depend on the size, composition and atomic ordering, and it should be important to adjust the above parameters for their functionality. One of the ways to form a multi-element cluster is to employ a low-energy collision between clusters. Here, we show characteristic results obtained in the collision between a neutral Ar cluster and a size-selected Co cluster ion. Low-energy collision experiment was accomplished by using a newly developed merging-beam apparatus. Cobalt cluster ions were produced by laser ablation, and mass-selected. On the other hand, argon clusters were prepared by the supersonic expansion of Ar gas. Both cluster beams were merged together in an ion gun, and ionic cluster complexes were mass-analyzed. In the collision of Co\(^{+}\) and Ar\(_n\), Co\(_2\)Ar\(_n\)\(_n\) (n = 1–30) were observed, and the total intensity of Co\(_2\)Ar\(_n\)\(_n\) (n \(\geq\) 1) is inversely proportional to the relative velocity between Co\(_2\) and Ar\(_n\). This suggests that the charge-induced dipole interaction between Co\(_2\) and a neutral Ar cluster is dominant in the formation of the cluster complex, Co\(_2\)Ar\(_n\).

3:30PM D27.00004 Investigations of ice nanoparticles and aerosols in molecular beams, Michal Farnik, J. Heyrovsky Institute of Physical Chemistry, ASCR, Dolejskova 3, 18223 Prague 8, Czech Republic — We have recently set up a versatile experiment which allows for different chemical environments and other atmospheric processes. We investigate (1) the UV-photochemistry using velocity map imaging techniques, and (2) the uptake cross section for the molecules on the ice nanoparticles from velocity measurements. In addition, we record (3) mass spectra of the particles implementing different ionization methods: electron ionization (EI) at variable electron energies, photoionization, and special method of electron photodetachment after Na-doping (NaPi). The unique combination of all these different methods performed with the same nanoparticles provides detailed molecular level information about the studied species and their (photo)physics and chemistry. In particular, an investigation of mixed water-nitric acid particles by means of EI and NaPi revealed the prominent role of the HNO\(_3\) molecule as the condensation nucleus. The uptake of atmospheric molecules by ice nanoparticles has been studied, and the pickup cross sections for these species exceed significantly the geometrical sizes of the ice nanoparticles. It has been argued that the large particles composed of several hundred water molecules which grow in the supersonic expansions tend to have highly irregular shapes called nanosnowflakes. Photodissociation of hydrogen halides on ice nanoparticles has been investigated, and shown to proceed via excitation of acidically dissociated ion pair and subsequent biradical generation and H\(_2\)O dissociation. The photodissociation of CF\(_2\)Cl\(_2\) molecules in clusters leads to efficient Cl-fragment caging caused by formation of halogen bond.

4:06PM D27.00005 What is the structure of aqueous-alkane nanodroplets?, Barbara Wyslouzil, Harshad Pathak, Ohio State University, Columbus, ABDALLA Obeidat, Jordan University of Science and Technology, Gerald Wilemski, Missouri University of Science and Technology — In situ small angle X-ray scattering (SAXS) experiments were conducted on D\(_2\)O-none nanodroplets produced in a supersonic nozzle. Fits to the scattering spectra, using standard models for multicomponent droplets such as well-mixed spheres and core-shell structures, were often poor and furthermore the amount of one of the condensed species often violated mass balance. Better fits were obtained using ‘lens-on-sphere’ models suggested by molecular dynamics simulations. Here the amount of nonane condensed, based on the SAXS fitting parameters, was quite close to that measured by infrared absorption spectroscopy although the amount D\(_2\)O condensed was only half of that measured spectroscopically.

1Supported by NSF grants CBET 1033439 and CBET 103387, and Jordan University of Science and Technology
the structure of water/nonane nanodroplets was investigated using classical molecular dynamics (MD) simulations of SPC/E water and a unified atom model of nonane. Because nonane and water are essentially immiscible fluids that only partially wet each other, one might expect unusual nanodroplet structures to arise. Indeed, nonspherical, phase-separated Russian Doll (RD) structures were found to occur for these nanodroplets over the entire temperature range studied in the MD simulations, 220K – 300K. An idealized, but realistic lens-on-sphere model for the observed RD structures consists of a spherical nonane lens that partially wets a spherical water droplet. This model was used to analyze the experimental small angle x-ray scattering measurements. The simulated contact angle of nonane on water was found to be quite sensitive to the value of the Lennard-Jones energy parameter $\varepsilon_{OC}$ for the cross-interaction between oxygen and carbon atoms. The standard geometric mean approximation for $\varepsilon_{OC}$ yielded contact angles in the range 70° - 80°, while a 19% increase in $\varepsilon_{OC}$ reduced the simulated contact angle close to the experimental value of 33.6° at 295 K.

NORDLANDER, Rice University, HUI WANG, University of South Carolina — Noble metal nanoparticles have been of tremendous interest due to their catalytic activity. These nanomaterials, which are often faceted, can possess unique optical properties that can be tuned by changing their composition. The optical properties of these nanomaterials are critically dependent on their crystallographic and electronic structure, as well as on the local environment.

Facets by metal oxide LSPRs is critically examined to suggest what future applications might be on the horizon. Spectroscopy, also contributes to ensemble line shapes, complicating direct interpretation of LSPR spectra. Finally, the possibility of electric field enhancement of nucleation, remains an enigma. Recent experiments revealed a negative charge affinity of 1-propanol molecules condensing on tungsten oxide seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. 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In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while prevailing first-principles calculations indicated a positive preference. In this study, we investigate the adsorption of organic molecules on charged seeds, while previ...
Protected Noble-Metal Clusters at the Transition from Molecules to Materials  
ROBERT L. WHETTEN, University of Texas, San Antonio — Protected noble-metal clusters are found at a molecular level of definite composition and structure up to a size of 145-165 metal atoms. Curiously, this size-range is also where several key signatures of metallic character begin to converge. These substances have been of great interest for many application-areas in the past couple decades, but the understanding of their structure and bonding, remarkable self-selection, electronic structure and optical properties has only recently started to reach a fundamental or molecular level of definition. This presentation emphasizes this recent progress and also outlines the prospects for extending the molecular domain of metallurgy well beyond the 200-atom range, thanks to advances in experimental & theoretical methods.

9:24AM F26.00004 ABSTRACT WITHDRAWN —

Rich Information on Quantum States and Ways to Calculate It in The Absorption Spectra of Au$_{144}$ Gold Cluster Compound  
XOCHITL LÓPEZ-LOZANO, ROBERT L. WHETTEN, Department of Physics & Astronomy, The University of Texas at San Antonio, HANS-CHRISTIAN WEISSKER, Aix-Marseille Univ., CNRS, CINaM — In recent decades, the prevalent view has been that noble-metal clusters of intermediate size necessarily have smooth optical absorption spectra of low information content in the near-IR, VIS and near-UV regions. At most, one expects a broad, smooth localized surface plasmon resonance feature. Recently, we demonstrate that, in contradistinction to the commonly held view, the optical absorption of the most widely applied gold cluster, the thiolate-protected Au$_{144}$ cluster, exhibits a rich spectrum of bands that are individually visible over the entire near-IR, VIS and near-UV region (1.0-4.0 eV), demonstrating high information content related to the quantum size effects which distinguish the nanoparticles from the bulk materials. In the calculation, the result is sensitive to the details of the structure. In the present work, we systematically compare the different structures actually used to date. We studied aspects like symmetry, geometry and type of ligands. In particular, we discuss the effect of their differences on the optical absorption spectra as well as how the theoretical methodology influences the final results.

Surface Properties of TMAA-dosed TiO$_2$ Nanocrystals prepared in situ on Au(111) substrate with Scanning Tunneling Microscopy (STM) and Temperature Programmed Desorption (TPD). Photodesorption of trimethyl acetic acid was chosen as a model for light-driven reaction dynamics since it is easily imaged with STM and since this system has been the subject of many earlier studies. For comparison, we use the dynamics of TMAA on TiO$_2$ rutile(110) by exposing it over the volume of the cluster even at moments of zero overall polarization. The difference between Ag and Au is clearly visible. Finally, we discuss the question of collective vs. molecular-like transitions; even for single transitions, the dynamics of the total density can be similar to the picture of a charge oscillation.

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10:12AM F26.00006 Surface Properties of Quantum-Sized Noble-Metal Clusters: Quantum Calculations and the Classical Picture of Charge Oscillations  
HANS-CHRISTIAN WEISSKER, CNRS - CINaM, Centre Interdisciplinaire de Nanoscience de Marseille, XOCHITL LÓPEZ-LOZANO, Department of Physics and Astronomy — The University of Texas at San Antonio One UTSA Circle, San Antonio, TX 78249 — The localized surface-plasmon resonance (LSPR) in metal clusters corresponds to a collective charge oscillation of quasi-free electrons of the metal. We use the real-time formulation [1] of time-dependent density-functional theory (TDDFT) with pseudopotentials to study the correspondence and differences of the quantum calculations with the classical picture. By means of animations, we discuss the real-time evolution of the electronic density for different geometries. While there is a clear correspondence between the overall picture of a charge oscillation and the actual dynamics in quantum-sized clusters, the situation is much more intricate owing to quantum effects and the spread of electronic density over the volume of the cluster even at moments of zero overall polarization. The difference between Ag and Au is clearly visible. Finally, we discuss the question of collective vs. molecular-like transitions; even for single transitions, the dynamics of the total density can be similar to the picture of a charge oscillation.

10:24AM F26.00007 Plasmon induced electric current in a molecular junction  
PARTHA PAL, NANNING, MATTSON, NAHAO CHANG, EDWARD FOLEY, RICHARD VAN DUYNE, TAMAR SEIDEMAN, Department of Chemistry, Northwestern University — We report light-triggered, plasmon-enhanced charge transport in a tip-molecule-surface molecular junction. Experimentally, enhancement of tunneling current is recorded when a chopped laser beam illuminates the junction. The enhancement is quenched when the sample is devoid of molecules and its amplitude increases steeply when the focus of the beam moves closer to the space between the tip and the mono layered sample. Finite difference time domain calculations indicate that significant electromagnetic field enhancements due to plasmonic activity, occurs in the space between the tip and the sample which is also the region where the tunneling current perturbation peaks. The perturbation in the transport characteristics at the tip-sample junction is theoretically estimated using a recent formulation for describing the transient electronic distribution due to plasmon decoherences. We find the enhancement in the electronic current to be directly proportional to the plasmon excitations only in the presence of a molecular linker which is in excellent agreement with the experimental results. Further analysis reveals that the nascent distribution allows injection of electrons through additional molecular resonances which were previously inaccessible, thus leading to an increased current.

10:36AM F26.00008 Long-range structural correlations in amorphous ternary In-based oxides  
RABI KHANAL, JULIA MEDVEDEVA, Missouri University of Science and Technology — In recent years, there is an increasing shift towards the use of oxide semiconductor materials in their amorphous form owing to several technological advantages and the fact that amorphous oxides exhibit similar or even superior properties than their crystalline counterparts. In this work we have systematically investigated the effect of chemical composition and oxygen stoichiometry on the local and long-range structure of ternary amorphous oxides, namely In-X-O with X=Sn, Zn, Ga, Cd, Ge, Sc, Y, or La, by means of ab-initio molecular dynamics. The results reveal that the local MO structure remains nearly intact upon amorphization and exhibit weak dependence on the composition. In marked contrast, the structural characteristics of the metal-metal shell, namely the M-M distances and M-O-M angles that determine how MO polyhedra are connected into a network, are affected by the presence of X. Complex interplay between several factors such as the cation ionic size, metal-oxygen bond strength, as well as the natural preference for edge, corner, or face-sharing between the MO polyhedra, leads to a correlated behavior in the long-range structure. These findings highlight the mechanisms of the amorphous structure formation as well as the species of the carrier transport in these oxides.

10:48AM F26.00009 TMAA surface-molecule photon interactions on Au-supported TiO$_2$ nanocrystals  
RICHARD OSGOOD, DENIS POTAPENKO, ZHISHENG LI, Columbia University — Nanostructured titanium dioxide is a versatile photocatalytic material. While its photocatalytic properties have been extensively studied in liquid/gas-phase environments, studies of the physics of photoinduced dynamics and reactions on bare well characterized titania nanoparticles using surface science tools have been lacking. Here we explore these photoinduced properties of TMAA-dosed TiO$_2$ nanocrystals prepared in situ on Au(111) substrate with Scanning Tunneling Microscopy (STM) and Temperature Programmed Desorption (TPD). Photodesorption of trimethyl acetic acid was chosen as a model for light-driven reaction dynamics since it is easily imaged with STM and since this system has been the subject of many earlier studies. For comparison, we use the dynamics of TMAA on TiO$_2$ rutile(110) by exposing it to monochromatized UV light and by injecting charges from the STM tip. We then demonstrated that 1–3 nm high and 10–25 nm wide nanocrystals of TiO$_2$ grown on Au(111) surface also exhibit photooxidation activity for TMAA when illuminated with UV light. TPD results, which provided surface-averaged information, agree well with STM data and demonstrate TMAA desorption on a single-molecule basis.

Tuesday, March 3, 2015 8:00AM - 10:48AM — Session F27 DCP: Focus Session: Emerging Ultrafast Technologies III  
204B - Jennifer Ogilvie, University of Michigan
8:00AM F27.00001 Anti-correlated vibrations drive fast non-adiabatic light harvesting

DAVID JONAS, University of Colorado — We have recently shown that intramolecular vibrations shared across pigments can drive electronic energy transfer beyond the Born-Oppenheimer framework developed by Forster. The key features of this mechanism are a small change in vibrational equilibrium (less than the zero point amplitude) upon electronic excitation of the pigments and vibrational resonance with the adiabatic electronic energy gap. For identical pigments, delocalized, anti-correlated vibrations increase the speed of energy transfer. The same anti-correlated vibrations are excited by an electronically enhanced Raman process on the ground electronic state of photosynthetic antennas, and these vibrational wavepackets generate all of the reported signatures of photosynthetic energy transfer in femtosecond two-dimensional Fourier transform spectra. The talk will discuss how these results are generalized for differences between donor and acceptor and for multiple vibrations.

1 This material is based upon work supported by the Air Force Office of Scientific Research under AFOSR Award No. FA9550-14-1-0258

8:36AM F27.00002 Two-Dimensional Line Shapes in Electronic-Vibrational Spectroscopy as a Measure of Correlated Spectral Dynamics of Electronic and Vibrational Degrees of Freedom

NICHOLAS LEWIS, HUI DONG, THOMAS OLIVER, GRAHAM FLEMING, University of California, Berkeley — 2D optical spectroscopies in many different frequency regimes have been useful to study the correlated spectral behavior for many different types of system degrees of freedom. The slope of the center-line of a feature in 2D electronic and 2D infrared spectroscopy has been shown to provide detailed information about the correlation functions that describe the system-bath coupling for the system degrees of freedom.1 Recently, we have demonstrated a new spectroscopic technique, 2D electronic-vibrational spectroscopy, that is capable of directly measuring the correlation between spectral motion of the electronic and vibrational degrees of freedom Here we demonstrate that the center-line slope of a 2DEV resonance can be directly related to the correlation function for the vibrational degrees of freedom on the excited state. We show experimentally that this can be observed in 2DEV spectra of the dye DTTCI. Finally, we show how 2DEV spectra can be used to directly measure the strength of system-bath coupling for the vibrational degrees of freedom on the excited state versus those on the electronic ground state.

1 K. Kwac and M. Cho, J. Phys. Chem. A 107, 5903
2 T. A. A. Oliver, N. H. C. Lewis and G. R. Fleming, PNAS 111, 0927

8:48AM F27.00003 Femtosecond Stimulated Raman Spectroscopy by Six-Wave Mixing

ANDREW MORAN, University of North Carolina — Knowledge of the structural changes that accompany photochemical reactions has motivated the development of a wide variety of time-resolved vibrational spectroscopies. For example, a technique known as femtosecond stimulated Raman spectroscopy (FSRS) has yielded important insights into numerous photochemical processes in the past 10-15 years. Simultaneous probing of all resonances in the fingerprint region of the vibrational spectrum and sensitivity to dynamics on the 100-fs time scale are the primary selling points for the FSRS technique. Despite its utility, FSRS is challenged by a large background of residual laser light and lower-order nonlinearities. In this talk, I will introduce a newly developed FSRS experiment in which five laser beams are used eliminate the background of residual laser light and lower-order nonlinearities present in the traditional three-beam FSRS geometry. Applications to photodissociation reactions in triiodide and heme proteins will be discussed. It is envisioned that this approach will be useful for investigating photoinduced dynamics in a wide variety of condensed phase systems.

9:24AM F27.00004 Quantum Process Tomography by 2D Fluorescence Spectroscopy

LEONARDO A. PACHON, Instate de Fisica, Universidad de Antioquia. Department of Chemistry and Chemical Biology, Harvard University, ALAN ASPURU-GUZIK, Department of Chemistry and Chemical Biology, Harvard University. — Characterization of quantum dynamics is one of the most important steps toward the implementation of any quantum technology and therefore, it is of fundamental relevance. Traditionally, dynamics are studied for particular initial preparations and hence, only partial information about the underlying physical processes is obtained. To overcome this drawback, a variety of proposals based on spectroscopic techniques have been suggested. Quantum Processes Tomography allows for the experimental reconstruction of the dynamics regardless the initial condition. Despite the success of QTP, the spectroscopic techniques they are based on require large samples to enhance the non-linear signal. Hence, particular features of the dynamics and realistic time scales are hidden by the incoherent average over the large structural and electronic heterogeneity. Based on recent progress on non-linear spectroscopies using collinear phase-modulated ultra-short pulses, which are suitable for single molecule spectroscopy, a formulation of single molecule QPT with classical light is provided here. This technique is applied to recover the dynamics of a model dimer. The single molecule character of this technique predicts longer coherence times than those techniques based on the phase-matching condition.

9:36AM F27.00005 Ultrafast 2D Fluorescence Spectroscopy using Spectrally Entangled Photon Pairs

MICHAEL RAYMER, University of Oregon — We propose entangled photon-pair two-dimensional fluorescence spectroscopy (EPP-2DFS) to probe the nonlinear electronic response of molecular systems. [1] The method, inspired by results in [2], uses a technique from quantum optics—a separated two-photon (Franzon) interferometer, which generates time-delayed packets of time-frequency-entangled photon pairs. This interferometer is incorporated into the framework of a fluorescence-detected 2D optical spectroscopic experiment [3]. The continuous stream of entangled photons are phase-modulated in the interferometer, and used to excite a two-photon-absorbing sample, whose excited-state population is selectively detected by simultaneously monitoring the sample fluorescence and the transmitted excitation fields. In comparison to standard ‘classical’ 2DFS techniques using coherent laser pulses and standard pulse-scanning sequences, advantages of this scheme include the suppression of uncorrelated background signals, the suppression of diagonal 2D spectral features, the enhancement and narrowing of off-diagonal spectral cross-peaks that contain information about electronic coupling, and the possibility for enhancement of simultaneous time- and-frequency resolution, including spectral selectivity within an inhomogeneously broadened distribution. These effects arise from the properties of parametric down-conversion light source, which effectively creates a different interaction-scanning protocol than in standard laser-pulse scanning. We numerically simulate the EPP-2DFS observable for the case of an electronically coupled molecular dimer. The EPP-2DFS spectrum is greatly simplified in comparison to its standard classical 2D counterpart. Our results indicate that EPP-2DFS can provide previously unattainable resolution to extract model Hamiltonian parameters from electronically coupled molecular dimers.

10:12AM F27.00006 Surface Sum Frequency Generation of III-V Semiconductors$^1$, ZHENYU ZHANG, JISUN KIM, Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA, E.W. PLUMMER, Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA, RAMI KHOURY, Department of Chemistry, Louisiana State University, Baton Rouge, LA, LOUIS HABER, Department of Chemistry, Louisiana State University, Baton Rouge, LA — Optical sum frequency generation (SFG) is a well-established technique for surface and interface studies but its use has been limited mainly to centrosymmetric materials so far. Here, we demonstrate that femtosecond broadband SFG spectroscopy has the ability to identify surface molecular vibrations on the archetypical non-centrosymmetric semiconductor GaAs (001), in which the bulk SFG signal typically dominates over surface SFG contributions. We present a conceptual framework to quantitatively describe the interaction and show that the process is highly sensitive to the relative optical phase of the stimulating field. To emphasize the utility of the technique, we demonstrate stimulated enhancement of second harmonic generation (SHG) from bovine collagen-I fibrils. Using a stimulating pulse fluence of only 3 nJ/cm$^2$, we obtain an SHG enhancement of $>10^4$ relative to the spontaneous signal. The stimulated enhancement is greatest in situations where spontaneous signals are the weakest — such as low laser power, small sample volume, and weak nonlinear susceptibility — emphasizing the importance of this technique for improving signal-to-noise ratios in biological imaging and interfacial spectroscopy.

$^1$Funded by EFRC

10:24AM F27.00007 Probing Molecular Organization and Electronic Dynamics at Buried Organic Interfaces, SEAN ROBERTS, University of Texas at Austin — Organic semiconductors are a promising class of materials due to their ability to meld the charge transport capabilities of semiconductors with many of the processing advantages of plastics. In thin film organic devices, interfacial charge transfer often comprises a crucial step in device operation. As molecular materials, the density of states within organic semiconductors often reflect their intermolecular organization. Truncation of the bulk structure of an organic semiconductor at an interface with another material can lead to substantial changes in the density of states near the interface that can significantly impact rates for interfacial charge and energy transfer. Here, we will present the results of experiments that utilize electronic sum frequency generation (ESFG) to probe buried interfaces in these materials. Within the electric dipole approximation, ESFG is only sensitive to regions of a sample that experience a breakdown of symmetry, which occurs naturally at material interfaces. Through modeling of signals measured for thin organic films using a transfer matrix-based formalism, signals from buried interfaces between two materials can be isolated and used to uncover the interfacial density of states.

10:36AM F27.00008 Stimulated Second Harmonic Generation for High-Sensitivity Interfacial Spectroscopy and Imaging, AARON GOODMAN, Department of Chemistry, Massachusetts Institute of Technology, WILLIAM TISDALE, Department of Chemical Engineering, Massachusetts Institute of Technology — Second-order nonlinear optical interactions such as sum- and difference-frequency generation are widely used for bioimaging and as selective probes of interfacial environments. However, inefficient nonlinear optical conversion often leads to poor signal-to-noise ratios and long signal acquisition times. Here, we demonstrate the dramatic enhancement of weak second-order nonlinear optical signals via stimulated sum- and difference-frequency generation. We present a conceptual framework to quantitatively describe the interaction and show that the process is highly sensitive to the relative optical phase of the stimulating field. To emphasize the utility of the technique, we demonstrate stimulated enhancement of second harmonic generation (SHG) from bovine collagen-I fibrils. Using a stimulating pulse fluence of only 3 nJ/cm$^2$, we obtain an SHG enhancement of $>10^4$ relative to the spontaneous signal. The stimulated enhancement is greatest in situations where spontaneous signals are the weakest — such as low laser power, small sample volume, and weak nonlinear susceptibility — emphasizing the importance of this technique for improving signal-to-noise ratios in biological imaging and interfacial spectroscopy.


11:15AM G26.00001 The Non-Adiabatic dynamics of Singlet Fission in Polyacenes$^1$, STEPHEN BRADFORTH, Univ of Southern California — Singlet fission involves the splitting of a single excitation into two coupled triplet excitations and is manifested in an increasing range of aromatic crystals and amorphous thin films. If the energy of the lowest triplet state is one half (or less) of the first singlet excited state, it is for tetracene or pentacene and their derivatives, singlet fission may occur between two adjacent chromophores. Since there is no change in the overall spin state of the system, singlet fission can be exceptionally fast, occurring on the fs – ps range. If the triplets can diffuse away from the fission site they are available for harvesting as a dissociated carriers with up to two charge carrier pairs per absorbed photon. The possibility of recovering excess energy above the material band gap (in this case determined by the triplet energy) when a higher energy photon is absorbed has led to great recent interest in exploiting this process for increased efficiency solar energy harvesting. The nature of the electronic couplings between the chromophores, intermediate electronic configurations, and the role of entropy in the spin-allowed primary fission event have all come under great scrutiny. Results from a series of femtosecond spectroscopy experiments on a variety of amorphous thin films, nanoparticles and isolated acene dimer compounds will be presented that shed light on the electronic intermediate states key to the efficiency and speed of this process.

$^1$Work supported as part of the Center for Energy Nanoscience, an Energy Frontier Research Center funded by the U.S. Department of Energy (DE-SC0001013)

11:51AM G26.00002 Extracting Molecular Dynamics from Ion Imaging Experiments of Carbonyl Sulfide, WEI WEI, COLIN WALLACE, SIMON NORTH, Texas A&M Univ — Photodissociation of carbonyl sulfide at 215nm are studied in details with sliced ion imaging experiments. Energy partitioning as well as vector correlations between carbonyl sulfide transition dipole moments, CO recoil velocity vector and angular momentum will be revealed. They can provide valuable information about symmetry of excited states which are involved in photodissociation process. These results can reveal information about non-adiabatic dynamics in carbonyl sulfide excited states. The results will be compared with both computational chemistry study conducted by G. McBane and coworkers. The result will also be compared with previous study on dynamics from carbonyl sulfide photodissociation at longer wavelength by Bersohn and coworkers.

12:03PM G26.00003 Vibronic interactions in multi-chromophores, LYUDMILA SLIPCHENKO, Purdue University — Understanding and control of excitation energy transfer and electron-phonon interactions is quintessential for advances in solar energy utilization. Recently, we developed a vibronic model that is capable of predicting vibronic spectra in complex multi-chromophore systems. Parameters to the model are obtained from electronic structure calculations on monomer units of a multi-chromophore. This model can account for multiple vibrational modes, asymmetric wave functions, and inter-chromophore vibrations. Using this model, we explored vibronic spectra in a series of flexible bichromophores with available high-resolution experimental spectra. One of the goals of this work was to understand the effects of asymmetry in monomer units on vibronic interactions in bichromophores. Detailed investigation of diphenylmethane, partially deuterated diphenylmethane, and diphenylethane resulted in intriguing observation that asymmetry leads to a partial localization of one of the exciton states but leaves the other one delocalized. Extension of the developed methodology to modeling spectroscopy and dynamics in synthetic and biological multi-chromophore systems such as photosynthetic proteins will be also discussed.
12:03PM G27.00003 Structural determination of metal nanoparticles from their vibrational (phonon) density of states1, IGNACIO GARZON, Universidad Nacional Autonoma de Mexico, HUZIEL SAUCEDA, Universidad Nacional Autonoma de Mexico — The vibrational (phonon) density of states of metal nanoparticles with size between 2-6 nm can be measured using nuclear resonant inelastic x-ray or plasmon resonance Raman scattering. In this work, we present atomistic calculations, based on a semiempirical tight-binding many-body Gupta potential, of the vibrational density of states (VDOS) for FCC, decahedral, and icosahedral (ICO) gold and silver nanoparticles with sizes ~ 4 nm (~ 2000 atoms). The calculated VDOS are compared with experimental data, recently published for gold and silver nanoparticles of similar size, obtained through plasmon resonance Raman scattering. The best agreement between the calculated and measured VDOS’s is obtained for the ICO morphology for both metal nanoparticles. These results indicate that most of the nanoparticles in the experimental samples should have icosahedral structures. The present study also shows that, as in the case of molecular systems and small clusters, vibrational spectroscopy of metal nanoparticles with few nanometers in size, together with theoretical calculations, are powerful tools for their structure determination. with your abstract body.

1Work supported by CONACYT-Mexico under Project 177981.

12:15PM G27.00004 Simulation studies of glassy nanoclusters, RICHARD BOWLES, Dept. Chemistry, University of Saskatchewan — Glassy materials are amorphous solids usually formed by rapidly cooling a liquid below its equilibrium freezing temperature, trapping the particles in a liquid-like structure at the glass transition temperature. While appearing throughout nature and industry, these systems continue to challenge the way we think about the dynamics and thermodynamics of condensed matter and a fundamental understanding of the glass state remains elusive. This talk describes molecular simulation studies of glassy behaviour in binary Lennard–Jones nanoclusters. We show that the relaxation dynamics of the clusters is nonuniform and the core of the cluster goes through a glass transition at higher temperatures than at the surface. As the nanoclusters are cooled, they also exhibit a fragile–strong crossover in their dynamics and we explore how this phenomena is linked to the potential energy landscape of the clusters. Finally, we compare the properties of nanoclusters formed through vapour condensation, directly to the glassy state, with those of glassy clusters formed through traditional supercooling. The condensation clusters are shown to form ultra-stable glassy states analogous to the ultra-stable glasses formed by thin film vapour deposition onto a cold substrate. In all, our work suggests that nanoscale clusters exhibit some unique glassy features, while also offering potential insights into the fundamental nature of the glass transition.

12:51PM G27.00005 Effects of Thermal Annealing and X-ray Exposure on Local Structures Surrounding Co in (Y, Co)-codoped CeO₂ Nanocrystals, TAI-SING WU, HORNG-TAY JENG, National Tsing Hua University, Taiwan, SHIH-LIN CHANG, National Synchrotron Radiation Research Center, Taiwan, YUN-LIANG SOO, National Tsing Hua University, Taiwan — Codoping of Y and Co in CeO₂ has been found to incur an unconventional bandgap narrowing effect in the host nanocrystal material. The dormant bandgap-tuning ability of Y appears to be turned on by the Co codopant in the oxygen-vacancy-rich CeO₂ host. The physical mechanism underlying such effect has also been revealed by DFT calculations. Synchrotron-Radiation-based X-ray absorption analysis has further demonstrated that the Co codopant atoms can be located in either of two different local bonding environments in the CeO₂ host. Thermal annealing is capable of driving Co atoms from one bonding environment to the other. On the other hand, when exposed to x-rays of sufficient photon energy, Co can resume the original local structure as in the as-made sample. A simple model is proposed to explain such intriguing interplay between the effects of annealing and x-ray exposure in these codoped nanoceria samples.

1:03PM G27.00006 The correspondence between the infrared vibrational spectra and the underlying hydrogen bonding network in aqueous clusters: caveats and tactics1, SATIRIS XANTHEAS, Pacific Northwest National Laboratory — The structural – spectral correspondence relates the observed infrared (IR) vibrational spectra to the underlying molecular structure. In the case of hydrogen bonded clusters the IR “fingerprint” region in the 3,000 – 4,000 cm⁻¹ range provides a direct probe of the connectivity and dynamics of the cluster’s hydrogen bonding network. For medium size (~20) aequous neutral and ionic clusters, the presence of several closely lying isomers that differ substantially in the oxygen atom network complicates both the sampling of the respective potential energy surfaces as well as the accurate determination of their energy order. Traditionally, a hierarchical procedure based on initial sampling with classical potentials and subsequent refinement with electronic structure methods has been used. We will highlight representative examples for the (H₂O)₂₀, (H₃O)₂₀, and H₃O⁺(H₂O)₂₀ clusters [1-3] where sampling with classical potentials fails to produce the most stable minima and outline approaches and strategies that are based on a combination of enhanced sampling of configurations in conjunction with electronic structure theory to obtain realistic cluster configurations that are consistent with the measured IR spectra.

1Work supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. Pacific Northwest National Laboratory (PNNL) is a multi-program national laboratory operated for DOE by Battelle.

1:39PM G27.00007 Studies of energetics and spectroscopy of water clusters: size evolution and connections to the spectrum of liquid water, ANNE MCCOY, Department of Chemistry and Biochemistry, The Ohio State University — In this talk, I will focus on recent work in our group on water clusters. The first part will focus on interpreting the origins of the band at 2100 cm⁻¹ in the absorption spectrum of liquid water. Based on its frequency, the band has long been assigned to a combination band involving intramolecular bend vibration and intermolecular librations. The intensity arises from changes in the transition moment for the HOH bend as the low-frequency librations form and break intermolecular hydrogen bonds. In the second part we investigate approaches for using Diffusion Monte Carlo for studying the zero-point averaged vibrational structure of water clusters. The weak coupling between the inter- and intra-molecular degrees of freedom makes these challenging systems for DMC. Approaches taken and insights gained from this work will be described.
1:51PM G27.00008 Infrared spectral challenges of individual, respirable, micron-sized dust particles: Strong phonons and their distorted lineshapes. JAMES COE, Ohio State Univ - Columbus — Consideration of cluster properties as they grow through the nanosize regime and into the micron-sized regime, leads to expectations of bulk-like trends which are well understood. However, individual micron-sized particles are of comparable size to the wavelength of probing infrared (IR) light, so vibrational spectra will be dominated by scattering effects and lineshapes will have dispersion and saturation distortions. Airborne dust particles of ~ 4 micron widths are of particular health interest because they get past the nose, throat, and thorax and can be inhaled into people’s lungs. This talk will describe the use of plasmonic metal mesh to obtain scatter-free, IR absorption spectra of single, ~ 4 micron respirable particles. A dust library of single particle IR spectra is being compiled to chemically characterize respirable dust and a Mie-Bruggeman model has been created to predict the IR spectra of collections of mixed-composition dust particles. Having dealt with scattering effects, the remaining difficulty involves the effect of strong phonons. Many of the most common mineral components of dust have strong phonons with intensity cross sections comparable to the size of the particle which leads to severe and interesting lineshape distortions.

2:30PM J26.00001 Corona Phase Molecular Recognition (CoPhMoRe) to Enable New Nanosensor Interfaces. MICHAEL STRANO, Massachusetts Inst of Tech-MIT — Our lab at MIT has been interested in how the 1D and 2D electronic structures of carbon nanotubes and graphene respectively can be utilized to advance new concepts in molecular detection. We introduce CoPhMoRe or corona phase molecular recognition [1] as a method of discovering synthetic antibodies, or nanotube-templated recognition sites from a heteropolymer library. We show that certain synthetic heteropolymers, once constrained onto a single-wall carbon nanotube by chemical adsorption, also form a new corona phase that exhibits highly selective recognition for specific molecules. To prove the generality of this phenomenon, we report three examples of heteropolymers–nanotube recognition complexes for riboflavin, L-thyroxine and estradiol. The platform opens new opportunities to create synthetic recognition sites for molecular detection. We have also extended this molecular recognition technique to neurotransmitters, producing the first fluorescent sensor for dopamine. Another area of advancement in biosensor development is the use of near infrared fluorescent carbon nanotube sensors for in-vivo detection [2]. Here, we show that PEG-ligated d(AAAT)₅ DNA wrapped SWNT are selective for nitric oxide, a vasodilator of blood vessels, and can be tail vein injected into mice and localized within the viable mouse liver. We use an SJL mouse model to study liver inflammation in vivo using the spatially and spectrally resolved nIR signature of the localized SWNT sensors.

3:06PM J26.00002 Detection of DNA and Protein using CVD Graphene-channel FET Biosensors. ABHILASH SEBASTIAN, ANIKET KAKATKAR, ROBERTO DE ALBA, HAROLD CRAIGHEAD, JEEVAK PARPIA, Centre for Materials Research, Cornell University — Graphene channel field-effect biosensors are demonstrated for detecting the binding of double-stranded DNA and poly-l-lysine. Sensors consist of CVD graphene transferred using a clean, etchant-free transfer method. The presence of DNA and poly-l-lysine are detected by the change in the Dirac Voltage (the voltage at which the graphene’s resistance peaks) of the graphene transistor. Sensors show large shifts in the Dirac voltage ~ 17 V after exposure to ~ 580 pM of poly-l-lysine and ~ 14 V upon exposure to 300 pM of DNA. The polarity of the response changes to positive direction with poly-l-lysine and negative direction with DNA. Sensors show detection limits of 8 pM for 48.5 kbp DNA and 11 pM for poly-l-lysine. The biosensors are easy to fabricate, reusable and are promising as sensors of a wide variety of charged biomolecules.

3:18PM J26.00003 High Yield and Scalable Fabrication of Nano/Bio Hybrid Graphene Field Effect Transistors for Cancer Biomarker Detection. PEDRO DUCOS, MADELINE DIAZ, Univ of Pennsylvania, MATTHEW ROBINSON, Fox Chase Cancer Center, A.T. CHARLIE JOHNSON, Univ of Pennsylvania — Graphene field effect transistors (GFETs) hold tremendous promise for use as biosensor transduction elements due to graphene’s high mobility, low noise and all-surface structure with every atom exposed to the environment. We developed a GFET array fabrication based on two approaches, pre-patterned transfer and post-transfer photolithography. Both approaches are scalable, high yield, and electrically stable. Functional groups for protein immobilization were added to the GFET using various bi-functional pyrene-based linkers. One approach immobilized an azide engineered protein through a “Staudinger Reaction” chemistry with NHS-phosphine reacting with a 1-aminopyrene linker. Another approach bound an engineered antibody via 1-pyrene butanoic acid succinimidyl ester, where an amine group of the antibody reacts to the succinimide of the linker. GFETs were studied by Raman spectroscopy, AFM and current-gate voltage (I-Vg) characterization at several steps of the fabrication process. A sensing response was obtained for a breast cancer biomarker (HER2) as a function of target concentration. We have started to design multiplexed sensor arrays by adding several functional groups to GFETs on a single chip. Simultaneous detection with these devices will be discussed.

3:30PM J26.00004 Infrared detection with colloidal quantum dots based on interband and intraband transitions. PHILIPPE GUYOT-SIONNES, University of Chicago — While much research on colloidal quantum dots is focused on their potential as visible emitter or light harvester, this talk will cover our investigations of the mercury chalcogenide colloidal quantum dot materials used for the mid-infrared ranges of 3-5 microns and 8-12 microns where the atmosphere is transparent. HgTe is a zero-gap semiconductor. As a result, colloidal quantum dots (CQD) of sizes between 10 and 20 nm readily lead to infrared gaps tuning between 3 and 12 microns respectively. It is also very promising that infrared photodetection using dried films of these CQDs has now been demonstrated up to 12 microns. Further improvement through chemistry are likely and will be required to raise the detectivity to the level required to transform thermal infrared detection technology. In contrast to HgTe CQDs which tend to be intrinsic, beta-HgS and HgSe CQDs are naturally n-doped, in the first such instance with CQDs. Furthermore, the doping is modulated by modifying the surface composition, and this effect is attributed to the tuning of the energy level with respect to the environment, via the surface electrostatics. With controlled doping, both HgSe and HgS CQDs have now led to the first operation of mid-infrared CQD photodetector based on the intraband absorption. This is a breakthrough in the field of colloidal quantum dots where interband transitions had been exclusively used for the past 30 years. One challenge with both interband and intraband infrared CQDs will be to reduce the nonradiative recombination, which will improve the detectivity as well as allow to use their infrared luminescence.
4:06PM J26.00005 Unraveling Molecular Structure in Stern Layer at Charged Water Interface using sum-frequency vibrational spectroscopy. YU-CHEH WEN, Institute of Physics, Academia Sinica, SHUAI ZHA, SHANSHAN YANG, CHUANSHAN TIAN, Department of Physics, Fudan University, Y. RON SHEN, Department of Physics, University of California, Berkeley — Charged aqueous interfaces, such as membrane/water and electrochemical interfaces, are essential in many chemical, biological, and environmental processes. Interactions between heterogeneous interfacial molecules and the consequent molecular network dictate properties and functions of the interfaces; however, the microscopic-level picture of the charged water interfaces remains substantially unclear. Here we demonstrate probing of the molecular structure in Stern layer at aqueous interfaces using sum-frequency vibrational spectroscopy. We show that at ionic surfactant/water interfaces, the hydrogen- (H-)bonding strength and network in the Stern layer depend sensitively on conformation and ionization of the surfactants, suggesting a relevant influence of the surfactant-water charge transfer. In addition, ion adsorption to the interface is shown to distort the interfacial water structure. Our study offers exciting opportunities to acquire microscopic insights into interfaces for catalytic and electrochemical applications.

4:18PM J26.00006 Mind the Entropy: Electronic and Thermal Fluctuations of Large Molecules on Metals. REINHARD MAURER, Yale University, WEI LIU, IGOR POLTAVSKYI, Fritz-Haber Institute of the Max-Planck Society, HARALD OBERHOFER, THOMAS STECHER, Technische Universitaet Muenchen, ALEXANDRE TKATCHENKO, Fritz-Haber Institute of the Max-Planck Society, KARSTEN REUTER, Technische Universitaet Muenchen. The prevailing working hypothesis in vacuum surface science is that equilibrium properties of adsorbed molecules are largely unaltered by finite temperature effects. In this work we illustrate that this is not the case for the adsorption geometry, energetics, and desorption temperature of the molecular switch Azobenzene adsorbed to Ag(111). Comparing with X-ray standing wave measurements and temperature programmed desorption experiments we find strong discrepancies to static Density-Functional Theory calculations. Anharmonic corrections and ab-initio molecular dynamics simulation of the free energy of desorption account for the thermal fluctuations and inclusion of many-body dispersion effects accounts for the electronic fluctuations that govern the interaction strength. In both cases more modest, typically employed approaches fail to capture the sizable entropy of desorption and the correct desorption temperature. This implies that an accurate description of adsorbate interactions and entropies of adsorption in most realistic functional hybrid metallic organic systems necessitates a full account of the inherent anharmonicity of adsorbate and substrate in addition to an accurate description of dispersion interactions.

4:30PM J26.00007 Stressed and Compressed Polymersomes. ROBERT HAYES, CHANGQIAN YU, STEVE GRANICK, Univ of Illinois - Urbana — Polymersomes are well-defined vesicular structures that have been studied extensively for encapsulation, controlled release and as cell mimics, inter alia. While polymersomes at ambient conditions are reasonably well-understood, comparatively little is known about how structure and properties change when subject to variations in their local environment. In this talk, atomic force microscopy is used to probe PEO-PBD polymersomes adsorbed at a solid liquid interface under osmotic pressure. We reveal interesting changes in shape and solution not captured by classical theory.

4:42PM J26.00008 Effect of CO2 on a polystyrene adsorbed nanolayer1. DEBORAH BARKLEY, NAISHENG JIANG, LEVENT SENDODUGULAR, XIAOYU DI, MANI SEN, MAYA K. ENDOH, TADANORI KOGA, Stony Brook University, Stony Brook, NY, BULENT AKGUN, Center for Neutron Research, National Institute of Standards and Technology, Bogazici University, Bebek, Istanbul, Turkey, MICHAEL DIMITRIOU, SUSHIL SATIJA, Center for Neutron Research, National Institute of Standards and Technology — We report the role of compressed carbon dioxide (CO2) in a mobility gradient of polymer chains near a planar solid substrate. A series of bilayers of bottom hydrogenated polystyrene and top deuterated polystyrene layers were prepared on Si substrates, and high pressure neutron reflectivity (NR) was used to study diffusive motion at the polymer/polymer interface. The interdiffusion is hindered when the distance is larger than 3Rg (Rg, radius of polymer gyration). This reduced chain diffusivity is attributed to CO2-induced polymer adsorption on the substrate, transforming the 0.6Rg thick region from the substrate interface into an irreversibly adsorbed polymer layer. The cohesion strength is attributed to loops in the adsorbed chains with which the neighboring chains can entangle.1T. K. acknowledges the partial financial support from NSF Grants (CMMI-084626 and CMIMI-1332499).

4:54PM J26.00009 First-principles investigation of CO2 absorption on III-nitride surfaces. YING-CHIN CHEN, HONG GUO, McGill Univ — Photoinduced chemical transformation of CO2 is a very interesting direction of greenhouse gas reduction. An accurate description of electronic structure at the interface between CO2 and the photocatalysts is important for understanding the process of artificial photosynthesis. In this work we report density functional theory (DFT) and many-body GW calculations to investigate CO2 adsorption on III-nitride semiconductor surfaces. The adsorption geometry is determined at the DFT level and the electronic structure is investigated at both DFT and GW levels. A detailed illustration of how the molecular orbital is renormalized is addressed.

5:06PM J26.00010 Ab initio molecular-dynamics study of EC decomposition process on Li2O2 surfaces. YASUNOBU ANDO1, Department of Materials Engineering, The University of Tokyo, TAMIO IKESHOJI, MINORU OTANI2, Nanosystem Research Institute, AIST — We have simulated electrochemical reactions of the EC molecule decomposition on Li2O2 substrate by ab initio molecular dynamics combined with the effective screening medium method. EC molecules adsorb onto the peroxide spontaneously. We find through the analysis of density of states that the adsorption state is stabilized by hybridization of the sp2 orbital and the surface states of the Li2O2. After adsorption, EC ring opens, which leads to the decomposition of the peroxide and the formation of a carboxy group. This kind of alkyl carbonates formed on the Li2O2 substrate was found in experiments actually.

5:18PM J26.00011 Understanding 3C-SiC/SiO2 interfaces in SiC-nanofiber based solar cells from ab initio theory1, TAUFIK ADI NUGRAHA, STEFAN WIPPERMANN, Max-Planck-Institute for Iron Research — Nanostructured materials such as e.g. hybrid nanocomposites consisting of inorganic semiconducting nanofibers and organic surfactants provide genuinely novel pathways to exceed the Shockley-Queisser limit for solar energy conversion. The synthesis of such functionalized nanofibers can be performed completely using only inexpensive wet chemical solution processing. However, the synthesis conditions often lead to complex interfacial structures involving thin oxide layers between the nanofiber and surfactants, whose atomistic details are poorly understood at best. Here we present a combined density functional theory and tight binding investigation of interfaces between 3C-SiC nanofiber surfaces and SiO2. Considering a wide variety of possible interfacial structures we utilize a grand canonical approach to generate a phase diagram and predict the structural details of the interface as a function of the chemical potentials of Si, O and H. This study provides indications about how the synthesis conditions lead to specific types of interfacial structures and their impact on the electronic properties of the interface.1The authors wish to thank U. Gerstmann, S. Greulich-Weber and W. G. Schmidt for helpful discussions. S. W. acknowledges BMBF NanoMatFutur Grant No. 13N12972.
Tuesday, March 3, 2015 2:30PM - 4:54PM –
Session J27 DCP: Focus Session: Chemical Physics of Clusters: Bridging from Angstrom-scale Clusters to Micron-scale Aerosol Particles III 204B - Cari Dutcher, University of Minnesota

2:30PM J27.00001 Solvation Effects on Structure and Charge Distribution in Anionic Clusters1
J. MATHIAS WEBER, JILA and Department of Chemistry & Biochemistry, University of Colorado at Boulder — The interaction of ions with solvent molecules modifies the properties of both solvent and solute. Solvation generally stabilizes compact charge distributions compared to more diffuse ones. In the most extreme cases, solvation will alter the very composition of the ion itself. We use infrared photodissociation spectroscopy of mass-selected ions to probe how solvation affects the structures and charge distributions of metal-CO2 cluster anions.

We gratefully acknowledge the National Science Foundation for funding through Grant CHE-0845618 (for graduate student support) and for instrumentation funding through Grant PHY-1125844.

3:06PM J27.00002 Proton transfer in acetaldehyde and acetaldehyde-water clusters: Vacuum ultraviolet photoionization experiment and theoretical calculations. OLEG KOSTKO, TYLER P. TROY, BISWAJIT BANDYOPADHYAY, MUSAHID AHMED, Lawrence Berkeley National Lab — Acetaldehyde, a probable human carcinogen and of environmental importance, upon solvation provides a test bed for understanding proton transfer pathways and catalytic mechanisms. In this study, we report on single photon vacuum ultraviolet photoionization of small acetaldehyde and acetaldehyde-water clusters. Appearance energies of protonated clusters are extracted from the experimental photoionization efficiency curves and compared to electronic structure calculations. The comparison of experimental data to computational results provides mechanistic insight into the fragmentation mechanisms of the observed mass spectra. Using deuterated water for isotopic tagging, we observe that proton transfer is mediated via acetaldehyde and not water in protonated acetaldehyde-water clusters.

3:18PM J27.00003 Does the 18-Electron Rule Apply to CrSi1221
MARISSA BADDICK ABREU, VIKAS CHAUHAN, ARTHUR REBER, SHIV KHANNA, Virginia Commonwealth University — Understanding the bonding between silicon and transition metals is valuable for devising strategies for incorporating magnetic species into silicon. CrSi12 is the standard example of a cluster whose apparent high stability has been explained by the 18-electron rule. We critically examine the bonding and nature of stability of CrSi12 and show that its electronic structure does not conform to the 18-electron rule. Through theoretical studies we find that CrSi12 has 18 effective valence electrons assigned to the Cr atom and an unoccupied 3d7 orbital. We demonstrate that the cluster’s apparent stability is rooted in a crystal field-like splitting of the 3d orbitals analogous to that of square planar complexes. CrSi12 is shown to follow the 18-electron rule and exhibits all the conventional markers characteristic of a magic cluster. We will also present results on the stability and electronic structure of FeSi12 clusters and in particular examine the valence configuration of FeSi12 since Fe has two additional valence electrons compared to Cr.

We acknowledge support from the Department of Energy (DOE) under Award Number DE-SC0006420.

3:30PM J27.00004 Effect of N- and P-Type Doping on the Oxygen-Binding Energy and Oxygen Spillover of Supported Palladium Clusters1
ARTHUR C. REBER, SHIV N. KHANNA, Virginia Commonwealth University — The oxygen-binding energy is one of the primary factors determining catalytic activity in oxidation reactions. One strategy for controlling the binding of a reactant to a surface is to dope the surface to create complementary donor–acceptor pairs. As oxygen is an acceptor, we have investigated the effect of doping on the oxygen-binding energy on Pd atoms and clusters supported on a rutile TiO2 (110) surface. We find that the P-type doping of the TiO2 surface dramatically reduces the O-binding energy to Pd. When extended to Pd1-supported clusters, we find that the P-type dopant decreases the energy for the oxygen to bind at spillover sites directly to the TiO2 surface. In PdO2, the oxygen-binding energy is reduced with P-type doping, suggesting that this strategy may be used to control the oxygen-binding energy to supported catalysts.

This work was supported by the Air Force Office of Scientific Research (AFOSR) Basic Research Initiative Grant FA9550-12-1-0481.

3:42PM J27.00005 Cluster Study of Anion Specificity in Solutions: From Molecular-Like Species to Nano-Sized Droplets1
XUE-BIN WANG, Pacific Northwest National Lab — In this talk, I will present our cluster approach using size-selected, low-temperature photoelectron spectroscopy and ab initio calculations to study a variety of complex anion solvation across the Hofmeister series. Pronounced anion specific effects and rich solute-solvent, solvent-solvent interactions have been discovered en-route to solvation evolution from molecular-like species to nano-sized droplets. We found significant solute anisotropy effects in preferably selecting solvent network to align solute permanent dipole with the solvent electric field in hydrated neutral clusters. Thermodynamic advantage of organic acids in facilitating formation of bisulfate ion clusters, an important issue related to atmospheric chemistry and aerosol particle formation will also be discussed.

This work was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Bioosciences.

4:18PM J27.00006 Ligand-modulated interactions between charged monolayer-protected Au144(SR)60 gold nanoparticles in physiological saline1
OSCAR VILLARREAL, LIAO CHEN, ROBERT WHETTEN, MIGUEL YACAMAN, Univ of Texas, San Antonio — We studied the interactions of functionalized Au144 nanoparticles (NPs) in a near-physiological environment through all-atom molecular dynamics simulations. The AuNPs were coated with a homogeneous selection of 60 thiolates: 11-mercapto-1-undecanesulfonate, 5-mercapto-1-pentanesulfonate, 5-mercapto-1-pentanamine, 4-mercapto-benzoate or 4-mercapto-benzamide. These ligands were selected to elucidate how the aggregation behavior depends on the ligands’ sign of charge, length, and flexibility. Simulating the dynamics of a pair of identical AuNPs in a cell of saline of 150 mM NaCl in addition to 120 Na+/Cl− counter-ions, we computed the aggregation affinities from the potential of mean force as a function of the pair separation. We found that NPs coated with negatively charged, short ligands have the strongest affinity mediated by multiple Na+ counter-ions residing on a plane in-between the pair and forming “salt bridges” to both NPs. Positively charged NPs have weaker affinities, as Cl− counter-ions form fewer and weaker salt bridges. The longer ligands’ large fluctuations disfavor the forming of salt bridges, enable hydrophobic contact between the exposed hydrocarbon chains and interact at greater separations due to the fact that the screening effect is rather incomplete.

Supported by the CONACYT, NIH, NSF and TACC.
3:00PM J27.00007 Structural and charge inhomogeneity in supported Pt clusters1, F.D. VILA, J.J. REHR, U. of Washington, A.I. FRENKEL, Yeshiva U. — Nanoparticle materials are ubiquitous in heterogeneous catalytic processes and there is broad interest in their physical and chemical properties. However, global probes such as XAS and XPS reveal their ensemble properties, missing details of their internal architecture. We have previously shown that a combination of theoretical and experimental techniques is needed to understand the intra-particle heterogeneity of these systems. Recent studies of CO- and H-covered Pt clusters on C and SiO2 exhibit a variety of spectral and structural trends as a function of temperature. Here we present DFT simulations showing opposite shifts in XES and XAS, as well as bond contraction with increasing temperature both arise from local electronic and structural changes upon desorption. For example, upon single CO adsorption, the Pt-Pt bonds formed by coordinated Pt atoms are locally expanded by 5%, with little change in the rest of the particle. Coordination also has a large effect on the net charge of the Pt atoms, with a net loss of charge upon adsorption. Finally, we show how high coverage inverts the charge distribution in the clusters.

1Supported by DOE grant DE-FG02-03ER15476, with computer support from DOE-NERSC.

4:20PM J27.00008 New Insights into the Structure of Multimetallic Nanoparticles and their Advanced Characterization, SUBARNA KHANAL, NABRAJ BHATTARAI, JESUS VELÁZQUEZ-SALAZAR, GREGORY GUIBBIERS, MIGUEL JOSE-YACAMAN, University of Texas at San Antonio — Noble multimetallic nanoparticles have led to exciting progress in a versatile array of applications. For the purpose of better tailoring of nanoparticle properties and understanding the correlation between their structures and properties, control over the composition, shape, size and architecture of bimetallic and multimetallic nanomaterials plays an important role on revealing their new or enhanced functions for potentials application. Advance electron microscopy techniques were used to provide atomic scale insights into the structure-properties of different materials: Pt-Pd, Au-Au,Cu, Cu-Pt, AgPd-Pt and AuCu/Pt nanoparticles. These multimetallic nanoparticles have raised interest for their various applications in fuel cells, ethanol and methanol oxidation reactions, hydrogen storage, and so on. The nanostructures were analyzed by transmission electron microscopy (TEM) and by aberration-corrected scanning transmission electron microscopy (Cs-corrected STEM), in combination with high angle annular dark field (HAADF), bright field (BF), energy dispersive X-ray spectroscopy (EDS), and electron energy loss spectroscopy (EELS) detectors. These techniques allowed us to probe the structure at the atomic level of the nanoparticles revealing new structural information and elemental composition of the nanoparticles.

Tuesday, March 3, 2015 5:45PM - 6:45PM — Session K27 DCP: DCP Business Meeting 204B —

5:45PM K27.00001 DCP BUSINESS MEETING —

Wednesday, March 4, 2015 8:00AM - 11:00AM — Session L26 DCP: Focus Session: At the Interface of Molecules and Materials III 204A - Michael Strano, Massachusetts Institute of Technology

8:00AM L26.00001 Exciton Dynamics in Quantum Dot Films and Interfaces1, WILLIAM TISDALE, Massachusetts Inst of Tech-MIT — Colloidal quantum dots (QD) are a promising material platform for solution-processable optoelectronic devices such as solar cells, light-emitting diodes, thermoelectric modules, and flexible electronics. Central to the operation of these devices is the formation, transport, and conversion of free charges and excitons. In the first part of the talk, I will present a comprehensive study of exciton diffusion in inhomogeneously broadened QD assemblies, including spectrally-resolved transient photoluminescence spectroscopy, transient photoluminescence quenching, time-resolved optical imaging, and kinetic Monte Carlo simulations. In the second part of the talk, I will show how nanoscale dielectric screening phenomena in atomically thin semiconductors such as MoS2 can lead to counterintuitive energy behavior from QD donors.

1Department of Energy, Office of Basic Energy Sciences: DE-SC0001088

8:36AM L26.00002 Ligand Chemistry and the Low-Frequency Vibrations of Semiconductor Nanocrystals1, ANNA JOLENE MORK, WILLIAM TISDALE, Massachusetts Institute of Technology — A variety of phonon-mediated processes centrally contribute to heat dissipation in colloidal quantum dot (QD) solids, and a method to tailor the QD vibrational spectrum may allow engineering of more efficient QD devices. Organic ligands, molecules attached to the surface of the inorganic core, are known to affect QD electronic transitions through the energy level alignment and degree of passivation; however, we demonstrate for the first time that ligands also affect the QD vibrational spectrum. We use low-frequency non-resonant Raman spectroscopy to non-destructively probe the acoustic phonon vibrational structure of CdSe QD cores with a variety of different attached ligands. The frequencies of the confined acoustic modes shift depending on the size and structure of the ligand, with more massive ligands resulting in red-shifted phonon energies. We develop a mathematical model based on vibrations of an elastic sphere to understand ligand-dependent shifts in the QD Raman spectrum upon ligand exchange. These data further our understanding of the factors affecting phonon energies and heat transport in QD solids.

1NSF GRFP, Eni-MIT Solar Frontiers

8:48AM L26.00003 Evolution of “waterproof” photoluminescent complexes of rare earth ions in crowded environment1, MICHAEL BLADES, Lehigh University, TETYANA IGNATOVA, UC Irvine, JUAN DUQUE, STEPHEN DOORN, Los Alamos National Lab, IVAN BIAGGIO, SLAVA V. ROTKIN, Lehigh University — Understanding behavior of rare-earth ions (REI) in crowded environments is crucial for several nano- and bio-technological applications. Evolution of REI photoluminescence in small compartments inside a silica hydrogel, mimic to a soft matter bio-environment, has been studied [doi: 10.1039/C4CP03424A] and explained within a solvation model. The model uncovered the origin of high rare earth photoluminescence efficiency to be the formation of REI complexes, surrounded by sodium deoxycholate molecules. Comparative study of these REI-deoxycholate complexes in bulk water solution and those enclosed inside the hydrogel revealed a strong correlation between an up to 5 times longer photoluminescence lifetime of REI and appearance of the deoxycholate ordered phase, further confirmed by dynamics of REI solvation shells, REI diffusion experiments and morphological characterization of microstructure of the hydrogel.

1Supported by NSF # ECCS-1202398.
9:00AM L26.00004 Nanointerfaces in InAs-SnS$_2$ nanocrystal-ligand networks: atomistic and electronic structure from first principles

EMILIO SCALISE, STEFAN WIPPERMANN, Max-Planck-Institute for Iron Research, GIULIA GALLI, University of Chicago — Our findings suggest that the formation of nanointerfaces is a promising route for solar energy conversion, light emission and electronic applications. Recent advances in wet chemical techniques allow for the synthesis of NCs, their assembly into superlattices and embedding into a host matrix using only inexpensive solution processing. However, the atomistic details of such composites are poorly understood, due to the complexity of the synthesis conditions and the unavailability of robust experimental techniques to probe nanointerfaces at the microscopic level. Here we present a density functional theory investigation of the interaction of SnS$_2$ ligands with InAs NCs. Employing a grand canonical approach, we consider a multitude of structures possibly realized at the NC-ligand interface, such as surface termination, reconstructions, passivation, substitution of subsurface atoms, ligand dissociation, NC core-shell formation and the adsorption of the ligands on NCs with different structures. This study provides guidance about the experimental conditions which lead to specific structural motifs and highlights the impact of structural details on the composite’s electronic properties.

9:12AM L26.00005 Defect Chemistry of Nanocrystalline Carbon, YUHuang WANG, University of Maryland — Defects can rule the properties of a crystal. This effect is particularly intriguing in atom-thick materials such as single-walled carbon nanotubes and graphene, where electrons, excitons, phonons, and spin may strongly couple at the defect sites due to reduced dimensionality. In this talk, we will discuss our recent progress in fundamental understanding and molecular control of sp3 defects in sp2 carbon lattices, and their applications. An sp3 defect (tetrahedral bonding, diamond-like) is created by covalently attaching a functional group to the sp2 carbon lattice (trigonal planar, honeycomb-like) of a carbon nanotube or graphene. The beauty of this type of defect is its well-defined structure and chemical tunability at the molecular level. Our experimental results have unveiled a series of intriguing and surprising roles of defects. Specific examples will be given to illustrate how defects may be used to drive reaction propagation on sp2 carbon lattices, brighten carbon nanotube photoluminescence, and create selective chemical sensors.

9:48AM L26.00006 Localized Excitons in Carbon Nanotubes, LYU咪LA ADAMSKA, STEPHEN K. DOORN, SERGEI TRETIAK, Los Alamos National Lab — It has been historically known that unintentional defects in carbon nanotubes (CNTs) may fully quench the fluorescence. However, some dopants may enhance the fluorescence by one order of magnitude thus turning the CNTs into ultra-bright, long-lifetime, cheap light absorbers in good emitters. We have correlated the experimentally observed photoluminescence spectra to the electronic structure simulations. Our experiment reveals multiple sharp asymmetric emission peaks at energies 50-300 meV red-shifted from that of the lowest bright exciton peak. Our simulations suggest an association of these peaks with deep trap states tied to different specific chemical adducts. While the wave functions of excitons in undoped CNTs are delocalized, those of the deep-trap states are strongly localized and pinned to the dopants. These findings are consistent with the experimental observation of asymmetric broadening of the deep trap emission peaks, which can result from scattering of acoustic phonons on localized excitons. Our work lays the foundation to utilize doping as a generalized route for wave function engineering and direct control of carrier dynamics in SWCNTs toward enhanced light emission properties for photonic applications.

10:00AM L26.00007 Understanding the effect of surface defects on sp2 carbon and HOPG, ANDREW KOZBIAL, VAHDH VAHDAT, HAITAO LIU, LEI LI, Univ of Pittsburgh, DEPARTMENT OF CHEMICAL & PETROLEUM ENGINEERING TEAM, DEPARTMENT OF CHEMISTRY TEAM — Basal planes of graphite are traditionally believed to be inert and electrochemical activity of graphitic materials was thought to be highly dependent on surface states. However, recent studies have shown the basal surface of graphite to be highly active and these results have significant implication on design of graphitic electrodes along with numerous other graphite, graphene, and carbon nanotube-based products. The mildly hydrophilic surface of fresh graphite subsequently adsorbs airborne contaminants causing the surface to transition towards hydrophobic behavior. A missing link between electrochemical activity and wettability requires elucidation of basal plane behavior and answering whether defect density on a graphite surface affects wettability. We have quantified defect density on various grades of highly ordered pyrolytic graphite (HOPG) through AFM imaging and contrasted wettability results to describe the effect of defect sites on wettability and surface contamination.

10:12AM L26.00008 Calculating exciton downconversion rates in Coulombically coupled chromophores, CRAIG CHAPMAN, GEORGE SCHATZ, Northwestern University — Exciton downconversion is a second order energy transfer process that splits a high energy exciton in a donor chromophore into multiple lower energy excitons in acceptor chromophores. Downconversion has been seen in a variety of materials including rare-earth doped glassy matrices, organic crystals, and semiconductor nanocrystals, and has the potential to efficiently convert a single high energy photon into a broad distribution of lower energy excitons. A comprehensive mechanistic understanding of the energy conversion process will allow for the rational engineering of materials that can control the flow of energy in a guided fashion. To this end we formulate and implement a method for calculating multi-chromophore Förster-like exciton transfer rates using transition charges obtained from time-dependent density functional theory.

10:24AM L26.00009 Raman spectroscopy of electric-field-tuned molecule-semiconductor interface, ALEXEY ZAYAK, FLOYD HILTY, ANDREW KUHLMAN, Bowling Green State University — In the search for methods of studying chemical properties of surfaces and atomic-scale heterogeneous interfaces, Raman scattering promises significant potential for measuring physical and chemical properties that vary on the scale of a few chemical bonds, reporting not only about a particular chemical species, but also about the immediate chemical environment. In this work we use first-principles (DFT) computations to investigate the chemical modification of Raman spectra of organic species after being chemically absorbed on semiconductor surfaces. We examine the binding of a trans-1,2-(4-pyridyl) ethylene molecule to the PbSe semiconductor surface and show that we can tune the degree of the interfacial chemical coupling by means of an external electric field, and at the same time, observe the induced changes in Raman spectra. In the process of applying electric bias, we observed a crossover between two regimes of the interfacial electron-vibron coupling: with vibration-induced charge transfer; and without it.

10:36AM L26.00010 Electronic structures at the interface between $\text{Au}$ and $\text{CH}_3\text{NH}_2\text{PbI}_3$, CONGCONG WANG, University of Rochester, XIAOLIANG LIU, Central South University, CHENGGONG WANG, University of Rochester, LU LU, Central South University, ZHENGBO XIAO, CHENG BI, JANSONG HUANG, University of Nebraska-Lincoln, YONGLI GAO, University of Rochester — Organometal trithiyl porosukite ($\text{CH}_3\text{NH}_2\text{PbI}_3$)-based solar cells have been developed rapidly in decades. The electronic properties of interfaces formed between $\text{Au}$ and $\text{CH}_3\text{NH}_2\text{PbI}_3$ are investigated with ultraviolet photoemission spectroscopy (UPS), X-ray photoemission spectroscopy (XPS) and inverse photoemission spectroscopy (IPES). The two-step method prepared $\text{CH}_3\text{NH}_2\text{PbI}_3$ film, coated onto the poly (3,4-ethylenedioxythiophene) (poly (styrenesulfonate) (PEDOT:PSS))/indium tin oxide (ITO) substrate, presents n-type semiconductor behavior with a band gap of 1.7 eV and a valence band (VB) edge of 1.0 eV below the Fermi energy ($E_F$). There is an interface dipole of 0.1 eV at $\text{CH}_3\text{NH}_2\text{PbI}_3$/$\text{Au}$ interface. The energy level of $\text{CH}_3\text{NH}_2\text{PbI}_3$ is lifted ca.0.4 eV with Au coverage of 64 Å upon it, resulting in band bending and a built-in field in $\text{CH}_3\text{NH}_2\text{PbI}_3$ that encourages hole transport to the interface. Hole accumulation near the interface facilitates the hole transfer from $\text{CH}_3\text{NH}_2\text{PbI}_3$ to $\text{Au}$. Furthermore, the decreasing offset between the VB maximum of $\text{CH}_3\text{NH}_2\text{PbI}_3$ and the $E_F$ indicates a decrease of energy loss as extracting holes from $\text{CH}_3\text{NH}_2\text{PbI}_3$ to Au coverage.

This work is supported by the National Science Foundation, the National Natural Science Foundation of China, the NSF of Hunan Province, China and the Freedom Explore Program of Central South Univ, China.
One-dimensional atomic chains: rich physics in simple structures

MINJIE LIU, VASILII I. ARTYUKHOV, BORIS I. YAKOBSON, Department of Materials Science and NanoEngineering, Rice University, Houston, TX — Carbyne—1D polymorph of carbon—has been hypothesized since 1960’s, however reproducible techniques of fabricating long carbon chains and measuring their properties have arrived only in the last decade. More recently, 1D chains of other compositions have been fabricated, such as CsI and BN. Here we report our first-principles calculations of a new class of 1D carbon polymorphs, termed carbyne, which show highly unusual magnetic and electronic properties. Reversibility of the chain-to-grid transformation is demonstrated by experiments.

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8:00AM L27.00001 Comprehensive thermochemistry for the hydration of copper ions, PETER ARMENTROUT, University of Utah — Cross sections for the threshold collision-induced dissociation (TCID) of Cu^2+(H_2O)_n, where n = 8-10, and of CuOH^+(H_2O)_n, where n = 1-4, are measured using a guided ion beam tandem mass spectrometer. In both cases, the primary dissociation pathway is found to be loss of a single water molecule followed by the sequential loss of additional water molecules. In the Cu^2+ complexes, charge separation to form CuOH^+(H_2O) and H^+(H_2O) is also observed and CuOH^+(H_2O) competitively loses both H_2O and OH. The data are analyzed using a statistical model accounting for internal and kinetic energy distributions, multiple collisions, and kinetic shifts to obtain 0 K bond dissociation energies (BDEs). In addition, BDEs for the loss of OH from CuOH^+(H_2O)_n, where n = 0-4 are derived using the experimental BDEs for dissociation of CuOH^+(H_2O)_n and literature values for Cu^+(H_2O)_n. Experimental BDEs are compared to theoretical BDEs determined at several levels of theory with reasonable agreement. Structural information regarding complexes of CuOH^+(H_2O)_n, where n = 2-9, are also obtained using infrared photodissociation spectroscopy (IRPD) in the OH stretching region and comparison to theoretical spectra. The IRPD spectra of all complexes where n ≥ 3 are consistent with structures generally having a coordination number (CN) of 4 although CuOH^+(H_2O)_7 exhibits bands characteristic of both CN = 4 and CN = 5 isoters.

8:36AM L27.00002 Collision induced dissociation study of azobenzene and its derivatives: computational and experimental results, MOHAMMADREZA REZAEE1, ROBERT COMPTON2, University of Tennessee, Knoxville — Experimental and computational investigations have been performed to study the bond dissociation energy of azobenzene and its derivatives using collision induced dissociation method as well as other energy and structural characteristics. The results have been verified by comparing with results obtained from computational quantum chemistry. We used different density functional methods as well as the Möllner-Plesset perturbation theory and the coupled cluster methods to explore geometric, electronic and the spectral properties of the sample molecules. Geometries were calculated and optimized using the 6-311++G(2d,2p) basis set and the B3LYP level of theory and these optimized structures have been subjected to the frequency calculations to obtain thermochemical properties by means of different density functional, Möller-Plesset, and coupled cluster theories to obtain a high accuracy estimation of the bond dissociation energy value. The results from experiments and the results obtained from computational thermochemistry are in close agreement.

8:48AM L27.00003 Hydration Structures and Thermodynamic Properties of Cationized Biologically Relevant Molecules, M^+(Indole)(H_2O)_n (M = Na, K; n = 3-6), HAOCHEN KE, JAMES LISY, Univ of Illinois - Urbana — The balance between various noncovalent interactions plays a key role in determining the hydration structures and thermodynamic properties of biologically relevant molecules in biological mediums. Such properties of biologically relevant molecules are closely related to their often unique biological functionalities. The indole moiety is a basic functional group of many important neurotransmitters and hormones and has been used as tractable model for more complex biomolecules. The cationized indole water cluster is a perfect system for the quantitative and systematic study of the competition and cooperation of noncovalent interactions, as electrostatic interactions can be adjusted by introducing different monovalent cations and hydrogen bonding interactions can be adjusted by varying the level of hydration. IRPD spectra with isotopic (H/D) analysis helped unravel the overlapping N-H and O-H stretching modes, a major challenge of earlier studies. Thermodynamic analysis using relative Gibbs free energies, for energy ordering, together with spectral analysis provided unambiguous assignment of spectral features and structural configurations. A systematic hydration model with an in-depth account of noncovalent interactions is presented.

9:00AM L27.00004 How big is the hydrated electron? Thermodynamics of electron solvation and its partial molar volume, DAVID BARTELS, Notre Dame Radiation Laboratory — Several models for the hydrated electron solvation structure have been proposed, which all can do a reasonable job of reproducing the room temperature optical spectrum. As Larsen, Glover and Schwartz [1] demonstrated, tweaking the electron-water pseudopotential can completely change the structure from a cavity to a non-cavity geometry. Deciding between the competing models then requires comparison with other observables. The resonance Raman spectrum and the temperature dependence of the optical spectrum can be cited as evidence in favor of a non-cavity structure [2]. In the present work we will re-examine the thermodynamics of hydration [3]. In particular, we will present new experimental and simulation results for the partial molar volume, which can bear directly on the cavity vs. non-cavity controversy.

photoexcitation resulting in complex fission, while the molecule or cluster being dominated by long-range correlation effects. Failure of conventional Hartree-Fock reference based approaches for treating these anionic states is discussed. Ab initio approaches that go beyond Hartree-Fock orbitals, such as Green’s function, and equation-of-motion methods are used to characterize nonvalence correlation-bound anion states of a variety of systems including C_{60}\text{ and } C_{60}\text{F}_{16}. Edge-bound nonvalence correlation-bound anionic states are established for polycyclic aromatics. Accurate one-electron model potential approaches, parametrized using the results of ab initio calculations, are used to study nonvalence correlation-bound anion states of large water clusters as well as “superatomic” states of fullerene systems.\[1\]

KENNETH JORDAN, University of Pittsburgh — Nonvalence correlation-bound anion states have been investigated using state-of-the-art ab initio methodologies to characterize nonvalence correlation-bound anion states of a variety of systems including C_{60} and C_{60}\text{F}_{16}. Edge-bound nonvalence correlation-bound anionic states are established for polycyclic aromatics. Accurate one-electron model potential approaches, parametrized using the results of ab initio calculations, are used to study nonvalence correlation-bound anion states of large water clusters as well as “superatomic” states of fullerene systems.\[1\]

Nano Lett. 2014, 14 (8), pp 4602-4606.\[2\]

4 Presently at University of California, Irvine

9:48AM L27.00006 Solute-Solvent Structural Changes that Accompany Ion Dehydration in Electrospray Ionization (ESI) as Revealed by Cryogenic (80 K) Ion Mobility-Mass Spectrometry (IM-MS)\[3\], DAVID RUSSELL, Texas A&M University — Peptide/protein conformer preferences are dictated by intra- and intermolecular interactions. Because of the large number of degrees-of-freedom in bulk solvent networks and the dynamic nature of hydrogen bonds, experimental studies of specific interactions of individual conformational states are difficult. Gas phase studies of solvent-free biomolecules provide a potential solution to this problem because inter- and intramolecular interactions are effectively decoupled. However, a potential concern is that during the transition from solution to gas phase the molecules encounter unique environments that can potentially affect their conformer preference. A number of studies have demonstrated that peptide/protein ions generated by ESI can retain memory of their solution structures, including retention of biological activity, suggesting that gaseous ions can be kinetically trapped in local minima along their potential energy surface owing to evaporative cooling and relatively slow rates of isomerization; however, the extent to which non-covalent interactions are affected remains unresolved. Here, we discuss recent cryogenic (80 K) IM-MS studies that capture the evaporation dynamics of a series of model peptide ions. Cryogenic-IM affords new insights as to the multiplicity of peptide ion conformations and how solute-solvent interactions alter both solute and solvent structures.

Funding from EPSRC (EP/G00224X and EP/L005913) is gratefully acknowledged.\[4\]

1 U. S. Department of Energy, Division of Chemical Sciences (BES DE-FG02-04ER15520)

10:24AM L27.00007 Mapping the UV Photophysics of Platinum Metal Complexes Bound to Nucleobases\[1\], ANANYA SEN, CAROLINE DESSENT, University of York — We report the first UV laser spectroscopic study of isolated gas-phase complexes of Platinum metal complex anions bound to a nucleobase as model systems for exploring at the molecular level the key photophysical processes involved in photodynamic therapy. Spectra of the Pt^{IV} (CN)\text{4}^- \text{CN} \text{•} \text{Uracil and Pt^{II} (CN)\text{2}^- \text{CN} \text{•} \text{Uracil complexes were acquired across the 220–320 nm range using mass-selective photodepletion and photofragment action spectroscopy. The spectra of both complexes reveal prominent UV absorption bands that we assign primarily to excitation of the Uracil } \pi \rightarrow \pi^* \text{ localized chromophore. Distinctive UV photofragments are observed for the complexes, with Pt^{IV} (CN)\text{4}^- \text{CN} \text{•} \text{Uracil photexcitation resulting in complex fission, while Pt^{II} (CN)\text{2}^- \text{CN} \text{•} \text{Uracil photoexcitation initiates a nucleobase proton-transfer reaction across 4.4–5.2 eV and electron detachment above 5.2 eV. The observed photofragments are consistent with ultrafast decay of a Uracil localized excited state back to the electronic ground state followed by intramolecular vibrational relaxation and ergodic complex fragmentation. In addition, we present recent results to explore how the photophysics of the Platinum complex-nucleobase clusters evolves as a function of nucleobase. Results are presented for Pt^{II} (CN)\text{2}^- \text{CN} \text{•} \text{Uracil complexed to Cytosine, Thymine and Adenine, reveal distinct decay dynamics which we attribute to the intrinsic decay dynamics of the nucleobase.}

1 JPC. Lett. 2014, 5, 3281 to 3285 and PCCP 2014, 16, 15490 to 15500


11:15AM M27.00001 Introduction, DAVID CHANDLER, Sandia National Laboratories —

11:27AM M27.00002 Herbert P. Broida Prize Talk: Molecular photofragmentation dynamics in the gas and condensed phase: similarities and differences\[1\], MICHAEL ASHFOLD, School of Chemistry, University of Bristol, Bristol, U.K., BSS 1TS — Phenols and azoles are important chromophores in the nucleobases and aromatic amino-acids that dominate the near-UV absorption spectra of many biological molecules. \pi \rightarrow \pi^* \text{ excitation is responsible for these strong UV absorptions, but these molecules also possess excited states from } \sigma^* \rightarrow \sigma \text{ electron promotions. } \sigma^* \text{ excited states typically have much smaller absorption cross-sections, but their photochemical importance is becoming ever more widely recognized [1]. We have used photofragment translational spectroscopy (PTS) methods (and complementary ab initio theory) to explore X-H bond fission (X = heteroatom) following UV photoexcitation of many such heteroaromatic molecules in the gas phase and, more recently, started ultrafast pump-probe studies of the same (and related) processes in solution. This presentation will (i) summarize the state of knowledge derived from PTS studies of phenol and related molecules in the gas phase [2], (ii) highlight the extent to which such knowledge can inform our interpretation of ultrafast pump-probe studies of the UV photofragmentation of similar molecules ((thio)phenols, anilines and ethers) in solution [3,4] and (iii) demonstrate how such solution phase studies offer a route to exploring photoinduced (\pi^* in state mediated) ring opening of heterocyclic molecules like furans and thiophenes [5].}

oxydehydrogenation, which produces an ordered atomic N layer on the surface when annealed to temperatures above 300 K. (The adsorption of ammonia on an oxygen covered Pt surface leads to the formation of an NH$_3$ microsity (LT-STM) is used to investigate the structure and reactivity of atomic nitrogen on Pt surfaces, which is important to a variety of catalytic processes.

Illinois at Chicago, SURFACE AND INTERFACE SCIENCE LABORATORY, RIKEN, JAPAN COLLABORATION — A low-temperature scanning tunneling microscopy (LT-STM) is used to investigate the structure and reactivity of atomic nitrogen on Pt surfaces, which is important to a variety of catalytic processes. The single molecule junction, a device in which two conducting leads are spanned by a single molecule, has become a powerful tool for studying charge transfer at the molecular level. While early experiments were focused on elastic electron conductance, today measurements of vibronic effects, molecular optical response, spintronics, thermal conductance, and quantum interference and decoherence effects are prominent areas of research. These new experimental advancements demand improved theoretical treatments which properly account for the interactions between different degrees of freedom: charge, electronic, vibrational, spin, etc.; all in physically relevant parameter ranges. This talk focuses on using a many-body states based approach to investigate the regime of strong interaction between these degrees of freedom, with relatively weak coupling between the molecule and the electric reservoirs created by the conducting leads. We focused on three related processes, electron transport, electronic energy transfer and molecular excitation.

In collaboration with Boris Fainberg, Faculty of Sciences, Holon Institute of Technology; Sergei Tretiak, Theoretical Division, Center for Integrated Nanotechnology, Los Alamos National Laboratory; and Michael Galperin, Department of Chemistry and Biochemistry, University of California San Diego — The field of molecular electronics has grown significantly since the first measurements of single molecule conductance. The single molecule junction, a device in which two conducting leads are spanned by a single molecule, has become a powerful tool for studying charge transfer at the molecular level. While early experiments were focused on elastic electron conductance, today measurements of vibronic effects, molecular optical response, spintronics, thermal conductance, and quantum interference and decoherence effects are prominent areas of research. These new experimental advancements demand improved theoretical treatments which properly account for the interactions between different degrees of freedom: charge, electronic, vibrational, spin, etc.; all in physically relevant parameter ranges. This talk focuses on using a many-body states based approach to investigate the regime of strong interaction between these degrees of freedom, with relatively weak coupling between the molecule and the electric reservoirs created by the conducting leads. We focused on three related processes, electron transport, electronic energy transfer and molecular excitation.

Grant agency of the Czech Republic, Grant No.: 14-08937S

2:03PM M27.00007 Probing Individual Atoms and Molecules on Pt(111)$^1$, ZHU LIANG, University of Illinois at Chicago, SURFACE AND INTERFACE SCIENCE LABORATORY, RIKEN, JAPAN COLLABORATION — A low-temperature scanning tunneling microscopy (LT-STM) is used to investigate the structure and reactivity of atomic nitrogen on Pt surfaces, which is important to a variety of catalytic processes. The adsorption of ammonia on an oxygen covered Pt surface leads to the formation of an NH$_3$-O$_2$ complex. Such a complex serves as a precursor to ammonia氧化解氢化, which produces an ordered atomic N layer on the surface when annealed to temperatures above 300 K. (√3×√3)R30°-N and p(2×2)-N phases are found to coexist at temperatures between 360 and 400 K. After exposing the N-covered surface to hydrogen gas at 300 K, NH molecules are present as scattered molecules, as well as in dense islands. Mechanisms of dissociation of NH and lateral movement of H have been explored by examining the threshold energies and reaction rates. Measuring the response of the motion against applied bias voltage reveals the threshold energy, which is the energy of the vibrational mode that is responsible for activating a given motion. A theoretical model is used to fit the spectra, from which an estimate of reaction rate is obtained. ND dissociation and D hopping have also been investigated to examine the role of tunneling in these reactions.

1Hyowon Kim, Hyun Jin Yang, and Junepyo Oh are acknowledged for their contributions to this work. Support and supervision by professor Yousoo Kim and professor Michael Trenary are gratefully acknowledged.

Wednesday, March 4, 2015 2:30PM - 4:42PM –
Session Q26 DCP: Focus Session: Non-Adiabatic Dynamics: New Insights from Experiment and Theory IV
204A - Scott Reid, Marquette University
As a result of further photon absorption modulated by one- and two-photon resonances, which provide sufficient energy to overcome the dissociation energy. From coherent vibrational motion governed by the potential energy surface of the ground state of the cation. Subsequent fragmentation of the cation takes place after the optical cycle with the electron carrying away essentially all of the energy, leaving behind little internal energy in the cation. Evidence for this observation comes from delay scans which show that among positional isomers the variations in relative energies, amounting to only a few meVs, are structure sensitive.

Molecules light-harvesting systems in photosynthetic complexes to understand the extent to which quantum effects are determinant in this nonadiabatic process. The formulated theory is applied to the context of photochemistry and fragmentation patterns in response to the laser field are structure sensitive; therefore, a molecule cannot simply be treated as a “bag of atoms” during intramolecular motions post ionization. The delay scans show that among positional isomers the variations in relative energies, amounting to only a few meVs, are structure sensitive.

Next, insights into the nonadiabatic dynamics of proton-coupled electron transfer reactions from the mixed quantum-classical Liouville approach will be discussed. The effect of a dielectric environment on a molecule can be profound, causing changes in nuclear configuration and electronic structure. Quantum chemical simulation of a solute-solvent system can be prohibitively expensive due to the large number of degrees of freedom attributed to the solvent. To remedy this, the solvent can be treated as a dielectric cavity. Mutual polarization of the solute and solvent must be considered for accurate treatment of an optically excited state (ES) with a state-specific solvent model (SSM). In vacuum, time dependent self-consistent field (TD-SCF) methods (e.g., TD-HF, TD-DFT) give variational excitation energies. With the well known Z-vector equation, a variational ES energy is used to explore the ES potential energy surface (PES) with analytical gradients.

Modification of the standard TD-SCF eigensystem to accommodate a SSM creates a nonlinear TD-SCF equation with non-variational excitation energies. This prevents analytical gradients from being formulated so that the ES PES cannot be explored. Here, we show how a variational formulation of existing SSMs can be derived from a Lagrangian formalism and give numerical results for the variability of calculated quantities. Model dynamics using SSMs are showcased.

The reliability of quantum chemical methods plays a critical role in performing nonadiabatic dynamics simulations. Unfortunately, the methods for computing excited states including larger regions of the energy surfaces are still computationally expensive or need support from higher level methods. In this talk the capabilities of multireference (MR) versus single reference (SR) methods will be discussed. In terms of SR approaches we focus our attention on the second-order algebraic diagrammatic construction method (ADC(2)). In addition to the direct calculation of nonadiabatic coupling vectors, we will also show how to compute wavefunction overlaps between consecutive time steps using various functional forms.

The surface hopping dynamics simulations are performed on the basis of the public domain program system NEWTON-X [M. Barbatti, M. Ruckenbauer, F. Plasser, J. Pittner, G. Granucci, M. Persico, and H. Lischka, WIREs:CMS 2014, 4, 26-33].

Unravelling Two State Reactivity: New Insights Combining Experimental, Ab Initio, and Statistical Modelling Techniques. SHAUN ARD, AFRL, JOSHUA MELKO, University of North Florida, OSCAR MARTINEZ, AFRL, VLADIMIRUSHAKOV, Max Plank Institute, ANYANG LI, RYAN JOHNSON, University of New Mexico, NICHOLAS SHUMAN, AFRL, HUA GUO, University of New Mexico, JURGEN TROE, Max Plank Institute, ALBERT VIGGIANO, AFRL — Non-Adiabatic dynamics have long played a role in understanding various ion molecule reactions. As calculation techniques have improved, even spin-allowed reactions have been found to be significantly impacted by low lying excited spin states, so-called Two-State reactivity. This talk will focus on recent studies of several canonical examples, FeO₂⁺, H₂FeO⁺, CH₄, and Fe⁺ + N₂O. Experimentally, the kinetics of these reactions are studied from 100 to 700K. Combined with computations of the reaction surface, statistical modelling employing the Statistical Adiabatic Channel Model (SACM) of this near thermal energy range gives unique insight into kinetic details of these systems. Implications of this combined approach, specifically towards better quantifying Two-State reactivity in ion-molecule reactions, will be discussed.

Variational state specific solvent models for excited states from time dependent self-consistent field methods. JOSIAH BJORGGAARD, KIRILL VELIZHANIN, SERGEI TRETIAK, Los Alamos National Laboratory — The electronic environment on a molecule can be profound, causing changes in nuclear configuration and electronic structure. Quantum chemical simulation of a solute-solvent system can be prohibitively expensive due to the large number of degrees of freedom attributed to the solvent. To remedy this, the solvent can be treated as a dielectric cavity. Mutual polarization of the solute and solvent must be considered for accurate treatment of an optically excited state (ES) with a state-specific solvent model (SSM). In vacuum, time dependent self-consistent field (TD-SCF) methods (e.g., TD-HF, TD-DFT) give variational excitation energies. With the well known Z-vector equation, a variational ES energy is used to explore the ES potential energy surface (PES) with analytical gradients.

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Electronic Structure and Potential Fitting Methods Suitable For Multi-state Reactive Surfaces. RICHARD DAWES, Missouri University of Science and Technology — Part of this talk describes the development of a new program (software code) which uses parallel processing on High-Performance Computing (HPC) clusters to construct PESs automatically. Thousands of ab initio data are computed at geometries chosen by the algorithm and fit to a functional form. The electronic structure of molecules is difficult to describe accurately using a single potential energy surface (PES) that can accommodate all of the electronic states of the molecule. Molecular interactions are treated using a classical environment.

The reliability of quantum chemical methods plays a critical role in performing reliable nonadiabatic dynamics simulations. Unfortunately, the methods for computing excited states including larger regions of the energy surfaces are still computationally expensive or need support from higher level methods. In this talk the capabilities of multireference (MR) versus single reference (SR) methods will be discussed. In terms of SR approaches we focus our attention on the second-order algebraic diagrammatic construction method (ADC(2)). In addition to the direct calculation of nonadiabatic coupling vectors, we also show how to compute wavefunction overlaps between consecutive time steps using various functional forms.

Comparison of the results concerning deactivation pathways and decay times is given for different methods including multireference configuration interaction, ADC(2) and time-dependent density functional theory (TDDFT) using various functionals. The surface hopping dynamics simulations are performed on the basis of the public domain program system NEWTON-X [M. Barbatti, M. Ruckenbauer, F. Plasser, J. Pittner, G. Granucci, M. Persico, and H. Lischka, WIREs:CMS 2014, 4, 26-33].

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Wednesday, March 4, 2015 2:30PM - 4:54PM –
Session Q27 DCP: Focus Session: Chemical Physics of Clusters: Bridging from Angstrom-scale Clusters to Micron-scale Aerosol Particles IV

2:30PM Q27.00001 Stability of Phosphine-Ligated Gold Cluster Ions toward Dissociation: Effect of Ligand and Cluster Size1. JULIA LASKIN, Pacific Northwest National Laboratory — Precise control of the composition of phosphine-ligated gold clusters is of interest to their applications in catalysis, sensing, and drug delivery. Reduction synthesis in solution typically generates a distribution of ligated clusters containing different number of gold atoms and capping ligands. Ligand binding energy is an important factor determining the kinetics of cluster nucleation and growth in solution and hence the resulting cluster distribution. Phosphines are popular capping ligands with tunable electronic and steric properties that affect their binding to the gold core. We examined the effect of the number of gold atoms in the cluster and the properties of the phosphine ligand on the gold cluster binding energy to the gold core using surface-induced dissociation (SID) of mass selected cluster cations produced through electrospray ionization. SID of vibrationally excited ions is ideally suited for studying gas-phase fragmentation of complex ions such as ligated gold clusters. The energetics, dynamics, and mechanisms of cluster ion fragmentation in the absence of solvent are determined through RRKM modeling of time and kinetic energy dependent SID spectra. This approach provides quantitative information on the ligand binding energies in phosphine-ligated gold clusters important for understanding their formation in solution. Furthermore, ligand binding energies derived from SID data provide the first benchmark values for comparison with electronic structure calculations.

1This work was supported by the US Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences.

3:06PM Q27.00002 Novel Electrocatalysts Prepared by Soft Landing of Mass-Selected Cluster Ions, GRANT JOHNSON, TREVOR MOSER, NIGEL BROWNING, MARK ENGELHARD, JULIA LASKIN, Pacific Northwest National Laboratory — Metal clusters, which possess defined size and composition depending on properties of precursor materials for use as catalysts, are promising materials for use in electrochemical reactions in fuel cells. A physical synthesis technique, magnetron sputtering combined with gas-aggregation, has been employed to produce anionic metal clusters in the gas-phase across a range of sizes, shapes, and compositions for mass-selection and deposition onto glassy carbon electrodes. Sputtering of multiple targets in the same region of gas aggregation is demonstrated to produce uncapped binary and ternary alloy clusters with defined composition and morphology that are not accessible through synthesis in solution. Introduction of reactive gases including alcoholics, alkanes, and amines into the sputtering region is shown to result in the formation of complex cluster morphologies containing carbon, nitrogen, and oxygen. A suite of cutting-edge characterization techniques is utilized to demonstrate how the size, shape, elemental composition, and surface density of clusters may be tuned through variations in source parameters such as the sputtering power, gas flow rates, and aggregation distance. The catalytic activity of the soft landed clusters towards the oxygen reduction reaction, a critical process occurring in hydrogen fuel cells, is measured using cyclic voltammetry. Alloy clusters containing reduced quantities of precious metals are shown to exhibit promising catalytic activity.

3:18PM Q27.00003 Quantum Monte Carlo study of charged transition-metal organometallic cluster systems1, KAMIL TOKAR, RENÉ DERIAN, IVAN STICH, Inst. of Physics, Slovak Academy of Sciences — Using accurate fixed-node quantum Monte Carlo (QMC) methods we study 1D clusters formed by transition metal atoms separated by benzene molecules (TMBz), both positively and negatively charged. TMZh are among the most important n-bonded organometallics, which, however, often require charged states for experimental studies. We have performed a systematic study of ground-state spin multiplets, ionization potentials, electron affinities, and dissociation energies of vanadium-benzene catonic and anionic half- and full-sandwiches. By comparison of QMC and DFT results, we find a very strong impact of electronic correlation on properties of these systems, such as dissociation energies, where ≈1 eV energy corrections are found. In particular, the anions are unstable at the DFT level and are stabilized only at the QMC level after sophisticated optimization of the trial wavefunction.

1Supported by APVV-0207-11 and VEGA (2/0007/12) projects.

3:30PM Q27.00004 Isolation and structural characterization of a silver-platinum nanocluster, Ag₄Pt₂(DMSA)₄1, ANTHONY PEDICINI, ARTHUR REBER, Virginia Commonwealth University, SCOTT BILTEK, AYUSMAN SEN, Pennsylvania State University, SHIV KHANNA, Virginia Commonwealth University — Cluster assembled materials offer an attractive prospect of making nanoscale materials with tunable characteristics. Here, we report the synthesis, isolation, and characterization of the ligand-protected bimatetalic cluster, Ag₄Pt₂(DMSA)₄ (DMSA—meso-2,3,-dimercaptosuccinic acid) and its analogue, Ag₄Pt₂(DMSA)₂. The procedure is similar to the one employed previously for the synthesis of Ag₄Ni₂(DMSA)₄. Theoretical studies show that the Pt and Ni atoms are square planar in configuration. Furthermore, the dependence on the optical spectrum due to congener replacement of the transition metal is highlighted. Since the crystal field splitting of 5d orbitals is typically larger than that for 3d orbitals, we show the Pt-based cluster has an optical spectrum that is significantly blue shifted as compared to the Ni-based cluster.

1This work was supported by an Air Force Office of Scientific Research (AFOSR) Basic Research Initiative Grant FA9550-12-1-0481.

3:42PM Q27.00005 Cluster size matters: Size-driven performance of subnanometer clusters in catalysis, electrocatalysis and Li-air batteries, STEFAN VAJDA, Argonne National Laboratory — This paper discusses the strongly size-dependent performance of subnanometer cluster based catalysts in 1) heterogeneous catalysis, 2) electrocatalysis and 3) Li-air batteries. The experimental studies are based on I. fabrication of ultrasmall clusters with atomic precision control of particle size and their deposition on oxide and carbon based supports; II. test of performance, III. in situ and ex situ X-ray characterization of cluster size, shape and oxidation state; and IV. electron microscopies. Heterogeneous catalysis. The pronounced effect of cluster size and support on the performance of the catalyst (catalyst activity and the yield of Cₓ products) will be illustrated on the example of nickel and cobalt clusters in Fischer-Tropsch reaction. Electrocatalysis. The study of the oxygen evolution reaction (OER) on size-selected palladium clusters supported on ultrananocrystalline diamond show pronounced size effects. While Pd₄ shows no reaction, Pd₆, or Pd₁₇ clusters are among the most active catalysts known (in terms of turnover rate per Pd atom). The system (soft-landed Pd₄, Pd₆, or Pd₁₇ clusters on an UNCD Si coated electrode) shows stable electrochemical potentials over several cycles, and the characterization of the electrodes show no evidence for evolution or dissolution of either the support Theoretical calculations suggest that this striking difference may be a demonstration that bridging Pd-Pd sites, which are only present in three-dimensional clusters, are active for the oxygen evolution reaction in Pd₄, Oₓ, Li-air batteries. The studies show that sub-nm silver clusters have dramatic size-dependent effect on the lowering of the overpotential, charge capacity, morphology of the discharge products, as well as on the morphology of the nm size building blocks of the discharge products. The results suggest that by precise control of the active surface sites on the cathode, the performance of Li-air cells can be significantly improved.
4:18PM Q27.00006 Theoretical Study of Chemisorption on Small Palladium Clusters, AIT HIRA, FRANK NARANJO, FELIPE MUNOZ, DANIELLE JARAMILLO, Northern New Mexico College — We continue our interest in the chemisorption of different atomic and molecular species on small clusters of metallic elements, by examining the interactions of H, H$_2$, Li and O adsorbates with Pd$_n$ clusters ($n = 2$ thru 20). Transition-metal clusters are specially suited for the study of quantum size effects and for formation of metallic states, and are ideal candidates for catalytic processes. Hybrid ab initio methods of quantum chemistry (particularly the DFT-B3LYP model) are used to derive optimal geometries for the clusters of interest. We compare calculated binding energies, bond-lengths, ionization potentials, electron affinities and HOMO-LUMO gaps for the clusters. Of particular interest are the comparisons of binding strengths at the three important types of sites: edge (E), hollow (H), on-top (T), threefold sites and fourfold sites. Effects of crystal symmetries corresponding to the bulk structures are investigated. The capacity of Pd clusters to adsorb H atoms will be compared to Ni clusters. 

1 Research Supported by National Science Foundation

4:30PM Q27.00007 Role of electronic structure and surface structuring effects in the synergistic catalytic activity of Ni-Pd nanoparticles, LINN LEPPERT, Theoretical Physics IV, University of Bayreuth, 95440 Bayreuth, RHETT KEMPE, Inorganic Chemistry II, University of Bayreuth, 95440 Bayreuth, STEPHAN KUEMMEL, Theoretical Physics IV, University of Bayreuth, 95440 Bayreuth — Nickel-palladium nanoalloys show a drastically enhanced catalytic activity in a variety of hydrogenation reactions as compared to pure nickel or palladium nanoparticles. We explore the mixing behavior, electronic structure and magnetic properties of nickel-palladium clusters using density functional theory to gain insight into this synergistic effect. We show that the binding energy of hydrogen to the metal nanoparticle’s surface, which can be tuned via the nickel-palladium composition, is the decisive factor determining how efficiently the reaction can take place. The optimal magnitude of the binding energy for intermediate nickel-palladium ratios can be traced back to a purely electronic effect: a balanced hybridization of the hydrogen s with the metal particle d and s states. This explanation not only holds for small clusters, but also for nickel-palladium surfaces. Finally, we demonstrate that catalytic activity on nickel-palladium surfaces might not only benefit from alloying, but also from the formation of nanostructures on surfaces.

4:42PM Q27.00008 Ultrasmall Carbide Nanospheres - Formation and Electronic Properties, PETRA REINKE, EHSAN MONAZAMI, University of Virginia, JOHN MCCLIMON, University of Pennsylvania — Metallic nanoparticles are highly coveted but are subject to rapid Ostwald ripening even at moderate temperatures limiting study of their properties. Ultrasmall transition metal carbide “nanospheres” are synthesized by a solid-state reaction between fullerene as carbon scaffold, and a W surface. This produces nanospheres with a narrow size distribution below 2.5 nm diameter. The nanosphere shape is defined by the scaffold and densely packed arrays can be achieved. The metal-fullerene reaction is temperature driven and progresses through an intermediate semiconducting phase until the fully metallic nanospheres are created at about 350 °C. The reaction sequence is observed with STM, and STS maps yield the local density of states. The reaction presumably progresses by stepwise introduction of W-atoms in the carbon scaffold. The results of high resolution STM/STS in combination with DFT calculations are used to unravel the reaction mechanism. We will discuss the transfer of this specific reaction mechanism to other transition metal carbides. The nanospheres are an excellent testbed for the physics and chemistry of highly curved surfaces.

Thursday, March 5, 2015 8:00AM - 11:00AM — Session S26 DCP: Focus Session: At the Interface of Molecules and Materials: IV 204A - Bruce Weisman, Rice University

8:00AM S26.00001 Variance Spectroscopy: A New Bridge between Ensemble and Single-Particle Studies, R. BRUCE WEISMAN, Rice University — We have developed a new experimental technique that probes variations in the spectra from small regions of heterogeneous bulk samples resulting from statistical variations in composition. The method is demonstrated using suspensions of single-walled carbon nanotubes (SWCNTs), which contain mixtures of distinct structural species emitting photoluminescence at characteristic short-wave infrared wavelengths. Using dilute SWCNT suspensions, focused excitation beams, multichannel detection, and quick data collection, we capture several thousand emission spectra representing different spatial regions of the sample. The data sets are analyzed to find emission mean and variance values as a function of wavelength. The combined mean and variance spectra contain information unavailable from conventional methods, including the abundances of different emissive species and their relative emission efficiencies. The variance data are also analyzed for correlations between intensity fluctuations at different wavelengths to give novel two-dimensional maps that reveal the spectra of homogeneous sub-populations within heterogeneously broadened bulk spectra. The off-diagonal features in these maps expose spatially correlated concentration variations for nanotubes of different types, which arise from earliest stages of aggregation. Variance spectroscopy should prove a powerful new experimental tool for characterizing nanoparticle samples.

8:36AM S26.00002 TBD, LIBAI HUANG, Notre-Dame University — No abstract available.

9:12AM S26.00003 Multiphoton Photoemission/Velocity Map Imaging Studies of Single Particle Plasmonics: A New Ultrafast Laser Microscopy Tool for Nanomaterials, DAVID NESBITT, JILA, University of Colorado — The ability to look with ultrafast laser microscopy at nanoparticles has lead to an explosion of novel research opportunities in chemistry, physics and engineering. By way of example, this talk will attempt to present recent “vignettes” from our group in ultrafast photoelectron study of novel plasmonic nanomaterials. In particular, scanning photoionization microscopy (SPIM) and dynamics of Au, Ag plasmonic rods, tubes, nanoshells, nanostars, etc have been investigated at the single nanoparticle level, exploiting ultrafast laser pulses tuned over the nanoparticle plasmon resonance features and monitored by time-resolved, coherent multiphoton electron photoemission and velocity map imaging methods. The focus will be on simple physical pictures that help explain and interpret the underlying chemical physics on the nanoscale level.

In collaboration with Andrej Grubisic, NASA and Jacob Pettine, JILA, University of Colorado.

9:48AM S26.00004 Femtosecond nanoplasmonic dephasing of individual silver nanoparticles, RICHA MITTAL, RACHEL GLENN, ILYAS SAYTASHEV, MARCOS DANTUS, Michigan State University — Localized surface plasmon emission from individual silver nanoparticles and cluster of 100nm silver nanoparticles are probed by 15fs laser pulse replica generated by a pulse shaper. The Fourier transform of the nanoplasmonic coherence oscillations reveals different frequency components, phases, and dephasing rates for each nanoparticle. We find broadly distributed coherence dephasing rates that correspond to the cluster size. Our results provide insight into inhomogenous and homogeneous broadening mechanisms in nanoplasmonic spectroscopy.
10:00AM S26.00005 Flicker Noise as a Probe of Electronic Interaction at Metal-Organic Interfaces. OLGUN ADAK, Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY, ETHAN ROSENTHAL, Department of Physics, Columbia University, New York, NY, JEFFEY MEISNER, Department of Chemistry, Columbia University, New York, NY, ERICK ANDRADE, ABHAY PASUPATHY, Department of Physics, Columbia University, New York, NY, COLIN NUCKOLLS, Department of Chemistry, Columbia University, New York, NY, MARK HYBERTSEN, Center for Functional Nanomaterials, Brookhaven National Labs, Upton, NY, LATHA VENKATARAMAN, Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY — Understanding the nature of the charge transport at metal-organic interfaces is fundamental for achieving functional organic electronic devices. The charge transport at such interfaces can be achieved by through-bond and through-space interaction. While through-bond interaction dominates the electronic coupling in most systems, through-space interaction plays important role when through-bond interaction is suppressed, for example, due to quantum interference. In this talk, we first shed light into the origin of the flicker noise phenomenon in single molecule junctions and show how it can be used to distinguish between through-bond and through-space interaction at metal-organic interfaces using a scanning-tunneling microscope based break junction technique.

10:12AM S26.00006 Dynamic Oxidation of Gallium Phosphide Surface Tracked by Near Ambient Pressure XPS1. SYLWIA PTASINSKA, XUEQIANG ZHANG, University of Notre Dame — Both from applied and fundamental points of view, it is important that we have a detailed molecular-level understanding of gas-solid interface interactions, especially under operational conditions. Recent progress in in-situ instrumentations (e.g., Near Ambient Pressure X-ray Photoelectron Spectroscopy—NAP XPS), has enabled us to explore the physicochemical processes at the gas-solid interface over a varied range of pressures (up to mbar range), bridging the gap in our knowledge of interfacial interactions. Our recent investigations have focused on dissociative adsorption of small gas-phase molecules onto III-V semiconductors, which leads to surface oxidation. In this work, we carried out a pressure- and temperature-dependent study of GaP(111) oxidation in an O2 environment. Dynamic changes in chemical evolutions at the O2/GaP(111) interface were reflected in Ga 2p, O 1s, and P 2p spectra. Different oxidation states were observed, involving Ga2O3, Ga2O5 and GaPO4 formation. A “phase diagram” of GaP(111) oxidation under various O2 pressures and temperatures can help us visualize transition states and gain more insights into chemical pathways leading to the final products of GaP oxidation. Further, an estimation of work function changes of the oxidized GaP surface was obtained under near ambient conditions.

1This material is based upon work supported by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences under Award Number DE-FC02-04ER15533.

10:24AM S26.00007 One Dimensional Surface Phonon Polaritons in Boron Nitride Nanotubes: High Field Confinement and Localization1. XIAOJI XU, Lehigh University, Bethlehem, PA, USA, BEHNOOD GHAMSARI, University of Ottawa, Ottawa, Ontario, Canada, DMITRI GOLBERG, WPI-MANA Centre of National Institute for Materials Science, Tsukuba, Ibaraki, Japan, PIERRE BERINI, University of Ottawa, Ottawa, Ontario, Canada, GILBERT WALKER, University of Toronto, Toronto, Ontario, Canada — We report the direct observation of one dimensional surface phonon polaritons (SPhPs) in boron nitride (BN) nanotubes at the mid infrared frequencies. High spatial resolution infrared near-field microscopy is used to spatially map the distribution of SPhPs in BN nanotubes. The polaritonic wavelength is experimentally found to be tuneable by the tubular diameter as well as the configurations of the conductive supporting substrate. Effective refractive index of the SPhPs is found to be as high as ~ 70 for a thin BN nanotube. Furthermore, strong field localization and mitigation of the polariton damping is achieved with the use of a rough gold substrate. The randomly spaced nanometer-sized gold grains on the substrate act as distributed reflectors for propagating SPhPs, and confined the surface waves in the one-dimension nanotube. Such geometry allows high field concentration at mid infrared frequencies for chemical sensing and nonlinear optics. Given the analogy between phonon polaritons and plasmon polaritons, BN nanotubes can be used for building blocks for nano-photonic devices in the mid infrared frequencies, with design principles learnt from well-established metallic plasmonics.

1 NSERC, ONR, MEXT Japan

10:36AM S26.00008 Characterization of Size, Anisotropy, and Density Heterogeneity of Nanoparticles by Sedimentation Velocity1. BORRIES DEMELER, University of Texas Health Sciences Center San Antonio — A critical problem in materials science is the accurate characterization of the size dependent properties of colloidal inorganic nanocrystals. Due to the intrinsic polydispersity present during synthesis, dispersions of such materials exhibit simultaneous heterogeneity in density, molar mass, and particle diameter. The density increments with respect to diameter and molar mass of these nanoparticles, if known, can then provide important information about crystal growth and particle size distributions. For most classes of nanocrystals, a mixture of surfactants is added during synthesis to control their shape, size, and optical properties. However, it remains a challenge to accurately determine the amount of passivating ligand bound to the particle surface post synthesis. The presence of the ligand shell hampers an accurate determination of the nanocrystal diameter. Using CdSe and PbS nanocrystals, and the silver nanoparticle (M4Ag44(p-MBA)30), as model systems, we describe how appropriate parameterizations of the flow equation can be used to extract high resolution composition information for mixtures of solutes that are heterogeneous in two out of three hydrodynamic parameters when the third is known. We show how this approach can yield important detail to the understanding of solution composition.

10:48AM S26.00009 Design of photo-absorption properties of hybrid organic-inorganic halide perovskite photovoltaic devices by cation manipulation1. OSCAR GRANAS, SEAS, Harvard University and Dept. of Physics and Astronomy, Uppsala University, DMITRY VINICHENKO, Dept. of Chemistry and Chemical Biology, Harvard University, EFTHMIOS KAXIRAS, Dept. of Physics, Harvard University — Photovoltaic devices based on hybrid organic-inorganic halide perovskite materials have lately sailed up as one of the most promising technologies for cost effective harvest of solar energy. In just a few years the efficiency has surpassed that of both conventional dye-sensitized- and organic solar cells. In this study we investigate the influence of the size of the cationic π-system on the electronic and structural properties of the perovskite photo-absorbing material. Using theoretical simulations we investigate key quantities for photovoltaic efficiency, such as band-gap, electron- and hole mass. Weshow that by changing the cation the band-gap and effective masses can be controlled. Structural changes are addressed, where we can see an enhanced influence of dispersion interaction as the cation polarizability increases. The effects of spin-orbit coupling is considered for both structural and electronic properties.

1Support from VR, the Ingegerd Bergh foundation, SNIC and XSEDE is gratefully acknowledged

Thursday, March 5, 2015 8:00AM - 11:00AM — Session S27 DCP: Focus Session: Solvation of Ions and Electrons II 204B - James M. Lisy, University of Illinois at Urbana-Champaign
8:00AM S27.00001 Spectral signatures of large amplitude vibrations in solvated ions. What do the intensities tell us about structure, bonding and dynamics?

8:36AM S27.00002 Ion Microsolvation Probed by Cryogenic Ion Trap Vibrational Spectroscopy

9:12AM S27.00003 Solation of ions investigated by DFT-MD simulations: from gas phase to oxide/liquid water interfaces

9:48AM S27.00004 Anomalous Vibrational Signatures of Ions and Solvation

10:24AM S27.00005 Modeling ion solvation in ethylene carbonate and propylene carbonate

10:36AM S27.00006 Mechanisms of Li-ion transport in bulk electrolytes and through solid-electrolyte interphases (SEI)
focus our attention on assessing the accuracy of predicted Transition-Metal XPS spectra. Many-Body Perturbation Theory introduction of Koopmans-compliant functionals 12 complexity of XPS signals makes it a hard task to go from a spectra to a list of chemical species and their associated oxidation states. Electronic structure sensitivity of electron binding energies VERT, NATHAN KEILBART, ISMAILA DABO, The Pennsylvania State University — X-Ray Photo-emission Spectroscopy (XPS) is one of the most accurate solvents such as ethylene carbonate (EC), ethyl methyl carbonate (EMC) and a mixture of the two. We observed that the diffusivity of Li+ is correlated to the degree of Li+ solvation. Corresponding analysis for PF6− shows greater diffusivity than Li+ associated with a weakly-bound, poorly defined first solvation shell. Using a recent analysis method to study the distribution of directional change from relative angles at successive time intervals, we also characterize the complex motion of these ions and find distinct patterns for each ion in different organic solvents. These results provide valuable insight that can be used to improve the cycling rate of Li-ion batteries and potentially lead to the design of new electrolytes for better overall battery performance.

Thursday, March 5, 2015 11:15AM - 2:15PM — Session T26 DCP: Computational Applications and Methods I 204A - Bruce Garrett, Pacific Northwest National Laboratory

11:15AM T26.00001 Attenuated second order Møller-Plesset perturbation theory: correcting finite basis set errors and infinite basis set inaccuracies, MATTHEW GOLDEY, Institute for Molecular Engineering, the University of Chicago, MARTIN HEAD-GORDON, Department of Chemistry, University of California, Berkeley — Second order Møller-Plesset perturbation theory (MP2) in finite basis sets describes several classes of noncovalent interactions poorly due to basis set superposition error (BSSE) and underlying inaccurate physics for dispersion interactions. Attenuation of the Coulomb operator provides a direct path toward improving MP2 for noncovalent interactions. In limited basis sets, we demonstrate improvements in accuracy for intermolecular interactions with a three to five-fold reduction in RMS errors. For a range of inter- and intramolecular test cases, attenuated MP2 even outperforms complete basis set estimates of MP2. Finite basis attenuated MP2 is useful for inter- and intramolecular interactions where higher cost approaches are intractable. Extending this approach, recent research pairs attenuated MP2 with long-range correction to describe potential energy landscapes, and further results for large systems with noncovalent interactions are shown.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We acknowledge computational resources obtained under NSF Award CHE-1048789.

11:27AM T26.00002 Vapor liquid equilibria of hydrofluorocarbons via first principles Monte Carlo simulations, NEERAJ RAI, HIMANSHU GOEL, Mississippi State Univ — The Kohn-Sham density functional theory (DFT) is a popular approach to compute condensed phase properties. In Kohn-Sham DFT, the local or semi local density functionals do not capture van der Waals interactions accurately. An accurate description of van der Waals interactions is essential in determining thermodynamic properties of molecules. The development of fully non local van der Waals density functional adequately describe dispersion interactions. In this work, we present first principles Monte Carlo simulations to obtain vapor liquid coexistence curves for hydrofluorocarbons by using Becke-Lee-Yang-Parr (BLYP) functional, dispersion corrected functionals, and with rVV10 nonlocal van der Waals density functional.

This work is supported by National Science Foundation

11:39AM T26.00003 Optical spectra and quasiparticle energies of molecules using a local basis set, MATHIAS LJUNGBERG, PETER KOVEL, FRANCESCO FERRARI, Donostia International Physics Center, Paseo Manuel de Lardizabal, 4. E-20018 Donostia-San Sebastián, DIETRICH FOERSTER, CPMO/HOMA, Université de Bordeaux 1, 351 Cours de la Libération, 33405 Talence, France, DANIEL SÁNCHEZ-PORTAL, Donostia International Physics Center, Paseo Manuel de Lardizabal, 4. E-20018 Donostia-San Sebastián — The Bethe-Salpeter equation (BSE) is the state of the art for computing optical spectra for solids and molecular clusters. Here we present an implementation of BSE for clusters that scales asymptotically like O(N3) with the number of atoms, achieved by exploiting the locality of the problem in the local basis set representation and by using the Haydock recursion method to compute the spectrum. Using a pseudo-Hermitian Lanczos algorithm we can go beyond the Tamm-Dancoff approximation within our iterative scheme. As a starting point for the BSE we compute quasiparticle energies with our low-scaling GW implementation [1], retaining the frequency dependence of all quantities and thus avoiding the plasmon-pole model or similar schemes. The initial wave functions are taken from a preceding SIESTA calculation. We discuss the influence of self-consistency on the quasiparticle energies [2] and its effect on the BSE spectra. We also investigate the satellite peaks that are present in the GW density of states. Computed GW/BSE spectra are shown for some organic molecules of medium size that are relevant for photovoltaic applications.


11:51AM T26.00004 Computational XPS from Koopmans-compliant Functional, NICOLAS POILVERT, NATHAN KEBLART, ISMAILA DABO, The Pennsylvania State University — X-Ray Photo-emission Spectroscopy (XPS) is one of the most accurate experimental probe when it comes to deciphering the chemical composition of materials like Transition-Metals and Transition-Metal Oxides. Because of the sensitivity of electron binding energies to the local chemistry surrounding an atom, XPS can also help identify atomic oxidation states. Nevertheless the complexity of XPS signals makes it a hard task to go from a spectra to a list of chemical species and their associated oxidation states. Electronic structure methods such as Density Functional Theory fall short when it comes to predicting electron binding energies because of large self-interaction errors. The recent introduction of Koopmans-compliant functionals on the other hand has led to the conclusion that UPS spectra can be accurately predicted at the level of Many-Body Perturbation Theory and beyond, retaining most of the conceptual and computational simplicity of DFT. In this talk, we will more particularly focus our attention on assessing the accuracy of predicted Transition-Metal XPS spectra.

12:03PM T26.00005 Computational studies of the acid catalysts and solvent effects on Diels-Alder cycloaddition and dehydration reactions: Maleic anhydride and 2,5 dimethylfuran. Taha Salavati-Fard, Stavros Caratzoulas, Douglas Doren, University of Delaware — Using DFT calculations, we present a detailed gas-phase mechanism for the conversion of DMF and maleic anhydride to 3,6 dimethyl phthalic anhydride. The conversion includes Diels-Alder cycloaddition followed by dehydration of cycloadduct. In addition, we consider the effects of solvent by making use of the PCM. We provide free energies of uncatalyzed, Lewis acid and Brønsted acid catalyzed reactions in vacuum and in a broad range of solvents. Our calculations show that a Lewis acid catalyzes the reaction through decreasing HOMO-LUMO gap of the addends. Also, a Brønsted acid changes the mechanism of reaction and is able to lower the activation free energy of cycloaddition, effectively. Furthermore, we show that as Lewis acids lower the activation barrier of dehydration reaction which is originally too high, a Brønsted acid changes the mechanism and is extremely effective in catalyzing the dehydration. Also, increasing dielectric constant of solvent decreases the activation barrier of uncatalyzed and Lewis acid catalyzed Diels-Alder reaction. For both the Lewis and Brønsted acid catalyzed Diels-Alder reaction, the dependency of activation free energy to increasing dielectric constant is much stronger when the acid is coordinated to DMF.

12:15PM T26.00006 First-principles Study of the Removal of Boron by Co-precipitation with Hydroxyapatite Using Dolomite as a Starting Material. Chenyang Li, Lazaro Calderin, Pennsylvania State University, Keiko Sasaki, Kyushu University, Ismaila Dabo, Pennsylvania State University, Pennsylvania State University Collaboration, Kyushu University Collaboration — Boron is a toxic chemical in drinking water and a major health concern worldwide. One method to reduce boron concentration in water consists of co-precipitating boron with hydrated minerals. Nevertheless, little is known about the chemical mechanisms underlying boron reactions with complex minerals. In this work, we have applied first-principles calculations based on density-functional theory (DFT) to characterize boron-bearing hydroxyapatite (HAp) resulting from co-precipitation with hydrated dolomite. DFT calculations have been performed to interpret X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) experiments and to characterize solid residues after boron removal with a focus on determining the absorption sites of B(OH)3 and B(OH)4 in the formed minerals. The computed results indicate that the absorption takes place at phosphate (PO4)3- sites. In addition, changes in the lattice parameters of B-bearing HAp as a function of boron concentration have been calculated and compared with experimental results. Good agreement of the decreasing trend in α-direction and the increasing trend in c-direction has been observed by our calculations. Raman and infrared (IR) spectra have been studied as well to achieve a better understanding the B-HAp structures.

12:27PM T26.00007 Effective Many-Body Interactions in Dipolar Fluids and their Effect on Structure: Can the Dipole-Dipole Interaction be Modelled as a Short-Ranged 3-Body Interaction? Julien Sindt, Philip Camp, University of Edinburgh — In the 1970s, Stell et al. showed that it is possible to map the partition function of a system of particles interacting via anisotropic dipolar pairwise interactions to that of a hypothetical system with isotropic many-body interactions. It follows that “polar and nonpolar fluids have the same critical exponents” irrespective of long-ranged Coulombic interactions. We have calculated the structural properties of a system of soft spheres with the leading-order 2- and 3-body terms of the isotropic many-body potential. We have compared radial distribution functions and structure factors obtained from molecular dynamics simulations of dipolar soft spheres (DSSs) under the same physical conditions. We find that the many-body potential overemphasises chaining when compared to the equivalent DSS system. The chain-inducing component is the three-body Axilrod-Teller potential, and by adjusting its contribution, it is possible to match the structure with that of the DSS fluid, showing that the many-body potential can be used as a proxy for the dipolar potential. We conclude by studying the gas-liquid phase transition, finding that the phase transition disappears beyond a threshold degree of chaining.

12:39PM T26.00008 A new lattice Monte-Carlo simulation for the dielectric inhomogeneity of ion-containing liquids. Xiaozheng Du, Issei Nakamura, State Key Laboratory of Polymer Physics and Chemistry, Chongchun Institute of Applied Chemistry, Chinese Academy of Sciences — We develop a novel lattice Monte-Carlo method to capture the effects of the reorganization of solvent dipoles under external electrostatic fields. Our simulation accounts for the effects of saturated dipoles near ions on the angstrom scale and hence spatial variations in the dielectric function. We will discuss the substantial disparity in the dielectric functions between like and unlike charges. Importantly, a contacting cation-anion pair cannot be literally taken as “charge-neutral species” in terms of the solvation energy. On the other hand, even when the two charges are separated by 1 nm, a significant correlation in the dielectric function may arise. Our simulation also provides the dependence of the bulk dielectric value on the ionic strength, which is consistent with experimental data.

12:51PM T26.00009 Energy levels of a particle confined in an ellipsoidal potential well. Roman Kezerashvili, New York City College of Technology, CUNY, USA, Tamar Kerevelidze, Tamaz Tchelidze, Tbilisi State University, Georgia — The Schrodinger equation is solved for a particle confined within the ellipsoidal potential well using the perturbation theory and the Hamiltonian diagonalization method. The explicit expressions are obtained for the energy levels that are the size and shape dependent and appropriate wave functions. The calculated energy levels are in a good qualitative and quantitative agreement with the result obtained by numerical solution of the Schrodinger equation. It is revealed that for the lowest states of a given symmetry the region of validity of the perturbation approximation is much larger than it follows from the usual condition of applicability of the perturbation theory. The optical properties of nanoparticles of a prolate and oblate ellipsoidal shape are discussed.

1:03PM T26.00010 Potential and kinetic energetic analysis of phonon modes in varied molecular solids. Brent Kraczek, US Army Research Laboratory — We calculate partitioned kinetic and potential energies of the phonon modes in molecular solids to illuminate the dynamical behavior of the constituent molecules. This enables analysis of the relationship between the characteristics of sets of phonon modes, molecular structure and chemical reactivity by partitioning the kinetic energy into the translational, rotational and vibrational motions of groups of atoms (including molecules), and the potential energy into the energy contained within interatomic interactions[1]. We consider three solids of differing size and rigidity: naphthalene (C10H8), nitromethane (CH3NO2) and α-HMX (C2H8N4O8). Naphthalene and nitromethane mostly act in the semi-rigid manner often expected in molecular solids. HMX exhibits behavior that is significantly less-rigid. While there are definite correlations between the kinetic and potential energetic analyses, there are also differences, particularly in the excitation of chemical bonds by low-frequency lattice modes. This suggests that in many cases computational and experimental methods dependent on atomic displacements may not identify phonon modes active in chemical reactivity. 1. Kraczek, Chung, J. Chem. Phys. 138:074505 (2013).
hydrazone-based switches.\footnote{Supported by AVP-0207-11 and VEGA (2/0007/12) projects.}

1:27PM T26.00012 Determination of the Torsional Potential Energy Surfaces of the Ortho-Meta-, and Para-Isomers of Dinitrobenzene, PAUL SMITH, MARIO BORUNDA, Oklahoma State Univ — The three unique isomers of dinitrobenzene, the ortho-, meta-, and para-isomers, have widely varying steric hindrances and bond hybridizations. The steric effects and the hybridized bonds cause the molecular energy to be dependent on the rotation of the nitro groups. We have calculated the torsional potential energy surfaces of each of the three dinitrobenzene isomers using density functional theory, obtaining a 33x33 plot of the energy of each molecule as a function of the torsional angles of the C-N bonds. The accuracy of the method used is determined by comparison with previous theoretical and experimental results. The potential energy surfaces provide valuable insight into the mechanics of conjugated molecules, and the method we present can be extended even to proteins, which have very complicated conformations and many conjugated bonds. This method makes the determination of the lowest energy conformations of complex molecules far more computationally accessible.

1:39PM T26.00013 Density Functional Plus Dynamical Mean Field Study of Spin Crossover Molecule, JIA CHEN, Department of Applied Physics and Applied Math, Columbia University, ANDREW MILLIS, Department of Physics, Columbia University, CHRIS MARIANETTI, Department of Applied Physics and Applied Math, Columbia University — We report a density functional plus dynamical mean field study of spin crossover molecule Fe(phen)2(NCS)2. The temperature dependent magnetic susceptibility, Fe-d spectral and total energy were calculated and compared with experimental magnetization, metal L-edge x-ray adsorption spectroscopy. The importance of dynamic effect on energetics is demonstrated by comparison with density functional plus U method, and the role of full charge self-consistency is identified. Moreover, the local spin density plus U (LSDA+U) method with exchange interaction explicitly included is shown to dramatically overemphasize magnetic interaction.

1:51PM T26.00014 The Effect of Structure Variations on Transition State Scaling Relations, PHILIPP PLESSOW, SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA, FRANK ABILD-PEDERSEN, SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA — Linear scaling relations for adsorption as well as transition state (TS) energies have proven extremely useful in the quest to identify, understand and predict reactivity trends of catalysts [1]. The existence of linear scaling relations for reaction intermediates can be understood in terms of simple bond order arguments and hence their accuracy depends on the variations in the adsorbate-surface bond [2]. Since structure and bonding of TS can vary substantially for different surfaces, it is much less clear that TS scaling relations should behave linearly at all. We investigated how the TS structure influences scaling relations and how scaling parameters relate to bond-orders. A model that accounts for varying geometry and goes beyond the linear approach is developed and applied to industrially relevant surface reactions.

2:03PM T26.00015 Machine learning of single molecule free energy surfaces and the impact of chemistry and environment upon structure and dynamics, RACHAEL MANSBACH, ANDREW FERGUSON, Univ of Illinois - Urbana — The conformational states explored by proteins and polymers can be controlled by environmental conditions (e.g., temperature, pressure, solvent) or molecular chemistry (e.g., chain length, side chains). It is of fundamental interest to quantify the impact upon molecular structure and function, and a prerequisite to the rational engineering of proteins and polymers with desired properties. Using the diffusion map nonlinear manifold learning algorithm, we have developed an approach to: (i) extract from molecular simulations the single molecule free energy surface governing the microscopic molecular behavior, (ii) quantify changes in its topography as a function of environmental conditions and molecular chemistry, and (iii) relate these perturbations to changes in molecular structure and dynamics. In a first application to an n-icosane chain, we have quantified the thermally accessible chain configurations as a function of temperature and solvent conditions. In a second application to a family of polyglutamate-derivative decameric homopeptides, we quantify the stability of the thermally accessible chain configurations as a function of solvent crucial for understanding the huge dipole moments (>10D) in the Z conformation and significantly smaller (∼5D) in the E conformation and at the transition state, pointing toward very different ordering in those states. Furthermore, the internal and free energy surfaces from thermodynamic integration are qualitatively very different with the free energy surface exhibiting much smaller energy differences between E and Z. In addition, the solvent causes a pronounced shift (∼30°) in the position of the Z states from internal and free energies. Both finding highlight the role of the entropy in the switching process and help a quantitative understanding of the switching in the solvent.


Thursday, March 5, 2015 11:15AM - 2:15PM
Session T27 DCP: Focus Session: Solvation of Ions and Electrons III
2048 - Etienne Garand, University of Wisconsin, Madison

11:15AM T27.00001 Solvation and Organization of Ions at the Air-Water Interface, HEATHER ALLEN, Ohio State University — The air-water interface has been the focus of research in the Allen Lab at Ohio State for more than a decade. We utilize nonlinear and linear optical spectroscopic methods to understand the local intermolecular interactions and organization of water itself with various solutes and monolayers. Motivated by atmospheric aerosol chemistry of marine and urban regions, and biophysical applications related to lung lining and biomembranes, monovalent and divalent cations and anions continue to be investigated by our group using conventional and heterodyne-detection vibrational sum frequency generation (VSFG) spectroscopy. Interest is in the surface propensity and availability for reaction at water surfaces. Ion valency, polarizability, size, shape, and identity of the counterion are critical factors in considering ion organization and subsequent changes in interfacial electric field at the air-water interface. The hydration water molecules play a key role in the interfacial organization of other species in the solution, and is studied directly as it reveals the details of ion interfacial distributions. Phospholipids and fatty acids are also investigated using both VSFG and Brewster angle microscopy (BAM). Head group differences, especially with regard to hydrogen bonding capability and extent, are discerning factors for surface organization and shape distinction at the water surface. In collaboration with Wei Hua and Dominique Verreault, Ohio State University.
11:51 AM T27.00002 Sensitivity of ultrafast vibrational dynamics of interfacial water to cations at silica/water interfaces, SHALAKA DEWAN, AASHISH TULADHAR, ERIC BORGUET, Temple Univ — Interfacial water structure is a key player in the chemistry of environmentally relevant processes, e.g., the dissolution of mineral surfaces. Since the properties of water are dominated by its hydrogen bonding network, understanding the local changes in this structure at the mineral/water interface is important. Vibrational sum-frequency generation (vSFG) spectroscopy is a tool that can probe the hydrogen bonding environment at buried interfaces. Time-resolved vSFG of the OH stretch is further sensitive to the changes in hydrogen bonding at surfaces. vSFG has demonstrated that interfacial water structure at silica is most sensitive to cations at neutral water pH 6-8. Further, at this pH, increasing the ionic strength slows the vibrational relaxation of O-H stretch of water from ~200 to ~600 fs. Here, we show that the slowing down of O-H dynamics on addition of cations is more pronounced at pH 6 than at pH 12, even though the surface is negatively charged in both cases. This suggests that, in addition to the salt-screening the surface charge, the cations actually change the local H-bonding environment of water differently at distinct bulk pH. Our results shed light on the ongoing debate on the role of ions in altering the structure of water at an interface.

12:03 PM T27.00003 Vibrational Spectroscopy of Hydrated MOH Clusters, BRETT MARSH, JONATHAN VOSS, JIA ZHOU, ETIENNE GARAND, Univ of Wisconsin, Madison — Hydrated metal ions have importance in a number of fields of chemistry including environmental chemistry, biochemical chemistry, and catalysis. Although the aqua complexes of transition metals are well studied there is a dearth of information on hydride containing metal clusters which have been implicated in catalytic mechanisms of water oxidation. In this work we use cryogenic ion vibrational spectroscopy (CVIS) to interrogate clusters of the form MOH(H2O)n (M= Fe, Co, Ni, Cu, Zn) in the hydride stretching region (2400-3800 cm⁻¹). Comparison of the spectral data to density functional theory calculations allow for unambiguous assignment of the observed spectral features. The resulting spectra show both a metal dependent and size dependent shift of the hydride stretching frequency in all clusters. The spectra also reveal that the first solvation shells of Fe, Co, Cu, and Zn containing clusters are composed of 4 ligands while the first solvation shell in Ni clusters is at least 6 ligands. This is markedly different from previous work on Ni(H2O)₆ molecules, Cu(H2O)₆, and Zn(H2O)₆ cluster in which the first solvation shells are 4 ligands, 2 ligands, and 3 ligands respectively. Aspects of hydration in the second solvation shell of these clusters will also be discussed.

12:15 PM T27.00004 Exploring Specific Ion Effects on Ion Hydration at Aqueous Interfaces, PAUL CREMER, Penn State University — We used sum frequency generation vibrational spectroscopy to probe the interactions of ions with self-assembled monolayers and proteins at aqueous interfaces. I will discuss the behavior of cations and anions as they relate to the Hofmeister series, which is a rank ordering of the efficacy of these species to influence the physical behavior of colloidal and interfacial systems in solution. Ion specific effects at these interfaces were found to be determined by several factors. These include the sign and magnitude of the surface potential, ion pairing effects in the double layer, as well as the presence of polar and nonpolar interfacial moieties. At negatively charged, hydrophilic surfaces, we found that Na⁺ adsorption and double layer formation were modulated by the type of the counterion in solution. The same ordering was observed for the anions whether this interface was relatively hydrophilic or hydrophobic. Changing the sign of the charge at the interface also led to a similar Hofmeister ordering. Moreover, at negatively charged hydrophilic surfaces, the smallest and best hydrated cations were mostly favored over more poorly hydrated cations. By contrast, well hydrated cations were repelled from more apolar surfaces.

12:15 PM T27.00005 Structural properties of simple aqueous solutions from ab initio simulations, ALEX P. GAIDUK, Institute for Molecular Engineering, University of Chicago, FRANCOIS GYGI, Department of Computer Science, University of California, Davis, GIULIA GALLI, Department of Molecular Engineering, University of Chicago — Although water and salt solutions have been studied for many decades, several aspects of their microscopic and electronic properties remain uncertain. One of the open questions is whether simple ions have long-range effects on the structure of liquid water. We performed extensive first-principles molecular dynamics simulations of a simple salt (NaCl) and found that the Na⁺ ion does not significantly change the structure of water beyond the first solvation shell. This has a far-reaching hydrogen-bond-breaking effect. We present an analysis of the structural modifications in terms of molecular polarizabilities and dipole angular correlations. Our results are in agreement with the traditional classification of Cl⁻ as a structure-breaker, but at variance with several theoretical and experimental studies which did not observe significant modifications of the structure of water outside the first solvation shell of ions. We also present an analysis of the electronic properties of the solutions [3].


Work supported by DOE BES DE-SC0008938. Computer time provided by the Argonne Leadership Computing Facility through the INCITE program.

1:03 PM T27.00006 Ultrafast vibrational spectroscopy (2D-IR) of anions in ionic liquids, SEAN GARRETT-ROE, University of Pittsburgh — Ionic liquids hold promise for applications in energy storage as the electrolyte in electric double-layer capacitors and other devices. Further optimizing device performance through their physical and chemical properties requires an improved understanding of the detailed interactions between cation and anion and how they reorganize in the presence of charge. Here we probe the dynamics of thioacyanate ions in several bulk imidazolium bis(trifluoromethylsulfonyl)amide ionic liquids from femtoseconds to 100 ps using ultrafast vibrational spectroscopy. Two-dimensional infrared (2D-IR) spectroscopy of thiocyanate ions detect both inertial motion (on the hundreds of femtosecond timescale) as well as slower, diffusive motions (on the tens of picosecond timescale). The 2D-IR experiments show that the rate of fluctuation of the electrostatic environment around the thiocyanate is sensitive (2D-IR) spectroscopy of thiocyanate ions detect both inertial motion (on the hundreds of femtosecond timescale) as well as slower, diffusive motions (on the tens of picosecond timescale). The 2D-IR experiments show that the rate of fluctuation of the electrostatic environment around the thiocyanate is sensitive to hydrogen bonding at the 2-position of the imidazolium ring. The correspondence of time-scales with molecular dynamics simulations suggests that the pico-second motions we observe are fluctuations around a local free-energy minimum while the tens of picoseconds timescales correspond to the rearrangement of some of the local molecular arrangements. Our measurements implicate the break-up of local ion cages as the activating event for the onset of translational motions which are responsible for viscosity and conductivity. We additionally test our hypothesis that the SCN anion is sensitive to the local environment by introducing co-solutes – counter-cations such as K⁺ and water. We observe contact-ion pairs, i.e., SCN- anions with a K⁺ counter charge in the first solvation shell through a static component in the frequency correlation function. We observe water-bound SCN- through changes in linewidth, population relaxation rates, and dynamics. The SCN- is an eloquent reporter of local structure and dynamics in these complex fluids.

1:39 PM T27.00007 Structural dynamics of solvated OH⁻ and H₃O⁺ in liquid water: an ab initio molecular dynamics study using PBE0 hybrid functional with van der Waals' interaction, LIXIN ZHENG, XIFAN WU, Temple Univ — The nature of solvation structure of hydroxide (OH⁻) and hydronium (H₃O⁺) solvated in liquid water is of fundamental interest, as it is the prerequisite to understand the autoprotolysis process, which is often a crucial step in chemical and biological activities. It has been revealed that the proton transfer (PT) process, especially in hydroxide case, is of great controversy and complexity compared to traditional textbook description. One major source of inaccuracy originates from the delocalization error and lack of dispersion force in the conventional adopted electron exchange correlation function in GGA functional leading to an over-structured H-bond (HB) structure. Now with state-of-the-art PBE0 hybrid density functional, and the inclusion of long-range van der Waals dispersion force, we are able to perform ab initio molecular dynamics with higher accuracy. Through the analysis of mean square displacement of ion, HB geometrical distribution and lifetime, and the strength change of HB, we are presenting a quantitatively accurate picture of proton transfer structural mechanism.
The splitting of H₂O into H₂ and O₂ is an important reaction for alternative energy sources, but it is hindered by the water oxidation step due to its unfavorable thermodynamics. Production of a suitable water oxidation catalyst (WOC) has posed a challenge to researchers for decades, and the reaction mechanism is not well understood. One of the most well-known and extensively studied WOCs is [Ru(tpy)(bpy)(H₂O)]²⁺ (tpy = 2,2':6,2"-terpyridine, bpy = 2,2'-bipyridine) and its derivatives. In this talk, infrared vibrational spectra (2400-3800 cm⁻¹) obtained by Cryogenic Ion Vibrational Spectroscopy (CIVS) of [Ru(tpy)(bpy)(H₂O)]²⁺ and its water clusters, [Ru(tpy)(bpy)(H₂O)]²⁺ ⋅ nH₂O, are presented. In particular, the OH stretches are used as a probe of solvation strength, and trends in their spectral shifts are examined as a function of cluster size. Determination of water binding geometries are facilitated by comparison with density functional theory (DFT) calculations. Additionally, IR and mass spectral data of electrochemically-produced intermediates of the water oxidation cycle are shown, which provide evidence of proton-coupled electron transfer (PCET) events, in agreement with proposed mechanisms.
3:30PM W26.00006 TDDFT+DMFT analysis of excitations and relaxation dynamics in alpha-
Ce\textsuperscript{1}, SYED ISLAMUDDIN SHAH, VOLODYMYR TURKOWSKI, TALAT S. RAHMAN, Department of Physics, University of Central Florida — We apply a combination of time-dependent density functional theory and dynamical mean-field theory (TDDFT+DMFT) to study the excitation spectrum and response of bulk alpha-Ce to an external perturbation by a laser pulse. The excitation spectrum is obtained by solving TDDFT Casida equation with the "free electron" spectrum calculated from density functional theory and the exchange-correlation (XC) kernel extracted from the DMFT charge susceptibility. We pay special attention to the complex role of the hybridization of the f- with the s-, p-, and d-electron states in the system spectrum. The nonequilibrium solution of the TDDFT equations shows that the short-lived local moments of f-electrons get suppressed as the hybridization strength between the f- and other orbitals increases. We also calculate the effective scattering times for the scattering of the f-electrons from the s-, p-, and d-states at different values of the local Coulomb repulsion and exchange J parameters from the corresponding expression for the orbital-resolved XC kernel, and analyze how these scattering processes may affect the dynamics of the system relaxation.

\textsuperscript{1}Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

DHARA TRIVEDI, Department of Physics & Astronomy, University of Rochester, LINJUN WANG, OLEG PREZHD, Department of Chemistry, University of Southern California — We carry out \textit{ab initio} nonadiabatic molecular dynamics (NAMD) simulations to study the fast relaxations of hot electrons in a CdSe quantum dot (QD). The reviewed system is a promising candidate for QD-sensitized semiconductor solar cells and the presence of well-separated conduction electron states opens the possibility of energy selectivity for hot carriers. We examine the intraband relaxation of the photoexcited electrons in the QD and the role of surface ligand in the process. A novel global flux surface hopping (GFSH) approach is adopted. We investigate the electron relaxation from the 1Pe to 1Se state in pure and 1,6-hexanediithiol ligated CdSe QD. The intraband relaxation is accelerated due to the Auger-type relaxation in the pure QD. The ligand forms a hole trapping state, which competes with the Auger-type relaxation impeding the electron-hole energy exchange. The present study establishes the basic theoretical model describing the relaxation processes in both scenarios. The model is supported by computational studies of relaxation dynamics in model QD-ligand complexes. The obtained interplay between the competing phonon-assisted Auger and ligand-induced trapping mechanisms has given us a comprehensive picture of the complex photoinduced dynamic related to QDs.

3:54PM W26.00008 New Developments in Ab Initio Multiple Spawning for Efficient Nonadiabatic Molecular Dynamics\textsuperscript{1}, BASILE F.E. CURCHOD, AARON SISTO, DAVID R. GLOWACKI, TODD J. MART\text{\textsc{\textregistered}}NEZ, Stanford University — Ab initio multiple spawning (AIMS) describes the nonadiabatic dynamics of nuclear wavepackets by means of a linear combination of frozen Gaussians. While the Gaussian centers follow classical trajectories, the expansion coefficients are propagated according to the time-dependent Schrödinger equation. As a result of the coupling between Gaussian functions, AIMS accurately describes coherence and decoherence effects close to nonadiabatic regions. This accuracy has further been validated by the excellent agreement reported between AIMS dynamics and experimental observations. In this Contribution, we will discuss new techniques used to extend the applicability of AIMS to (i) larger molecules, (ii) long-time simulations, and (iii) dynamics involving an important number of electronic states. We will present different examples of nonadiabatic molecular dynamics in organic and atmospheric photochemistry, resulting from the interface between AIMS and the GPU-accelerated electronic structure code TeraChem. New methods improving the AIMS efficiency for larger systems will be discussed, such as the stochastic-selection AIMS. Finally, we will highlight early results on the extension of AIMS to the combined description of both internal conversion and intersystem crossing phenomena.

\textsuperscript{1}B.F.E.C. acknowledges the Swiss National Science Foundation ( fellowship P2ELP2_151927) for financial support.

4:06PM W26.00009 Effects of Thermal and Quantum Fluctuations on Dipole-moment distribution of \textit{H}_2\textit{O} molecules in ice \textit{I}_\text{h}\textsuperscript{1}, PEDRO MOREIRA, UFSCar, MAURICE DE KONING, Unicamp — Molecular dipole moments are the fundamental entities that underpin the dielectric behavior of molecular materials. Here, we discuss the molecular-dipole distributions of water molecules in ice \textit{I}_\text{h}, considering the roles of proton-disorder, as well as the effects of thermal and quantum fluctuations. For this purpose we employ \textit{ab initio} Born-Oppenheimer and Path-Integral Molecular Dynamics simulations and compute molecular dipole moments using maximally-localized Wannier functions. We discuss trends in the dipole-moment distributions as a function of temperature.

4:18PM W26.00010 Screened Hybrid Exact Exchange Schemes to Adsorption Energies on Perovskite Oxides, ELTON SANTOS, Department of Chemical Engineering, Stanford University, Stanford, California 94305, USA, ALEKSANDRA VOJVODIC, SLAC National Accelerator Laboratory, Menlo Park, CA, 94305, JENS K. NORSKOV, Department of Chemical Engineering, Stanford University, Stanford, California 94305, USA — The bond formation between an oxide surface and oxygen, which is one of the important intermediates for oxygen evolution reaction, is investigated using hybrid functionals. We show that there exists a linear correlation between the adsorption energies of oxygen on LaMnO\textsubscript{3} (M=Sc-Cu) oxides at hybrid calculations to those computed using semilocal density functionals through the magnetic properties of the bulk phase. The energetics of the spin-polarized surfaces follow the same trend as corresponding bulk systems, which can be treated at a much lower computational cost. The difference in adsorption energy due to magnetism is linearly correlated to the magnetization energy of bulk, i.e., the energy difference between the spin-polarized and the non spin-polarized solutions. This suggests that one could estimate the correction to the semilocal density functional adsorption energies directly from the hybrid bulk magnetization energy.

4:30PM W26.00011 Kinetic compensation effect in thermal desorption, NAYELI ZUNIGA-HANSEN, Austin Peay State University, LEONARDO E. SILBERT, Southern Illinois University Carbondale, MERCEDES CALBI, University of Denver — The parameters which characterize the rates of many thermally activated processes are often extracted using the Arrhenius equation. A series of closely related thermally activated processes exhibit systematic variations in the energies of activation, \textit{E}_a, and preexponential factor, \textit{A}, in response to a perturbation, which leads to the concept of ‘kinetic compensation’, such that the different parameters in the Arrhenius equation balance each other out thereby leading to an implicitly assumed constant rate. However, the compensation effect has not been generally demonstrated and its origins are not completely understood. Using kinetic Monte Carlo simulations on a model interface, we explore how site-adsorbate and adsorbate-adsorbate interactions, and surface structural changes influence surface coverage and the kinetic parameters during a typical temperature programmed desorption process. We find that the concept of the compensation effect for interacting species breaks down and the time characterizing desorption increases with increasing interaction strength due to an increase in the effective activation energy. At the ‘molecular’ level the changes are the result of enhanced site correlations with increasing adsorbate interaction strength suppressing the onset of desorption.
4:42PM W26.00012 First principles molecular dynamics simulations of the static, dynamic and electronic properties of the liquid silver-tin alloy\(^1\), Lazaro Calderin, The Pennsylvania State University, PA, USA.

David Gonzalez, Luis E. Gonzalez, Universidad de Valladolid, Valladolid, Spain — We report an ab-initio molecular dynamics study of several structural and dynamic properties of the liquid Ag-Sn alloy at three concentrations and a temperature of 1273 K. The calculated structural results show good agreement with the available experimental data and accurately reproduce the measured total static structure factors.\(^1\) The heterocoordinating tendencies in the alloy have been analyzed in terms of some short range order parameters. As for the dynamical properties, the single particle dynamics in the liquid alloy has been studied by evaluating several velocity correlation functions and the associated diffusion coefficients. Results are also reported for other transport coefficients, such as the adiabatic sound velocities and shear viscosities. Finally, from the spectra of the longitudinal current correlation functions, the longitudinal dispersion curves have been computed.\(^1\) I. Kaban, W. Hoyer, A. Ilinski, O. Slukhovskii and S. Slyusarenko, J. Non-Cryst. Solids, 331, 254-262 (2003)

\(^1\) We acknowledge financial support from Spanish MSI (project FIS2012-33126).

4:54PM W26.00013 Orbital-free ab initio molecular dynamics study of the free liquid surface of Sn. From pseudopotential generation to structural and dynamic properties\(^1\), Beatriz Gonzalez del Rio, Luis Enrique Gonzalez Teasedo, Universidad de Valladolid — We report results of an orbital-free ab initio molecular dynamics (OF-AIMD) study of the free liquid surface of Sn at 1000 K. A key ingredient in the OF-AIMD method is the local ionic pseudopotential describing the ions-valence electrons interaction. We have developed a force-matching method\(^1\) to derive a local ionic pseudopotential suitable to account for a rapidly varying density system, such as in a free liquid surface. We obtain very good results for several structural properties. We have also studied the evolution of some dynamical properties when going from the central region (where the system behaves like the bulk liquid) towards the free liquid surface.


5:06PM W26.00014 ABSTRACT WITHDRAWN

5:18PM W26.00015 ABSTRACT WITHDRAWN

Thursday, March 5, 2015 2:30PM - 5:30PM

Session W27 DCP: Charge Transport and Plasmonics 204B - David Nesbitt, University of Colorado at Boulder

2:30PM W27.00001 Lifetimes for fast charge transfer of core excited molecules on gold and graphene, Gian Paolo Brivio, ETSF, CNISM, Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Milano, Italy, Guido Fratesi, ETSF, CNISM, Dip. di Fisica, Università di Milano, Milano, Italy, and Dip. di Scienza dei Materiali, Milano-Bicocca, Milano, Italy, He Lin, Abhilash Ravikumar, Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Milano, Italy, Olgun Adak, Latha Venkataraman, Department of Applied Physics, Columbia University, NY, Gregor Kladnik, Dean Cvetko, Physics department, Faculty for mathematics and physics, University of Ljubljana, Ljubljana, Slovenia, and CNR-IOM, Laboratorio TASC, Trieste, Italy, Alberto Morgante, CNR-IOM, Laboratorio TASC, Trieste, Italy and Department of Physics, University of Trieste, Trieste, Italy — The charge transfer time from an excited organic molecule both adsorbed on gold and graphene is studied in terms of the resonant linewidth of the molecular orbital energy levels interacting with the valence band of the substrate. The calculations are performed by density functional theory including the van der Waals contribution. Experiments are carried out by the core level resonant spectroscopies with fs resolution. The core valence exciton is described by a static perturbation of the atomic potential. The calculated widths are consistent with the experimental transfer times. They display a dependence on the molecular adsorption angle both in theory and experiments, and this effect is predicted to be function of the excited orbital.

2:42PM W27.00002 Rhodium nanoparticles for Ultraviolet Plasmonics, Anne Watson, Xiao Zhang, Duke University, Rodrigo Alcaraz de la Osa, Juan Sanz, Francisco Fernandez, Fernando Moreno, University of Cantabria, Gieb Finkelstein, Jie Liu, Henry Everitt, Duke University — We introduce the non-oxidizing catalytic noble metal rhodium for ultraviolet (UV) plasmonics. 8 nm tripod-shaped planar Rh nanoparticles (NPs) were synthesized by a modified polyol reduction chemistry. They display a dependence on the molecular adsorption angle both in theory and experiments, and this effect is predicted to be function of the excited orbital.

2:54PM W27.00003 ABSTRACT WITHDRAWN

3:06PM W27.00004 Analyzing biphasic surface plasmon resonance data, Purushottam Tiwari, Xuewen Wang, Jin He, Yesim Darici, Florida International University — Surface plasmon resonance (SPR) is a widely used label-free biophysical technique to quantitatively study biochemical processes. Analysis of monophasic SPR profiles by fitting using a single exponential function is straightforward. However, there is no simple procedure for SPR data fitting with double exponential functions. An existing approach is to fit the biphasic SPR profiles with numerical solutions of the rate equations. This procedure requires some prior knowledge of the underlying interaction mechanism, and the extracted rate constants often have large uncertainties. We propose a new method of analyzing the biphasic SPR data using the three commonly employed biphasic models. Our method is based on a general analytical solution of the biphasic rate equations. Our method can be used to determine the underlying biphasic interaction mechanism from the analysis of the SPR data, and to extract the rate constants with high confidence levels.
We present new insights into the role dimensionality plays in the lead-molecule coupling scheme at molecular electronic junctions. A key ingredient of our approach is the development of a noise spectroscopy formalism. As defined, \( \Gamma(E) \) describes resonances of non-Lorentzian nature and can be decomposed into components associated with the left and right leads, respectively; and it is particularly useful in understanding transport properties in terms of molecular orbitals in asymmetric junctions. We compute this quantity via an ab initio NEGF approach based on density functional theory and illustrate its utility with several junctions of experimental relevance, including recent work on rectification in Au-graphite junctions.

This work is supported by the DOE, and computational resources are provided by NERSC.

4:06PM W27.00009 Quantum model of capacitance of nanostructures \(^1\), JUNQIANG LU, University of Puerto Rico at Mayaguez — Modeling high-frequency electronic properties of nanostructures in nanocircuits presents particular challenge because of contribution from electrodes. In this talk, I present the difference in modeling steady and dynamic electronic transport properties of nano-gap structures and a quantum model to measure capacitance of nanostructures.

\(^1\)This work is supported by NSF-EPSCOR program (Grants 1002410 and 1010094) and an award from Research Corporation for Science Advancement. JQIL is also grateful for the support from the Faculty of Arts and Sciences, University of Puerto Rico at Mayaguez.

4:18PM W27.00010 Finding Destructive Interference Features in Molecular Transport Junctions \(^2\), MATTHEW REUTER, Institute for Advanced Computational Science and Department of Applied Mathematics & Statistics, Stony Brook University, THORSTEN HANSEN, Department of Chemistry, University of Copenhagen — Associating molecular structure with quantum interference features in electrode-molecule-electrode transport junctions has been difficult because existing guidelines for understanding interferences only apply to conjugated hydrocarbons. Herein we use linear algebra and the Landauer-Büttiker theory for electron transport to derive a general rule for predicting the existence and locations of interference features. Our analysis illustrates that interferences can be directly determined from the molecular Hamiltonian and the molecule-electrode couplings, and we demonstrate its utility with several examples.

\(^2\)This work is supported by the DOE, and computational resources are provided by NERSC.

4:30PM W27.00011 The role of dimensionality on the molecule-lead coupling in molecular electronic junctions \(^3\), TAMAR ZELOVICH, Tel Aviv University, LEEOR KRONIK, Weizmann Institute of Science, ODED HOD, Tel Aviv University — Present new insights into the role dimensionality plays in the lead-molecule coupling scheme at molecular electronic junctions. A key ingredient of our approach is a transformation of the Hamiltonian matrix from an atomic to a state representation of the molecular junction. This provides direct access to the different couplings between the molecular states and the energy manifold of the leads, which underlie the transport properties of molecular junctions. We explore several tight-binding junction models and predict the appearance of coupling bands that depend on the dimensionality and shape of the leads. We believe that a similar analysis may contribute to the understanding of many phenomena characteristic to the fields of nano- and molecular-electronics.
4:42PM W27.00012 ‘Soft’ amplifier circuits based on field-effect ionic transistors, NIELS BOON, MONICA OLVERA DE LA CRUZ. Northwestern University — Soft materials can be used as building blocks of electronic devices with extraordinary properties. We demonstrate that an ionic analogue of the semiconductor field-effect transistor (FET) could be used for voltage and current amplifiers. Our theoretical model incorporates readily-available soft materials, such as conductive porous membranes and polymer electrolytes to represent a current-gating device that can be integrated in electronic circuits. By means of Nernst-Planck numerical simulations as well as an analytical approach towards expressions that describe steady-state currents, we find that the behavior in response to various input voltages can be categorized into ohmic, sub-threshold, and active modes. This is fully analogous to what is known for semiconductor FETs. Pivotal FET properties such as threshold voltage and transconductance must be related to half-cell redox potentials as well as polyelectrolyte and gate material properties. We further extend the analogy with semiconductor FETs through numerical simulations of elementary amplifier circuits in which we successfully substitute the semiconductor transistor by an ionic FET.

4:54PM W27.00013 Curl flux, coherence, and population landscape of molecular systems: Nonequilibrium quantum steady state, energy (charge) transport, and thermodynamics, ZHEDONG ZHANG, JIN WANG, SUNY Stony Brook — We established a theoretical framework in terms of the curl flux, population landscape, and coherence for nonequilibrium quantum systems at steady state, through exploring the energy and charge transport in molecular processes. The curl quantum flux plays the key role in determining transport properties and the system reaches equilibrium when flux vanishes. The novel curl quantum flux reflects the degree of non-equilibriumness and the time-irreversibility. We found an analytical expression for the quantum flux and its relationship to the environmental pumping (non-equilibriumness quantified by the voltage away from the equilibrium) and the quantum tunneling. Furthermore, we investigated another quantum signature, the coherence, quantitatively measured by the non-zero off diagonal element of the density matrix. Quantum flux is promoted by the coherence in the regime of small tunneling while reduced by the coherence in the regime of large tunneling, due to the non-monotonic relationship between the coherence and tunneling. For the systems coupled to bosonic (photonic and phononic) reservoirs the flux is significantly promoted at large voltage while for fermionic (electronic) reservoirs the flux reaches a saturation after a significant enhancement at large voltage.

5:06PM W27.00014 EPR Studies of orthorhombic Jahn-Teller effect in single crystal of ferroelectric Cu(II):Cd$_2$(NH$_4$)$_2$(SO$_4$)$_3$, YERIMA BENSON, Department of Physics, Covenant University, Ota, Ogun State, Nigeria, DILIP DE, Department of Physics, Modbi Adamawa University of Technology, Yola, Nigeria — In this paper we report the first EPR observation and theoretical explanation of orthorhombic Jahn-Teller effect in Cu(II) doped single crystal of ferroelectric cadmium ammonium sulphate: Cu(II):Cd$_2$(NH$_4$)$_2$(SO$_4$)$_3$. The isotropic EPR spectra of the $^{127}$I$^+$ ion (in regular octahedral symmetry) at higher temperature becomes anisotropic at low temperature with clear manifestation of orthorhombic g and hyperfine tensors at 15 K. The static Jahn-Teller(JT) effect can only be explained theoretically by assuming the three JT potential wells energetically inequivalent, unlike the potential wells in most of the Cu(II) doped crystalline materials where JT effect manifests. The measured splitting of the JT potential wells in this ferroelectric crystal fall in the sub millimeter wave region pointing to possible application of the material.

5:18PM W27.00015 Probing molecular dynamics at the nanoscale via an individual paramagnetic center, TOBIAS STAUDACHER, 3rd Institute of Physics and Research Center SCOPE, University Stuttgart, NICOLE RAATZ, SEBASTIEN PÉZZAGNA, JAN MEIJER, Institute for experimental physics II, University of Leipzig, FRIEDMANN REINHARD, Walter Schottky Institut, Technical University Munich, CARLOS MERILES, CUNY-City College of New York, JOERG WRACHTRUP, 3rd Institute of Physics and Research Center SCOPE, University Stuttgart — We use shallow NVs to probe mesoscopic proton ensembles from different substances deposited on the diamond surface. We resort to a form of correlation spectroscopy to construct the equivalent of a nuclear “free-induction-decay” (FID), which, unlike the NMR counterpart, does not require nuclear spin pre-polarization. This pseudo FID has a limit decay time governed by the NV spin-lattice relaxation time $T_1$ (typically longer than the NV coherence lifetime $T_2$), which allows us to attain spectral resolution superior to that possible with standard magnetometry techniques. Upon applying this scheme to solid- and liquid-state substances we find substantial differences in the correlation signal lifetime, which we associate with the presumably different molecular dynamics.

Friday, March 6, 2015 8:00AM - 11:00AM — Session Y26 DCP: Surfaces, Interfaces, Colloids and Catalysis I 204A - Jinglie Ping, University of Pennsylvania

8:00AM W27.00001 CO Adsorption on Pd(111) at 0.5ML: a First Principles Study, ZAHR HAOSHMAND GHAREHBAGH, DUY LE, TALAT S. RAHMAN, University of Central Florida, Department of Physics, Orlando FL 32816-2385, USA — While the adlayer structures formed by CO molecules on Pd(111) are well-understood both experimentally and theoretically, for low and high coverages, it is still a matter of discussion for medium coverage (0.5ML). At this medium coverage, it is well-known that the c(4 × 2) phase is formed but the adsorption sites of CO molecules have been reported differently by various studies: at the bridge sites, at the hollow sites, or at both bridge and hollow sites. Using density functional theory calculations we studied the overlayer structure of CO at 0.5ML on Pd(111) with all possible highly symmetric adsorption sites leading to c(4 × 2) structures. We will show that, on the same surface, CO molecules adsorb either only on bridge or hollow sites and that there is no overlayer structure in which CO binds at both bridge and hollow sites. By means of ab initio thermodynamics simulation, we will also report the conditions (temperature, pressure) in which each overlayer structure exists.

1Work support in part by NSF Grant CHE-1310327

8:12AM W26.00002 Theoretical investigation of oxygen adsorption on Pu-Ga alloy (111) surface, SARAH C. HERNANDEZ, University of Texas at Arlington, THOMAS J. VENHAUS, Los Alamos National Laboratory, MUHAMMAD N. HUDA, University of Texas at Arlington — All electron density functional theory was implemented to study the adsorption of atomic oxygen on a 3.125 at. % Ga stabilized f-Pu (111) surface. A 4-layer periodic slab, with 8 atoms per layer, was used to model the surface, and the location of the Ga within the surface was considered. High symmetry on-surface and interstitials adsorption sites were explored, which also included the adatom placed in different local environments (i.e. oxygen coordinated with/without a Ga atom). Full relaxation of the atomic positions of the Pu-Ga slab and O atom were employed. The inclusion of spin-orbit-coupling was preformed for the lowest energetic structure. The goal of these calculations was to the probe the effects that Ga may have within the surface when O is adsorbed. We found that oxygen binds strongly at an on-surface site with chemisorption energy of -5.06 eV and prefers to be three-fold coordinated in a Pd-like environment. Ga participating in chemical bonding with the O adatom chemisorptions energies were unfavorable. Interstitials sites were also unfavorable, which implies that diffusion of O into the subsurface is an activated process. Furthermore, a geometric analysis of the slab after O adsorption showed local oxygen-induced distortions, which will be discussed in detail.

1We gratefully acknowledge support by the US Department of Energy through the Los Alamos National Laboratory LDRD Program.
8:24AM Y26.00003 Stabilization of CH$_2$ on Ru(0001) by hydrogen co-adsorption. SERGEY V. LEVCHENKO, XUNHUA ZHAO, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG, Berlin, FRITZ-HABER-INSTITUT DER MPG, BERLIN TEAM — Based on indirect experimental evidence, CH$_2$ was proposed as a building block for hydrocarbon chain growth on the Ru(0001) surface during the Fischer-Tropsch process. However, previous calculations agreed that CH$_2$ is not stable on Ru(0001) at the reaction conditions, and should quickly convert into CH. Employing density-functional theory, we show that this disagreement can be reconciled if coadsorbed hydrogen is present on the surface. The atomic structure of various CH$_2$+H$_2$ phases is obtained with genetic algorithm. CH$_2$ dissociation barriers are calculated using the string method. We further demonstrate, by calculating the surface phase diagram for one-carbon species on Ru(0001) as a function of H$_2$ chemical potential, that the stabilization of CH$_2$ by co-adsorbed hydrogen requires non-equilibrium conditions. The calculated barrier for the CH$_2$ dissociation in the presence of hydrogen is significantly increased, and is close to the one recently measured by vibrational sum-frequency generation spectroscopy [1]. Our results also explain why CH$_2$ was not observed when C or CH are hydrogenated on Ru(0001), although it is observed after methane decomposition.


8:36AM Y26.00004 ABSTRACT WITHDRAWN —

8:48AM Y26.00005 ABSTRACT WITHDRAWN —

9:00AM Y26.00006 Structure and Electron Localization of Reduced Ceria Surfaces. RENAT SABIRIANOV, Univ of Nebraska - Omaha, KHADLOUN TARAWNEH, Princess Sumaya University for Technology, NABIL AL-AQTASH, PRINCESS SUMAYA UNIVERSITY FOR TECHNOLOGY - We present the results of an adsorption study on ZIF-8 through application of the “point B” method. The isosteric heat of adsorption of Xe on ZIF-8 was determined from the isotherm data. We will also discuss in detail the potential energy surface and the associated barrier for a surface vacancy transition on the (100) surface. The extra adsorption step is a consequence of the “gate opening” transition that occurs due to the structural transition present in the isotherm data as a quasi-vertical substep. We used this feature to explore the temperature dependence of the structural transition. We have found that the transition occurs below the saturated vapor pressure only for temperatures below 93.93 K. The adsorption measurements.

9:12AM Y26.00007 ABSTRACT WITHDRAWN —

9:24AM Y26.00008 Towards Controlling the Structural Evolution and Kinetic Properties of Monolayer (Hyd)oxide-Metal Interfaces. ZHENHUA ZENG, JOSEPH KUBAL, JEFF GREELEY, Purdue University — Ultrathin (hydr)oxide films grown on transition metal surfaces have widespread applications in processes related to electrocatalysis, photocatalysis, coating and corrosion inhibition, and heterogeneous catalysis, among others. These hybrid systems with novel properties are often prepared and characterized under very specific conditions, such as ultra-high vacuum. When subsequently used in various applications, however, significant structural evolution, which depends strongly on the reaction conditions in-situ, is expected and has been widely observed. Nevertheless, the atomic-level details of these structural changes are generally unknown, particularly in the case of electrocatalytic environments. In order to identify structure-property relationships and, ultimately, predict new materials with improved performance, the development of such understanding is essential. In the present study, on the basis of detailed density functional theory calculations, and using Ni (hydr)oxide films on Pt(111) and Au(111) electrodes as model systems, we describe a detailed structural analysis of film growth and electrocatalytic analysis of hydrogen evolution at three-phase boundaries under alkaline electrochemical conditions.

9:36AM Y26.00009 Study of Xenon Adsorption on Zeolitic Imidazolate Framework – 8 (ZIF-8). DONUKA GALLABA, BRICE RUSSELL, ALDO MIGONE, Department of Physics, Southern Illinois University, Carbondale IL 62901 — We have investigated Xe adsorption on ZIF-8 for temperatures in the range between 138 and 158 K. ZIF-8 is known to undergo a structural (“gate-opening”) transition as a function of increasing pressure (or loading) for a number of adsorbates (N$_2$, Ar, CO, O$_2$). For isotherms measured at sufficiently low temperatures, the gate-opening transition manifests itself as an additional (higher pressure) substep in the adsorption isotherm data. Xe isotherms measured above 145 K do not show the additional isotherm feature, while those measured below do. The extra adsorption step is a consequence of the “gate opening” transition that occurs due to the re-orientation of the organic linkers in the ZIF-8. This re-orientation is an open challenge in automotive emission control industry. Our method can expand the range of catalytically active elements to those which are not conventionally considered for catalysis and which are more economical, e.g., Cr (for NO$_x$ direct decomposition and CO oxidation) instead of conventional precious metal catalysts.

1Primary support from Toyota Motor Engineering and Manufacturing, North America, Inc.

10:00AM Y26.00011 Ferroelectric based catalysis: Switchable surface chemistry, ARVIN KAKEHANI, SOHRAB ISMAIL-BEI, Yale University — We describe a new class of catalysts that uses an epitaxial monolayer of a transition metal oxide on a ferroelectric substrate. The ferroelectric polarization switches the surface chemistry between strongly adsorptive and strongly desorptive regimes, circumventing difficulties encountered on non-switchable catalytic surfaces where the Sabatier principle dictates a moderate surface-molecule interaction strength. This method is general and can, in principle, be applied to many reactions, and for each case the choice of the transition oxide monolayer can be optimized. Here, as a specific example, we show how simultaneous NO$_2$ direct decomposition (into N$_2$ and O$_2$) and CO oxidation can be achieved efficiently on CrO$_2$ terminated Pt/TiO$_2$, while circumventing oxygen (and sulfur) poisoning issues. One should note that NO$_2$ direct decomposition has been an open challenge in automotive emission control industry. Our method can expand the range of catalytically active elements to those which are not conventionally considered for catalysis and which are more economical, e.g., Cr (for NO$_x$ direct decomposition and CO oxidation) instead of canonical precious metal catalysts.
10:12AM Y26.00012 Acceleration of non-PGM Electrocatyst Design For Fuel Cells Through Site Specific XPS Predictions from First-principles Simulations, BORIS KIEFER, New Mexico State University, SADIA KABIR, KATERYNA ARTYUSHKHOVA, PLAMEN ATANASSOV, University of New Mexico — One of the most pressing problems in the 21st century is the provision of environmentally consistent energy technologies especially for space limited non-stationary applications. Fuel Cells are promising candidates for addressing and mastering this challenge. Alternative materials to platinum catalysts which continue to attract significant attention are non-PGM FeNx/C based materials. The understanding of the geometry and chemistry of catalytically active defect moieties is a prerequisite for the rational improvement and design of non-PGM electrocatalysts. XPS, a widely used surface analytical technique, generally shows broad N1s peaks with abundance weighted contributions from every defect motif. Due to the lack of appropriate reference materials it is currently impossible to de-convolute the N1s peak into defect specific contributions. In order to remove this limitation we have performed density-functional-theory (DFT) based calculations for a variety of in-plane FeNx (x=2-4) defects. Using DFT we predict, for the first time, defect chemistry and geometry induced N1s binding energy shifts in these materials. In combination with our XPS experiments and catalyst performance we find that higher FeNx defect abundance correlates with improved catalyst performance.

10:24AM Y26.00013 Electrolytes near structured dielectric interfaces, HUANXIN WU, YUFEI JING, Northwestern University, FRANCISCO SOLIS, Arizona State University, MONICA OLVERA DE LA CRUZ, ERIK LUIJSEN, Northwestern University — The ion distribution in an electrolyte near a dielectric interface has important consequences for numerous applications. To date, most studies have focused on planar interfaces, where, e.g., simulations can take advantage of the image-charge method. However, for surfaces that display structure on the nanoscale, dielectric effects may be significantly different. Here, we investigate such interfaces via a combination of computer simulations and Poisson–Boltzmann theory. We demonstrate how, even for systems with piecewise uniform dielectric constant, surface structure affects the induced polarization charge as well as the ion distribution near the interface, in particular for asymmetric salts. We explore the role of ion concentration, dielectric mismatch and characteristic length scale of the surface structure.

10:36AM Y26.00014 Charge dependent condensation of macro-ions at air-water interfaces, MRINAL BERA, MARK ANTONIO, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL-60439, USA — Ordering of ions at and near air-water interfaces is a century old problem for researchers and has implications on a host of physical, chemical and biological processes. The dynamic nature of water surface and the surface fluctuations created by thermally excited capillary waves have always limited measurement of near surface ionic-distributions. We demonstrate that this limitation can be overcome by using macro-ions of sizes larger than the capillary wave roughness ~3Å. Our attempts to measure distributions of inorganic macro-ions in the form of Keggin heteropolyanions (HPAs) of sizes ~10Å have unraveled novel charge-dependent condensation of macro-ions beneath air-water interfaces. Our results demonstrate that HPAs with ~3 charges condense readily beneath air-water interfaces. This is in contrast to the absence of surface preference for HPAs with ~4 charges. The similarity of HPA-HPA separations near air-water interfaces and in bulk crystal structures suggests the presence of the planar Zundel ions (H3O+2), which interact with HPAs and the water surface to facilitate the charge dependent condensation beneath the air-water interfaces.

Friday, March 6, 2015 11:15AM - 1:51PM – Session Z26 DCP: Surfaces, Interfaces, Colloids and Catalysis II


11:15AM Z26.00002 Friction boosted by spontaneous epitaxial rotations, DAVIDE MANDELLI, SISSA, ANDREA VANOSSI, CNR-IOM Democritos and SISSA, NICOLA MAFINI, Universit degli studi di Milano, SISSA and CNR-IOM Democritos, ERIJO TOSATTI, ICTP, SISSA and CNR-IOM Democritos — It is well known in surface science that incommensurate adsorbed monolayers undergo a spontaneous, energy-lowering epitaxial rotation from an aligned to misaligned relative to a periodic substrate. We show first of all that a model 2D colloidal monolayer in an optical lattice, of recent importance as a frictional model, also develops in full equilibrium a small rotation angle, easy to detect in the Moire pattern. The colloidal monolayer misalignment is then shown by extensive sliding simulations to increase the dynamic friction by a considerable factor over the aligned case. More generally, this example suggests that spontaneous rotations are rather ubiquitous and should not be ignored in all tribological phenomena between mismatched lattices.

1This work was mainly supported by the ERC Advanced Grant No. 320796-MODPHYSFRICT, and partly by SINERGIA contract CRSII2 136287, by PRIN/COFIN Contract 2010LKKJBX 004, by COST Action MP1303.
11:39AM Z26.00003 Surface Electric Potential of Macroions between the Limits of Small Ions and Charged Nanocolloids, BENJIN JING, Y. ELAINE ZHU. Department of Chemical and Biomolecular Engineering, University of Notre Dame—The surface electric potential of macroions in the size of 1–10 nm in aqueous solutions is critical to understand the supramolecular assembly involving biomacromolecules, charged nanoparticles and nanoclusters and their resulting material properties. However, the electric potential of these macroions could not be accurately determined because their sizes fall in between the limits of small ions and plain charged nanocolloids, while solving the non-linear Poisson-Boltzmann equation remains a grand challenge to date. In this work, we investigate polydialyolic osmesosiloxane (POSS) with 8 amine terminal groups as a model macroion. With the help of a recently developed fluorescence correlation spectroscopy (FCS) technique, fluorescence correlation spectroscopy (FCS) and excitation power (PCHI) to quantitatively measure the local proton concentration, which is the local co-ion concentration in vicinity of POSS with 1.5 nm in diameter. By changing the ionic strength of aqueous solution and the distance between pH-sensitive fluorescence probe and POSS, we quantitatively determine the proton concentration gradient. The distance dependent local pH can be simply analyzed to obtain the surface electric potential of the POSS macroion without the necessity to solve the non-linear Poisson-Boltzmann equation.

11:51AM Z26.00004 X-ray absorption spectroscopy of lithium sulfur battery reaction intermediates, KEVIN WUJCIK, Dept. of Chemical and Biomolecular Engineering, University of California, Berkeley, TOD PASCAL, DAVID PRENDERGAST. Molecular Foundry, Lawrence Berkeley National Laboratory, NITASH BALSARA, Dept. of Chemical and Biomolecular Engineering, University of California, Berkeley—Lithium sulfur batteries have a theoretical energy density nearly five times greater than current lithium ion battery standards, but questions remain regarding the reaction pathways through which soluble lithium polysulfide (Li2Sx, “x” ranging from 2 to 8) reaction intermediates are formed. Complicating spectroelectrochemical approaches to elucidate redox pathways is the challenge of obtaining spectral standards for individual Li2Sx species. Lithium polysulfides cannot be isolated as individual component and exist only in solution as a distribution of different Li2Sx molecules formed via disproportionation reactions (e.g. 2Li2S4 goes to Li2S3 + Li2S5). X-ray absorption spectroscopy (XAS) at the sulfur K-edge has recently been employed as a technique to study Li-S chemistry. We have recently obtained XAS standards for individual Li2Sx species via first principles DFT simulations and the excited electron and core hole approach. Here, experimental sulfur K-edge XAS of Li2Sx species dissolved in poly(ethylene oxide) are compared to spectra obtained from analogous theoretical calculations. The impact that polysulfide solution concentration and the presence of other lithium salts (e.g. LiNO3) have on X-ray spectra of Li2Sx species is discussed.

12:03PM Z26.00005 Depth profile of halide anions under highly charged biological membrane, WOONGMO SUNG, Department of Physics, Sogang University, WENJIE WANG, Ames National Lab., JONGGWAN LEE, Department of Physics, Sogang University, DAVID VAKVIN, Ames National Lab., DOSEOK KIM, Department of Physics, Sogang University—Halide ion (Cl− and I−) distribution under a cationic Langmuir monolayer consisting of 1,2-dipalmitoyl-3 trimethylammonium-propane (DPTAP) molecules was investigated by vibrational sum-frequency generation (VSFG) and X-ray spectroscopy. From VSFG spectra, it was observed that large halide anions (I−) screen surface charge more efficiently so that interfacial water alignment becomes more randomized. On the other hand, number density of ions directly measured by X-ray fluorescence spectroscopy at grazing incidence angle reveals that the ion densities within 6 ~ 8 nm are the same for both I− and Cl−. Since the observed ion densities in both cases are almost equal to the charge density of the DPTAP monolayer, we propose that larger halide anions are attracted closer to the surface making direct binding with the charged headgroups of the molecules in the monolayer, accomplishing charge neutrality in short distance. This direct adsorption of anions also disturbs the monolayer structure both in terms of the conformation of alkyl chains and the vertical configuration of the monolayer, with iodine having the stronger effect. Our study shows that the length scale that ions neutralize a charged interface varies significantly and specifically even between monovalent ions.

12:15PM Z26.00006 Electrochemical Growth of Ag Junctions and Diffusion Limited Aggregate (DLA) Fractal Simulation, ZAK OLSON, SAM TUPPAN, WOO-JOONG KIM, Seattle Univ, SEATTLE UNIVERSITY TEAM—We attempt construction of a single atom connection between two copper wires. By applying a DC voltage across the wires when immersed in a silver nitrate solution, we deposit silver until a junction is formed. The deposited silver forms a fractal structure that can be simulated with a diffusion limited aggregation model.

12:27PM Z26.00007 Single crystal growth and properties of two layered oxytellurides1, TIGLET BESARA, DANIEL RAMIREZ, THEO SIEGSTR, National High Magnetic Field Laboratory/Florida State University, JIFENG SUN, JEFFREY WHALEN, TAKAHISA TAKUMOTO, STEPHEN MCGILL, RYAN STILLWELL, STANLEY TOZER, National High Magnetic Field Laboratory, DAVID SINGH, Oak Ridge National Laboratory—We report on the synthesis, structure, and physical properties of two layered oxytellurides: Ba2Yb2O5Te and Ba2Te. Both compound were grown in single crystalline form using a molten metal flux, and crystallize in a tetragonal space group: P4/nmm for Ba2Yb2O5Te and P4/mmm for Ba2Te. Ba2Yb2O5Te consists of Ba2Yb2O5 perovskite double layers separated by a CsCl-type BaTe slab, while Ba2TeO consists of an inverse PbO-type BaO layer separated by an NaCl-type BaTe slab. Ba2TeO displays short range 2D magnetic ordering below 4 K, and a sharp optical absorption feature at 1.27 eV consistent with a F2g/2 → F2g/2 transition of Yb3+. For Ba2TeO, optical measurements display a sharp increase in absorbance, a manifest of a band edge. DOS corroborates the band gap, at 2.93 eV, indicating semiconducting behavior.

1DOE DE-SC0008832 (TB, DR, JS, TS), NSF DMR-1157490 (NHMFL)

12:39PM Z26.00008 ABSTRACT WITHDRAWN

12:51PM Z26.00009 Superhydrophilic - Superhydrophobic Transition in Vertically Aligned Titania Nanotubes, OOMMAN VARGHESE, RAM NEUPANE, MAGGIE PAULOSE, University of Houston—Both hydrophilic (wetting) and hydrophobic (non-wetting) surfaces find applications in a variety of technological areas. For example, hydrophilic surfaces are used in microfluidic devices to provide antifogging and antifouling functions whereas hydrophobic coatings are used in clothes to attribute stain resistance. While in superhydrophilic surfaces the contact angle that water droplets make with the surface is nearly zero, the surfaces that make contact angles greater than about 120° are considered superhydrophobic. Oxide ceramics generally exhibit hydrophilic behavior. Surface texturing or organic coatings are often used to make the surface hydrophobic or superhydrophobic. We prepared highly ordered titania nanotube arrays on titanium foils using anodic oxidation that showed superhydrophilic behavior upon fabrication. We noticed a strong correlation between fabrication conditions and the wettability. We have become successful in converting such a superhydrophilic nanostructure into superhydrophobic without modifying the surface with organic molecules or texturing. Contact angles in excess of 145° have been obtained. We will present these results and discuss the physiochemical processes that decide wetting properties of oxide nanostructures.
1:03PM Z26.00010 Size-dependent melting of single and stacked silver alkanethiolate layers: experiment and phenomenological model

1Supported by NSF-DMR-1409953 and NSF-DMR-1006385.


1:27PM Z26.00012 Effects of Surface Treatments on Nylon 6,6 via Non-thermal Atmospheric Plasma for Thermoplastic Adhesives

1:39PM Z26.00013 Theoretical evidence for unexpected O-rich phases at corners of MgO surfaces

2Supported by NSF-DMR-1409953 and NSF-DMR-1006385.