APS March Meeting 2011
Dallas, Texas
http://www.aps.org/meetings/march/index.cfm
this concept by extending our measurements to a small molecule (HCl).

by ionizing a second electron via a laser-induced tunneling gate. Since our tunneling gates are optically controlled, the second gate can be opened at any angle

scheme we directly observe the periodic charge redistribution in the valence shell of singly charged noble gas atoms that was predicted by Santra and coworkers

electrons in rare gas atoms with intense laser pulses. We find a strong spatial propensity in the sequential double tunnel ionization regime. For instantaneous

hand, laser tunnel ionization has been known to access multiple electronic states. Recent evidence, corroborating the notion that tunneling can prepare these

multiple ionization in the tunneling limit proceeds sequentially - each successive ionization stage loosing memory of previous electronic correlations. On the other

using multiphoton ionization remain an exception. One reason may be that recollision aside, studies in rare gas atoms have largely suggested that multiphoton

streaking allows a direct look at electronic correlations and rearrangement processes. Photoemissions from solid surfaces reveal an attosecond time delay between conduction electrons and core electrons and provide time-resolved information on
electron transport, plasmon excitation, and dissipation. Attosecond pulses allow not only to probe but also to control and manipulate electronic dynamics which we will illustrate for two-electron emission from atoms and molecular break-up.

Which novel information can be extracted from time-resolved spectroscopies that cannot be gained from precision experiments in the spectral domain? In this talk, these issues will be addressed with the help of a few examples. Attosecond streaking allows a direct look at electronic correlations and rearrangement processes.

In collaboration with J. Feist, S. Graefe, C. Lemell, S. Nagele, R. Pazyurek, F. Krausz, V. Yakovlev, L. Collins, and B. Schneider, work supported by

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8:36AM A38.00002 Simulation of Transmission Electron Microscopy in Time Domain1, JIA-AN YAN, Department of Physics, Georgia Southern University, J. DRISCOLL, KALMAN VARGA, S.T. PANTELIDES, Department of Physics, Vanderbilt University — Based on the time-dependent Schrodinger equation, a new method of simulating transmission electron microscope (TEM) images by directly propagating an electron wave packet in real time and real space is presented. Compared to other widely used methods, the new technique yields an accurate description of the electron scattering in solid thin films for both low and the high-energy electrons. We demonstrate the method by simulating TEM images for silicon crystalline films and low-energy-electron diffraction (LEED) images of Si surfaces and graphene. The time-dependent simulations described here could be useful for studying ultrafast electron dynamics in solids.

8:48AM A38.00003 Ultrafast imaging of nanoclusters with intense x-ray laser pulses, CHRISTOPH BOSTEDT, Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA 94025 — Ultrafast x-ray scattering opens the door for unprecedented insight into the structure and dynamics of matter with atomic resolution. Any sample in an x-ray laser flash, however, will be converted into a highly excited, non-equilibrium plasma during the pulse. The scatter signal itself is sensitive to changes in the electronic structure of the sample leading to distortions of the signal intensities with respect to the ground state configuration. On the other hand, the information about the electronic structure carried by the scatter signal can be exploited to gain insight into transient electronic states on the femtosecond time scale of the x-ray pulse. We have performed single shot — single particle scattering experiments on clusters to investigate the interplay between excitation and scattering in nanoscale objects with x-ray pulses from both, the FLASH and LCLS free electron lasers. Atomic clusters have been proven ideal to investigate the interaction between intense light pulses and matter in a wide spectral regime from the infrared to x-rays due to their finite size and simple electronic structure. Spectroscopy data recorded in coincidence with the scattering patterns revealed strong power-density dependent ionization dynamics of the clusters. The scattering patterns themselves provide information on the 2-dim as well as 3-dim structure of clusters and of cluster ensembles. Modeling the scattering patterns indicates that the optical constants of the clusters, which are inherently coupled to its electronic structure and thus charge states, change during the femtosecond pulse. Time resolved experiments with pump -- probe techniques have started which allow following the evolution of cluster ionization up to several ps.

9:24AM A38.00004 Thermal transport in thin films measured by time-resolved grazing-incidence x-ray diffraction1, D.A. WALKO, Advanced Photon Source, Argonne National Laboratory, Y.-M. SHEU, University of Michigan, M. TRIGO, D.A. REIS, SLAC National Accelerator Laboratory and Stanford University — Depth- and time-resolved x-ray diffraction were used to study thermal transport across single crystal Bi films grown on sapphire, to determine the thermal conductivity of the films and the Kapitza conductance of the interfaces. Ultrafast Ti:sapphire laser pulses heated the films; x-ray diffraction measured the subsequent lattice expansion. Use of grazing incidence geometry provided depth sensitivity with the x-ray angle of incidence near the critical angle, in contrast to symmetric Bragg geometries which only measure the average temperature of the film. The shift of the film’s Bragg peak position with time was used to determine the film temperature, averaged over an x-ray penetration depth that could be selected by choice of the angle of incidence. Films that were thick compared to the laser penetration depth exhibited a large temperature gradient at early times; in this case, measurements with the incident angle below and above the critical angle were more sensitive to the film conductivity and Kapitza conductance, respectively. For thinner films, however, cooling was dominated by the Kapitza conductance on all accessible time scales.

1 This work was supported in part by DOE grant DE-FG02-09ER46554.

9:48AM A38.00003 Ultrafast imaging of nanoclusters with intense x-ray laser pulses, CHRISTOPH BOSTEDT, Linac Coherent Light Source, SLAC National Accelerator Laboratory, Menlo Park, CA 94025 — Ultrafast x-ray scattering opens the door for unprecedented insight into the structure and dynamics of matter with atomic resolution. Any sample in an x-ray laser flash, however, will be converted into a highly excited, non-equilibrium plasma during the pulse. The scatter signal itself is sensitive to changes in the electronic structure of the sample leading to distortions of the signal intensities with respect to the ground state configuration. On the other hand, the information about the electronic structure carried by the scatter signal can be exploited to gain insight into transient electronic states on the femtosecond time scale of the x-ray pulse. We have performed single shot — single particle scattering experiments on clusters to investigate the interplay between excitation and scattering in nanoscale objects with x-ray pulses from both, the FLASH and LCLS free electron lasers. Atomic clusters have been proven ideal to investigate the interaction between intense light pulses and matter in a wide spectral regime from the infrared to x-rays due to their finite size and simple electronic structure. Spectroscopy data recorded in coincidence with the scattering patterns revealed strong power-density dependent ionization dynamics of the clusters. The scattering patterns themselves provide information on the 2-dim as well as 3-dim structure of clusters and of cluster ensembles. Modeling the scattering patterns indicates that the optical constants of the clusters, which are inherently coupled to its electronic structure and thus charge states, change during the femtosecond pulse. Time resolved experiments with pump – probe techniques have started which allow following the evolution of cluster ionization up to several ps.

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9:36AM A38.00005 Probing electron correlations by laser-induced tunnel ionization, ANDRÉ STAUDTE, National Research Council of Canada — Pairwise electron correlation has been intensely studied by projecting two electrons to the continuum simultaneously via a well controlled perturbation, e.g. a collision with an energetic electron, a fast ion or a single XUV photon. Electron correlation studies using multiphoton ionization remain an exception. One reason may be that recollision aside, studies in rare gas atoms have largely suggested that multiphoton multiple ionization in the tunneling limit proceeds sequentially - each successive ionization stage loosing memory of previous electronic correlations. On the other hand, laser tunnel ionization has been known to access multiple electronic states. Recent evidence, corroborating the notion that tunneling can prepare these correlated multielectron states in a coherent superposition, suggests that sequential multiple ionization may provide insight into dynamical correlations in the parent ion. Here, we demonstrate how dynamics of electron correlation can be investigated using laser-induced tunnel ionization by interrogating valence shell electrons in rare gas atoms with intense laser pulses. We find a strong spatial propensity in the sequential double tunnel ionization regime. For instantaneous emission, we find that the two electrons are preferentially emitted in perpendicular directions. Applying laser scanning tunneling microscopy in a pump-probe scheme we directly observe the periodic charge redistribution in the valence shell of singly charged noble gas atoms that was predicted by Santra and coworkers and recently inferred in an attosecond pump-probe experiment using XUV probe pulses. In contrast to single photon ionization, tunneling is highly directional. Here, we exploit that property of tunnel ionization to remove an electron from a rare gas atom along a specific spatial direction. We then probe the correlation by ionizing a second electron via a laser-induced tunneling gate. Since our tunneling gates are optically controlled, the second gate can be opened at any angle and at any time relative to the first. Hence, not only spatial but also temporal variations of the correlation can be probed. We demonstrate the generality of this concept by extending our measurements to a small molecule (HCl).
10:12 AM A38.00006 2D Fano-resonances in momentum space, WAI-LUN CHAN, JOHN TRITSCH, ANDREI DOLOCAN, XIAOYANG ZHU, University of Texas at Austin — Using the model system of molecular quantum wells and image potential states at the Cu$_2$/Au(111) interface and the experimental technique of time- and angle-resolved two photon photoemission spectroscopy, we probe many body interaction in coupled two-dimensional (2D) systems. Transiently populated 2D bands with different effective masses are found to intersect with each other in the reciprocal space. At the points of intersection, we observe strong modulations in the photoemission intensity as a function of parallel momentum vector. The intensity modulation in the reciprocal space can be explained by the well-known Fano resonances – the interference between different quantum mechanical pathways in optical excitation. The experimental results agree semi-quantitatively with simulation based on optical Bloch’s equations. Differing from conventional Fano resonances in energy space, our observation establishes the existence of 2D Fano resonance in momentum space.

Monday, March 21, 2011 11:15AM - 2:15PM
Session B38 DCP: Earle K. Plyler Prize Session I: Spectroscopy A130/131

11:15 AM B38.00001 Earle K. Plyler Prize for Molecular Spectroscopy Talk: Coherent Ultra-fast Multidimensional Spectroscopy of Molecules; From NMR to X-rays, SHAUL MUKAMEL, University of California, Irvine — Multidimensional spectroscopic techniques which originated with NMR in the 1970s have been extended over the past 15 years to the optical regime. NMR spectroscopists have developed methods for the design of pulse sequences that resolve otherwise congested spectra, enhance selected spectral features and reveal desired dynamical events. The major experimental and computational advances required for extending these ideas to study electronic and vibrational motions on the femtosecond timescale will be surveyed. The response of complex molecules and semiconductor nanostructures to sequences of optical pulses provides snapshots of their structure and dynamical processes. Two-dimensional correlation plots of the signals show characteristic cross-peak patterns which carry information about hydrogen bonding, secondary structure fluctuations of proteins and amyloid fibrils, and coherent and incoherent energy and charge transfer in photosynthetic complexes. Double quantum coherence signals that are induced by correlations among electrons or excitons allow the visualization of correlated wavefunctions. Future extensions to the attosecond regime using xray pulses will be discussed. Since core excitations are highly localized at selected atoms, such signals can monitor the motions of valence electron wavepackets in real space with atomic spatial resolution. Common principles underlying coherent spectroscopy techniques for spins, valence electrons, and core electronic excitations, spanning frequencies from radio waves, infrared, ultraviolet all the way to hard X-rays will be discussed.

12:03 PM B38.00003 The Solvated Electron in Acetonitrile, STEPHANIE DOAN, ARTHUR BRAGG, BENJAMIN SCHWARTZ, Dept. Chem. & Biochem., UCLA — The nature of solvated electrons in liquid acetonitrile is of great interest as it appears that excess electrons in this solvent are stabilized in two forms, a dipole-bound (DB) electron (i.e. a typical solvated electron) and a valence-bound electron (VB) electron (e.g. a solvated CH3CN dimer anion). Previous work has suggested that these two species are in equilibrium and can interconvert. We performed 3-pulse transient hole-burning experiments aimed at better understanding the nature of the VB and DB electrons. We found that photoexcitation of VB electrons produces an increased population of DB electrons, but that exciting DB electrons does not produce VB electrons. This suggests a significant asymmetry in the solvent motions that accompany photoexcitation of the electron: it is easier for a DB electron to relax back into the solvent location from which it came than for the local solvent structure to change enough to create a VB electron, whereas excitation of a VB electron disrupts the local solvent structure to the point where the excited electron can relax into the bulk solvent rather than back to the molecules on which it initially resided.

12:15 PM B38.00004 Dynamics of electron solvation in I$^-$(CH$_3$OH)$_n$ clusters (4 ≤ n ≤ 11), RYAN YOUNG, University of California, Berkeley — The dynamics of electron solvation following excitation of the charge-transfer-to-solvent (CTTS) precursor state in iodide-doped methyl clusters, I$^-$(CH$_3$OH)$_{n=4-11}$ are studied with time-resolved photoelectron imaging (TRPEI). This excitation produces a 1$^-$(CH$_3$OH)$_n$ cluster that is unsatellite with respect to electron autodetachment, and whose autodetachment lifetime increases monotonically from ~800 fs to 85 ps as n increases from 4-11. Vertical detachment energy (VDE) and width of the excited state feature in the photoelectron spectrum show complex time dependence suggesting two competing mechanisms of the detachment. The VDE decreases over the first 200 ps, then rises exponentially to a minimum with a ~1 ps time constant, decreasing by as much as 180 meV with timescales from 4-10 ps. The early dynamics are assigned to electron transfer from the iodide to a localized portion of the methanol cluster, while the longer-time changes in VDE are attributed to solvent reordering, possibly in conjunction with ejection of neutral iodine from the cluster. Changes in the observed width of the spectrum largely follow those of the VDEs; the dynamics of both are attributed to the major rearrangement of the solvent cluster during relaxation. The relaxation dynamics are interpreted as a reorientation of at least one methanol molecule and the disruption and formation of the solvent network in order to accommodate the excess charge.

12:27 PM B38.00005 Vibronic Enhancement of Exciton Sizes and Energy Transport in Photosynthetic Complexes, ANDREW MORAN, JORDAN WOMICK, BRANTLEY WEST, STEPHEN MILLER, University of North Carolina — This talk investigates the impact of vibronic couplings on the electronic structures and relaxation mechanisms of two cyanobacterial light harvesting proteins, allophycocyanin (APC) and c-phycocyanin (CPC). Both APC and CPC possess three pairs of pigments (i.e., dimers), which undergo electronic relaxation on the sub-picosecond time scale. Electronic relaxation is approximately 10 times faster in APC than in CPC despite the nearly identical structures of their pigment dimers. Femtosecond laser spectroscopies conducted in conjunction with a Frenkel exciton model find that photo-induced electronic relaxation in these two proteins is understood on the same footing only when the vibronic couplings in high-frequency modes are properly taken into account. In addition to incorporating high-frequency intramolecular modes in the spectral density, we simulate electronic relaxation dynamics using a model in which the excitions delocalize in a vibronic basis. General implications of the present findings for energy transport in artificial systems (e.g., crystalline organic semiconductors) are discussed.
12:39PM B38.00006 Nonlinear Coherent Optical Imaging for Biomedicine: The Quest for Ultimate Sensitivity  
SUNNEY XIE, Harvard University — Recent advances in nonlinear coherent optical imaging, particularly stimulated Raman scattering microscopy, have allowed highly sensitive label-free imaging of living cells and organisms based on molecular spectroscopy. Using the ultimate sensitivity of nonlinear optical microscopy, the detection of a single-molecule absorption signal at room temperature has been achieved. These unprecedented sensitivities offer exciting possibilities for biomedicine.

1:15PM B38.00007 Optical Control of Conjugated Oligomer Planarity  
SERGEI TRETIAK, Los Alamos National Laboratory, JENNY CLARK, Cavendish Laboratory, University of Cambridge, GUGLIELMØ LANZANI, Lanzani — Using a sequential photo-excitation mechanism we observe the ultrafast conformational planarization of a large fluorene oligomer at ~ 60fs timescale. Novel non-adiabatic excited state molecular dynamics (NA-ESMD) framework incorporating quantum transitions has been used to rationalize this phenomenon. Simulation show the ultrafast relaxation of the photoexcited wavepacket toward the lowest electronic excited state along the torsional coordinate. The process effectively ‘locks’ the oligomer into a planar state within 100 fs, with excess energy being dissipated into other vibrational modes. Ultrafast control of molecular conformation, as demonstrated here, could have impacts for molecular conformational switches for memory or molecular electronics.

1:27PM B38.00008 Using 2D Fourier-transform spectroscopy to separate homogeneous and inhomogeneous line widths of heavy- and light-hole excitons in weakly disordered semiconductor quantum wells  
STEVEN CUNDIFF, ALAN BRISTOW, TIANHAO ZHANG, MARK SIEMENS, JILA, NIST and University of Colorado, RICHARD MIRIN, NIST-Boulder — Optical two-dimensional Fourier-transform spectroscopy is used to study the heavy- and light-hole excitonic resonances in GaAs quantum wells with weak structural disorder. Homogeneous and inhomogeneous broadening contribute differently to the two-dimensional resonance line shapes, allowing separation of homogeneous and inhomogeneous line widths. The heavy-hole exciton exhibits more inhomogeneous than homogeneous broadening, whereas the light-hole exciton shows the opposite. This situation arises from the interplay between the length scale of the disorder and the exciton Bohr radius, which affects the exciton localization and scattering. Utilizing this separation of line widths, excitation-density-dependent measurements reveal that many-body interactions alter the homogeneous dephasing, while disorder-induced dephasing is unchanged.

1:39PM B38.00009 Oxygen atom roaming and multiple dissociation pathways of NO_3  
MICHAEL GRUBB, MICHELLE WARTER, KURT JOHNSON, SIMON NORTH, Texas A&M University — The role of nitrate radical (NO_3) photolysis in atmospheric has long been known, but mysteries remain regarding the mechanism of the dissociation. In particular, the NO + O_2 channel has proven to be a challenge both theoretically and experimentally. High resolution velocity map ion imaging studies reveal that there are two distinct mechanisms to form the NO + O_2 products. Additionally, the dominant of these mechanisms appears to be the non-traditional state “roaming” mechanism recently identified in formaldehyde dissociation. The roaming mechanism involves large amplitude motion associated with a frustrated radical dissociation before roaming oxygen atom abstraction to form O_2. The identification of roaming in the NO_3 reaction may imply the widespread importance of this type of mechanism in atmospheric chemistry.

1:51PM B38.00010 First Principle Simulations of the Infrared Spectrum of Liquid Water using Hybrid Density Functionals  
CUI ZHANG, DAVIDE DONADIO, FRANCOIS GYCI, GIULIA GALLI, University of California, Davis — We report on calculations of the infrared spectrum (IR) of liquid water carried out using first principle molecular dynamics and the hybrid functional PBE0. We find results in much better agreement with experiment than those obtained using semi-local, gradient corrected exchange correlation functionals. In particular the description of the IR stretching band is greatly improved and in good accord with recent measurements. When adopting the PBE0 functional, substantial improvement is also found in the description of the structural properties of the liquid, consistent with a smaller average number of hydrogen bonds, and a reduced molecular dipole moment, as revealed by our analysis of maximally localized Wannier functions. Finally the average electronic gap of the liquid is increased by 15% with respect to PBE, when computed at the PBE0 level of theory, and is in fair agreement with experiment. Work supported by NSF/OCI-0749217.

KJUEONG KWAC, EITAN GEVA — Liquid mixtures of methanol-d and carbon tetrachloride provide attractive model systems for investigating hydrogen-bond structure and dynamics. The hydrogen-bonded methanol oligomers in these mixtures give rise to a very broad hydroxyl stretch IR band (~150 cm^-1). We have employed mixed quantum-classical molecular dynamics simulations to study the nature of hydrogen-bond structure and dynamics in this system and its spectroscopic signature. In our simulations, the hydroxyl stretch mode is treated quantum mechanically. We have found that the absorption spectrum is highly sensitive to the type of force fields used. Obtaining absorption spectra consistent with experiment required the use of corrected polarizable force fields and a dipole damping scheme. We have established mapping relationships between the electric field along the hydroxyl bond and the hydrogen-stretch frequency and bond length thereby reducing the computational cost dramatically to simulate the complex nonequilibrium dynamics underlying pump-probe spectra.


11:15AM B39.00001 Single-image molecular analysis for accelerated fluorescence imaging  
YAN MEI WANG, University of Washington — We have developed a new single-molecule fluorescence imaging analysis method, SIMA, to improve the temporal resolution of single-molecule localization and tracking studies to millisecond timescales without compromising the nanometer range spatial resolution [1,2]. In this method, the width of the fluorescence intensity profile of a static or mobile molecule, imaged using submillisecond to milliseconds exposure time, is used for localization and dynamics analysis. We apply this method to three single-molecule studies: (1) subdiffraction molecular separation measurements, (2) axial localization precision measurements, and (3) protein diffusion coefficient measurements in free solution. Applications of SIMA in flagella IFT particle analysis, localizations of UgtP (a cell division regulator protein) in live cells, and diffusion coefficient measurement of LacI in vitro and in vivo will be discussed.


11:51AM B39.00002 Super-resolution imaging of multiple fluorescent proteins with highly overlapping emission spectra in living cells. MUDALIGE GUNEWARDENE, University of Maine, FEDOR SUBACH, Albert Einstein College of Medicine, TRAVIS COUL, Yale University, GREGORY PENONCELLO, MANASA GUDHETI, University of Maine, VLADISLAV VERKHUSHA, Albert Einstein College of Medicine, SAMUEL HESS, University of Maine — Diffraction limits resolution in far field microscopy. Single molecule localization based superresolution imaging has surpassed such limitations and is rapidly gaining popularity, yet limited availability of cell-compatible photoactivatable fluorescent probes with distinct emission spectra have impeded simultaneous visualization of multiple molecular species in living cells. We introduce PAmKate, a monomeric far-red photoactivatable fluorescent protein (PAFF), which has facilitated simultaneous imaging of three PAFFs in biological samples with fluorescence photoactivation localization microscopy (FPALM). Successful probe identification was achieved by measuring the fluorescence emission intensity in two distinct spectral channels spanning approximately 100 nm of the visible spectrum. Raft- and cytoskeleton-associated proteins were simultaneously imaged in both live and fixed fibroblasts co-expressing Dendra2-hemagglutinin, PAmKate-transferrin receptor and PAmCherry-β-actin chimeras, revealing evidence for specific interactions between membrane proteins and membrane-associated actin structures.

12:03PM B39.00003 Single-image diffusion coefficient measurements of proteins in free solution. SHANNON KIAN ZAREH, MICHAEL DESANTIS, JONATHAN KESSLER, YAN MEI WANG, Washing University in St. Louis, Physics department — Diffusion coefficient measurement of biomolecules is important for particle size determination, reaction rate characterization, and molecular dynamics investigation. Here we present a simple and fast method for determining diffusion coefficient of nanometer- and sub-nanometer-sized fluorophores, such as GFP, in free solution by analyzing their single fluorescence images with sub-millisecond exposure times. In this method, the standard deviation (SD) of a diffusing molecule’s intensity profile is used to determine its diffusion coefficient. Our SD vs. diffusion coefficient expression is consistent with our simulation and experimental measurement results, rendering this sub-millisecond-long method to be an improvement of at least 100-fold in temporal resolution over current diffusion coefficient measurement methods, such as single-particle-tracking and FCS.

12:15PM B39.00004 Quantifying kinetics and dynamics of DNA repair proteins using Raster-scan Image Correlation Spectroscopy. SALIM ABDISALAAM, University of Texas at Arlington/UT Southwestern Medical Center, MILAN POUDEL, DAVID CHEN, UT Southwestern Medical Center, GEORGE ALEXANDRAKIS, University of Texas at Arlington/UT Southwestern Medical Center — DNA double strand breaks are potentially dangerous lesions as their incomplete repair may lead to carcinogenesis. In this study the confocal Raster-scan Image Correlation Spectroscopy technique is used to study kinetics and dynamics of double strand break repair proteins after γ-irradiation of mammalian cells. Diffusion and binding constants were obtained by fitting with different physical models. Results were compared to ones obtained by creating high density DNA damage with a laser and subsequently performing Fluorescence Recovery after Photobleaching over the damage area. This work presents similarities and differences in double strand break repair response between γ-irradiation versus laser damage. This is of importance to answering the question of whether the popular use of laser induced DNA damage is a sufficient surrogate for predicting the radiation treatment response of cancer cells.

12:27PM B39.00005 Overview of single-molecule methods including high-force, force-fluorescence, and dual-trap studies for probing molecular and cellular machinery. MATTHEW LANG, Vanderbilt University — High force optical trapping, including double trap geometry and simultaneous visualization with single molecule fluorescence imaging enables a wide range of measurement capabilities applicable for probing molecular and cellular machinery. A series of single molecule measurement methods will be presented. Force-fluorescence microscopy enables visualizing amyloid fibers while physically probing their structures including direct unfolding and rupture of fibers with a high force optical trap. Force spectroscopy is employed to probe the strength of single peptide aptamer bonds. A dual-trap geometry allows for direct tracking of unfolding and translocation machinery of the biological motor ClpXP. Force fluorescence microscopy directly visualizes T-cell activation. Automation and flexibility in our instruments coupled with advances in physical assay design strategies are leveraged to access a broad set of molecular and cellular measurement targets.

1:03PM B39.00006 ABSTRACT WITHDRAWN —

1:15PM B39.00007 3D single molecule tracking in thick cellular specimens using multifocal plane microscopy. SRIPAD RAM, E. SALLY WARD, University of Texas Southwestern Medical Center, RAIMUND J. OBER, University of Texas at Dallas — One of the major challenges in single molecule microscopy concerns 3D tracking of single molecules in cellular specimens. This has been a major impediment to study many fundamental cellular processes, such as protein transport across thick cellular specimens (e.g. a cell-monolayer). Here we show that multifocal plane microscopy (MUM), an imaging modality developed by our group, provides the much needed solution to this longstanding problem. While MUM was previously used for 3D single molecule tracking at shallow depths (~ 1 micron) in live-cells [1], the question arises if MUM can also live up to the significant challenge of tracking single molecules in thick samples. Here by substantially expanding the capabilities of MUM, we demonstrate 3D tracking of quantum-dot labeled molecules in a ~10 micron thick cell monolayer. In this way we have reconstructed the complete 3D intracellular trafficking itinerary of single molecules at high spatial and temporal precision in a thick cell-sample.


Funding support: NIH and the National MS Society.

1:27PM B39.00008 Single Molecule Analysis of Serotonin Transporter Regulation Using Quantum Dots. JERRY CHANG, Vanderbilt University, IAN TOMLINSON, MICHAEL WARNEMENT, ALESSANDRO USTIONE, ANA CARNEIRO, DAVID PISTON, RANDY BLAKELY, SANDRA ROSENTHAL — For the first time, we implement a novel, single molecule approach to define the localization and mobility of the brain’s major target of widely prescribed antidepressant medications, the serotonin transporter (SERT). SERT labeled with single quantum dot (Qdot) revealed unsuspected features of transporter mobility with cholesterol-enriched membrane microdomains (often referred to as “lipid rafts”) and cytoskeleton network linked to transporter activation. We document two pools of surface SERT proteins defined by their lateral mobility, one that exhibits relatively free diffusion in the plasma membrane and a second that displays significantly restricted mobility and localizes to cholesterol-enriched microdomains. Diffusion model prediction and instantaneous velocity analysis indicated that stimuli that act through p38 MAPK-dependent signaling pathways to activate SERT trigger rapid SERT protein translocation within membrane microdomains. Cytoskeleton disruption showed that SERT lateral mobility behaves a membrane raft-constrained, cytoskeleton-associated manner. Our work identifies an unsuspected aspect of neurotransmitter transporter regulation that we propose reflects the dissociation of inhibitory, SERT-associated cytoskeletal anchors.
1:39PM B39.00009 Casein Kinase 2 Reverses Tail-Independent Inhibition of Kinesin-1. JING XU, ZHANYONG SHU, PREETHA ANAND, BABU REDDY, SILVIA CERMELLI, THOMAS WHISENANT, UC Irvine, STEPHEN KING, University of Missouri-Kansas City, LEE BARDWELL, LAN HUANG, STEVEN GROSS, UC Irvine — Kinesin-1 is a plus-end microtubule-based molecular motor, and defects in kinesin transport are linked to diseases including neurodegeneration. Kinesin can auto-inhibit via a direct head-tail interaction, but is believed to be active otherwise. In contrast, this study uncovers a fast but reversible inhibition distinct from the canonical auto-inhibition pathway. The majority of the initially active kinesin (full-length or tail-less) loses its ability to bind/interact with microtubule, and Casein Kinase 2 (CK2) reverses this inactivation (up to 4-fold) without altering kinesin’s single motor properties. Motor phosphorylation is not required for this CK2-mediated kinesin activation. In cultured mammalian cells, knockdown of CK2 level, but not kinase activity, was sufficient to decrease the force required to stall lipid droplet transport, consistent with a reduction in the number of active motors. We propose that CK2 forms a positive regulating complex with the motor. This study provides the first direct evidence of a protein kinase positively regulating kinesin-transport, and uncovers a pathway whereby inactive cargo-bound kinesin can be activated.

1 This work is supported by NIGMS grants GM64624 and GM079156 to SPC, GM-74830 to LH, NIGMS grants GM176516 and GM63366 to LB, and AHA grant 825278F to JX.

1:51PM B39.00010 Asymmetric Configuration and Directed Movement of Brownian Motors. OLEG ANDREEV, University of Rhode Island, VLADISLAV MARKIN, University of Texas Southwestern Medical Center, URI TEAM, UTSMC TEAM — It is assumed that a Brownian motor is a system that can rectify thermal fluctuations into directed movement. The intriguing question is how this is achieved: what is the mechanism for transferring random pulses from the environment into directed movement. A number of models have been proposed, which, in general, assume the existence of an “asymmetric flashing potential” that makes the motor’s diffusion predominately in one direction. In this work, we introduce a model of Brownian motors based on asymmetric friction rather than on asymmetric flashing potential. We show that asymmetric friction can break the symmetry of a molecule’s “random walk” by changing the step size depending on direction. Our model assumes the presence of a symmetrical Brownian force (Gaussian function, average force is 0), an isotropic viscous force, which is proportional to the velocity value but opposite in direction, and an asymmetric friction force, whose value depends on the direction. We present a mathematical model that explains the directed movement for several Brownian motor types.

2:03PM B39.00011 GSK-3 regulates transport of kinesin-1 driven cargos in vivo. CHRISTINA LEIDEL, Department of Physics, University of Texas at Austin, CAROLE WEAVER, LUKASZ SZPANKOWSKI, LAWRENCE S.B. GOLDSTEIN, HHMI, Department of Cellular and Molecular Medicine, School of Medicine, University of California, GEORGE T. SHUBEITA, Department of Physics, University of Texas at Austin, CENTER FOR NONLINEAR DYNAMICS, DEPARTMENT OF PHYSICS, UNIVERSITY OF TEXAS AT AUSTIN COLLABORATION, HHMI, DEPARTMENT OF CELLULAR AND MOLECULAR MEDICINE, UNIV. OF CALIFORNIA COLLABORATION — The Glycogen Synthase Kinase 3 (GSK-3) has been linked to many aspects of the development of Alzheimer’s disease and was proposed to be involved in the transport of the Amyloid Precursor Protein (APP) by kinesin-1 motors. Using Drosophila embryos and larvae with altered GSK-3 expression, we characterize motor transport of cargos including APP and lipid droplets using DIC microscopy, high-resolution video tracking, fluorescence, and in vivo stall force measurements with optical tweezers. By comparing cargo velocities and run lengths we find that GSK-3 is a required negative regulator of in vivo transport. Stall force measurements on lipid droplets reveal that enhanced transport under conditions of reduced GSK-3 is a result of a larger number of active motors hauling the cargo. Our findings have implications on the use of GSK-3 inhibitors in treatment of Alzheimer’s disease.

Monday, March 21, 2011 2:30PM - 5:06PM — Session D38 DCP: Earle K. Plyler Prize Session II: Spectroscopy A130/131

2:30PM D38.00001 Ultrafast Nonlinear Optical Spectroscopy or where would we be without Shaul Mukamel? GRAHAM FLEMING, University of California Berkeley — The development of ultrafast nonlinear optical spectroscopy owes much to the pioneering work of Shaul Mukamel in developing a unifying framework and language with which to understand and relate the content of different types of experiment. The culmination of this work, to date, is in the development of multidimensional optical spectroscopies. In this talk, I will describe recent work in my group on two dimensional electronic spectroscopy of photosynthetic light-harvesting complexes and, if time permits, single walled carbon nanotubes and molecular systems relaxing via conical intersections.

3:06PM D38.00002 2D IR Spectroscopy of Protein Conformation, Folding, and Binding. KEVIN JONES, ANDREJ TOKMAKOFF, ZIAD GALIM, JOSHUA LESSING, C. SAM PENG, MIT Department of Chemistry — 2D IR spectroscopy is an increasingly powerful tool for investigation of protein structure and dynamics. As an ultrashort spectroscopy, it provides information on protein structure and conformational variation with high time resolution, providing a tool to study the dynamics of folding and binding. Some of the unique characteristics of 2D IR result from the powerful structure based modeling that is available for amide vibrations. This talk will cover recent examples from our group in which different forms of protein 2D IR and computational spectroscopy are used to reveal conformational heterogeneity in peptides, the folding and binding of proteins, and protein-water interactions. When combined with temperature-jump experiments, the formation and interchange of these structures is probed.

3:18PM D38.00003 Three-dimensional Fourier-transform spectroscopy of potassium vapor. HEBIN LI, ALAN BRISTOW, MARK SIEMENS, GALAN MOODY, STEVEN CUNDIFF, JILA, University of Colorado and National Institute of Standards and Technology, Boulder, CO 80309 — We have implemented three-dimensional (3D) Fourier-transform spectroscopy to study potassium vapor contained in a ~20 μm transmission cell with argon buffer gas. The four-wave mixing signal is measured in three time dimensions corresponding to the delays between three ~100 fs, phase-stabilized excitation pulses that are arranged in the box geometry. The emission is detected using a phase-stabilized reference pulse by spectral interferometry, and other time axes are Fourier transformed to construct the 3D spectra. The 3D spectra contain the full information of third-order coherent response of the vapor, yet the contribution from each of the single-quantum excitation pathways is unambiguously isolated. Projecting a 3D spectrum onto a specific two-dimensional (2D) plane retrieves rephasing, non-rephasing, and T-scan 2D spectra, as well as the spectra that are not accessible by conventional 2D scans. The spectral features which overlap in congested 2D spectra can be isolated for studying unique processes represented by a single pathway.

3:30PM D38.00004 Reflection Geometry Electronic Two-dimensional Fourier Transform Spectroscopy. THOMAS W. JARVIS, ZHENG SUN, XIAOQIN LI, Department of Physics, University of Texas at Austin, Austin, Texas 78712, MIKHAIL EREMENCHOUK, MICHAEL N. LEUENBERGER, NanoScience Technology Center & Department of Physics, University of Central Florida, Orlando, Florida 32826 — Studying dynamics in nanostructures is vital to develop new opto-electronic devices and to understand fundamental processes in the solid state. Electronic Two-dimensional Fourier Transform Spectroscopy (2DFTS) is a powerful technique that coherently probes the nonlinear optical polarization, establishing correlations between absorption and subsequent emission or dispersion. We perform 2DFTS in reflection, a novel experimental geometry that allows us to probe structured materials. The coupling features and dimensionally extended lineshapes revealed by 2DFTS provide a description of decoherence and dephasing processes, coherent and incoherent energy transfer, and relaxation.
and attraction length scales, these nanoparticles exhibit an interesting hierarchy of phases made up of multiple interpenetrating structures. The number of DNA strands, and on the development of theories for the clustering and self-assembly kinetics of a specific case. Due to a separation of repulsion and attraction lengths, these nanoparticles exhibit an interesting hierarchy of phases made up of multiple interpenetrating structures.

1 A. T. Zayak, et al., arXiv:1011.1873v1

Contrary to [2], we clearly observe phase-dependent control of photoproduct yield over a wide range of excitation energies. Above the excitation limit of 200 GW/cm², our results do however come into agreement with [2], but only for a single observation wavelength (650 nm) whereas the spectra of a unambiguously show drastic changes in the protein due to its ionization. At these excitation levels, the deleterious side channel precludes correct determination of the amount of 13-cis isomer. As such, we argue that it is impossible to make assignments of mechanistic details of control at a high field that in effect “kills” the protein. [1] V. I. Prokhorenko, A. M. Nagy, S. A. Waschuk, L. S. Brown, R. R. Birge, and R. J. D. Miller, Science 313, 1257-1261 (2006). [2] A. C. Florea et al., PNAS 106, 10896-10900 (2009).

Present: University of Hamburg, Physics Department, Germany

4:30PM D38.00007 Toward Investigating Protein Folding Using the Combination of Computer Simulation and Spectroscopy. WEI ZHUANG — Protein folding is an important problem that is attracting scientists from a wide range of disciplines. One of the major challenges comes from the gap between the experimental and the theoretical studies. We proposed a computational protocol of simulating the T-jump peptide unfolding experiments and the related transient IR and 2DIR spectra based on the Markov State Model (MSM) and Nonlinear Exciton Propagation (NEP) methods. MSMs partition the conformation space into a set of non-overlapping metastable states, and we can calculate spectra signal for each of these states using NEP method. Thus the overall spectroscopic observable for a given system is simply the sum of spectra of different metastable states weighted by their populations. Simulated spectra based on MSM have a much better agreement with the equilibrium experimental 2DIR spectra compared to MD simulations starting from the folded state. MSMs are also capable of simulating the unfolding relaxation dynamics upon the temperature jump. The agreement of the simulation using MSMs and NEP with the experiment provides a justification for our protocol as well as a physical insight underlying the spectroscopic observables.

4:42PM D38.00008 Supersymmetry and fluctuation relations for currents in closed networks. VLADIMIR CHERNYAK, Wayne State University, NIKOLAI SINITSYN, Los Alamos National Laboratory — The discovery of fluctuation theorems and nonequilibrium work relations has stimulated considerable interest in nonequilibrium statistical mechanics and theory of counting statistics. It is important to obtain exact relations that do not directly rely on the thermodynamic concepts, such as work or entropy, but rather describe unambiguous microscopic characteristics, such as statistics of particle currents in systems driven by time-dependent fields. We identify hidden supersymmetry in evolution, governed by the master equation, that survives on the level of the counting statistics of stochastic particle currents. Supersymmetry connects the evolutions in the spaces of populations (boson component) and empirical currents (fermion component). We present exact relations for statistics of currents in strongly driven mesoscopic stochastic systems. Being reminiscent of known fluctuation theorems, a part of our exact result is not directly related to the condition of microscopic reversibility but rather follows from supersymmetry of the counting statistics of currents.

4:54PM D38.00009 Understanding Metal-Adsorbate Binding with Surface-Enhanced Raman Spectroscopy: Theory and Experiment. ALEXEY ZAYAK, Molecular Foundry, LBNL, HYUCK CHOO, EECS, UC Berkeley, YING HU, Bioengineering Dpt., Rice University, JEFFREY BOKOR, EECS, UC Berkeley, STEFANO CABRINI, JAMES SCHUCK, JEFFREY NEATON, Molecular Foundry, LBNL. Building on recent work [1], we use a combination of density functional theory (DFT) calculations and surface-enhanced Raman spectroscopy (SERS) measurements to explain experimentally observed variations in SERS data of an organic molecule, trans-1,2-two (4-pyridyl) ethylene (BPE). For the BPE on Au surfaces, our DFT calculations provide a quantitative description of chemical enhancement (CE), and elucidate that variations reported in experiments arise from a convolution of two factors: a nonuniform frequency dependent electromagnetic enhancement, and dependence of CE on the sample incubation time. The later reveals aspects of the binding kinetics of BPE to Au surfaces.

1 We acknowledge support from DOE and DARPA. Computational resources provided by NERSC.

Monday, March 21, 2011 2:30PM - 5:30PM
Session D41 DCP: LeRoy Apker Prize Session: Clusters and Nanoscale Systems A115/117

2:30PM D41.00001 LeRoy Apker Award Talk: Self-Assembly of DNA-Functionalized Nanoparticles. CHIA WEI HSU, Wesleyan University / Harvard University — Nanoparticles tethered with DNA strands can self-assemble into highly organized structures through the bonding of complementary nucleobases. These are promising building blocks for the bottom-up nanotechnology, and computational tools are useful to probe the behaviors of such complex materials. In this talk I will summarize my work on the phase behavior of nanoparticles tethered with a small number of DNA strands, and on the development of theories for the clustering and self-assembly kinetics of a specific case. Due to a separation of repulsion and attraction length scales, these nanoparticles exhibit an interesting hierarchy of phases made up of multiple interpenetrating structures.
characterize the structures with a microscope and compare observed averages with statistical mechanical predictions.

Each disc contains two MSPs, wrapping around the edge of a leaflet of the bilayer. Although nanodiscs have become an important and versatile tool among model membrane systems to functionally reconstitute membrane proteins, they are yet to be utilized as building blocks in material science. However their highly monodisperse nanoscale structure make them ideal for this purpose. Here we report the first superstructures of nanodiscs self-assembled via membrane anchored single stranded DNA. The discs assemble into columnar stacks with high aspect ratio. The MSPs provide another powerful feature, as the His-tags of the protein can be used to attach the discs to colloids or other molecules of interest. This has strong potential for assembly of nanomaterials with greater degrees of complexity.

Orthogonal DNA-colloid Clusters

We experimentally investigate the self-assembly of colloids labelled with different DNA strands into small clusters. We coat 1 micron diameter spheres with 65 base DNA strands having highly specific “sticky ends.” Particles with different surface-bound DNA sequences represent different particle “types.” We tune the short-ranged, pairwise interactions between some types to be attractive and interactions between other types to be purely repulsive; in this sense, the interactions are orthogonal. The magnitude of attraction (and repulsion) is constant across various types. We control the number and types of colloids at the single particle level, and distinguish the type of each particle from the types of their binding partners within each cluster. In an example experiment, 2 particles of each of 3 different types explore a volume less than 100 picoliters and assemble into equilibrium configurations. We characterize the structures with a microscope and compare observed averages with statistical mechanical predictions.

We acknowledge support from NSF through MRSEC (DMR-0820484), NIRT (ECCS-0709323), and IGERT programs.

Size Characterization of Surfactant and Polymer Coated Gold Nanorods

The autocorrelation function of the scattered light intensity was determined for a series of scattering angles under V and VV scattering geometries. The data were fit to a model of rotational and translational diffusivities. From this fit, we estimate the effective length (L) and diameter of the coated nanorods in solution. Au NRs coated with 50k PS show greatly reduced rotational diffusion compared to CTAB-coated NRs. Since the rotational diffusion coefficient scales as 1/L^2, this implies significant extension of the coated PS chains in toluene. We investigate this phenomenon for PS grafted onto Au nanoparticles and nanorods of varying aspect ratio to determine the impact of surface curvature on polymer layer thickness.

This work was supported by the AFOSR under MURI grant FA9550-06-1-0337.

A ligand phase transition on nanorods and its effect on their surface forces

The elemental nanoparticles were prepared by heating an ethylene glycol (EG) solution containing CuCl_2·6H_2O to its boiling temperature, adding an appropriate amount of NaOH, and allowing the reaction to proceed at reflux for 30 minutes prior to the addition of NaOH. The resulting precipitate was then extracted, dried, and characterized by scanning electron microscopy (SEM) with elemental analysis, x-ray diffraction (XRD), and in the case of the elemental Ni nanoparticles, vibrating sample magnetometry (VSM) measurements. The best fit lattice parameters obtained from the elemental Ni and Cu nanoparticles were 0.35289(28) and 0.36171(23) nm, respectively, in good agreement with the corresponding bulk values. On the other hand, the measured saturation magnetization of about 49 emu/g was somewhat smaller than the bulk Ni value. In the case of the Cu/Ni nanoparticles, the best fit lattice parameters for the Ni and Cu components of the core/shell structure were 0.35299(26) and 0.36101(10) nm, indicating the formation of an essentially pure Ni shell and a slight amount of Ni incorporation in the Cu core.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Chemical Preparation and Characterization of Elemental Cu, Ni, and Cu/Ni Core/Shell Nanoparticles

The as-prepared nanoparticles were characterized by scanning electron microscopy (SEM) with elemental mapping, x-ray diffraction (XRD), and vibrating sample magnetometry (VSM) measurements. Chemical composition maps of the particles revealed a well-defined core/shell structure consisting of a Cu core about 100-150 nm in diameter surrounded by a Ni shell about 30-40 nm in thickness. XRD measurements indicated that while the Cu core contained a small amount of incorporated Ni, the shell was essentially pure Ni. The solid-state transformation from the as-prepared core/shell structure to an essentially homogeneous Cu-Ni alloy was studied by high temperature VSM and XRD measurements as a function of annealing temperature and time. These measurements reveal that the core/shell structure remains largely intact to temperatures above 400 °C and that complete homogenization occurs at temperatures above about 600 °C.

Solid-State Homogenization Reactions in Cu Core/Ni shell Nanoparticles

The solid-state transformation from the as-prepared core/shell structure to an essentially homogeneous Cu-Ni alloy was studied by high temperature VSM and XRD measurements as a function of annealing temperature and time. These measurements reveal that the core/shell structure remains largely intact to temperatures above 400 °C and that complete homogenization occurs at temperatures above about 600 °C.
through studies of the detachment energies, gaps in the electronic spectrum, variations in binding energy, and nature of the electronic states. Particularly stable structure studies within a gradient corrected density functional approach. The stability and electronic properties of these clusters have been characterized containing up to 5 Pb and up to 7 In atoms have been investigated using negative ion photodetachment spectroscopy along with first-principles electronic states. Emphasis has been placed on developing accurate and dependable bases to be used to study nano-sized systems. The binding energy, coordination Conjugate Gradient relaxations were performed on clusters ranging in size from 50 to 150 atoms using the SIESTA code to find the geometries of metastable Of particular concern is the bonding behavior between the two chemical elements, one tending to form metallic bonds, the other covalent. DFT calculations and comparisons revealed surface and internal dielectron, $e_2^−$, localization modes and elucidated the mechanism of the reaction ($H_2O$)$_{2n}$ → ($H_2O$)$_{2n-2}$($OH^-$)2 + H2 (for n ≥ 105), which was found to occur via concerted approach of a pair of protons belonging to two water molecules located in the first shell of the dielectron internal hydration cavity, culminating in hydrogen formation 2H2 + $e_2^−$ → H2. Instability of the dielectron internal localization impedes the reaction for smaller (n < 105) clusters.

5:18PM D41.00008 The Discovery of a New Class of Magnetic Superhalogens, P. JENA, M.M. WU, H. WANG, Y. KO, Q. WANG, Q. SUN, B. KIRAN, A. KANDALAM, K. BOWEN, VIRGINIA COMMONWEALTH UNIVERSITY TEAM, PEKING UNIVERSITY COLLABORATION, JOHNS HOPKINS UNIVERSITY COLLABORATION, MCNEESE STATE UNIVERSITY COLLABORATION — We report the discovery of a new class of magnetic superhalogens and their unusually stable molecular anions. These are formed when a hot plume of manganese atoms is cooled through collisions with an inert gas in the presence of chlorine atoms. The anions, with a composition of (Mn$_x$Cl$_{2y+1}$)$^{-}$ (x = 1, 2, 3, . . .), appear as prominent (magic) peaks in mass spectra. Using calculations based on density functional theory and experiments utilizing anion photoelectron spectroscopy, we traced the origin of their unusual stability to the half-filled d-shell of the Mn atoms in anionic clusters and the large electron affinities of their neutral counterparts. The calculated and measured electron affinities are almost twice as high as that of the chlorine atom. However, unlike conventional superhalogens which are non-magnetic and consist of a single metal atom at the core surrounded by halogen atoms, the superhalogens discovered here are magnetic and have (MnCl$_x$)$^{-}$ moieties as a core to which a chlorine atom is attached. In addition, our calculations show that Mn atoms carry large magnetic moments and Mn$_x$Cl$_{2y+1}$ superhalogen moieties can serve as building blocks of a new category of salts with magnetic properties.

4:30PM D41.00009 Dielectron Attachment and Hydrogen Evolution Reaction in Water Clusters1, ROBERT BARNETT, Georgia Institute of Technology, RINA GINGER, ORI CHERNOVSKY, Tel-Aviv University, UZI LANDMAN, Georgia Institute of Technology — Binding of excess electrons to nano-size water droplets, with a focus on the hitherto largely unexplored properties of doubly-charged clusters, were investigated experimentally using mass spectrometry and theoretically with large-scale first-principles quantum simulations. Doubly-charged clusters were measured in the range of 83 ≤ n ≤ 123, with (H$_2$O)$_{2n}$ clusters found for 83 ≤ n < 105, and mass-shifted peaks corresponding to (H$_2$O)$_{2n-2}$($OH^-$)$_2$ detected for n ≥ 105. Simulations revealed surface and internal dielectron, $e_2^−$, localization modes and elucidated the mechanism of the reaction (H$_2$O)$_{2n}$ → (H$_2$O)$_{2n-2}$($OH^-$)$_2$ + H$_2$ (for n ≥ 105), which was found to occur via concerted approach of a pair of protons belonging to two water molecules located in the first shell of the dielectron internal hydration cavity, culminating in hydrogen formation 2H$_2$ + $e_2^−$ → H$_2$. Instability of the dielectron internal localization impedes the reaction for smaller (n < 105) clusters.

4:42PM D41.00010 Investigations into aggregate growth dynamics via in situ structural quantification of flame synthesized silica nanoparticle aggregates, DURGESH RAJ, GREGORY BEAUCAGE, University of Cincinnati, JAN ILAVSKY, Argonne National Laboratory, HENDRIK KAMMLER, Clarient Corporation, SOTIRIS PRATJINIS, ETH Zurich — Ramified aggregates are formed in many dynamic processes such as in flames. The structures are disordered and present a challenge to quantification. The topological quantification of such nanostructured materials is important to understand their growth processes. Small-angle X-ray scattering (SAXS) is widely used to characterize such nanoparticle aggregates. Recently, we have developed a method for the quantification of topology in aggregated material using SAXS. This methodology will be used to describe topologies from in-situ SAXS studies on flame synthesized silica aggregates on millisecond time scales. This is an important step to facilitate understanding of the growth dynamics and the structural rearrangements that occur during flame synthesis.

5:06PM D41.00012 Anion Photoelectron Spectroscopy and First-Principles Study of PbxIn Clusters1, S. VINCENT ONG, Virginia Commonwealth University, JOSHUA MELKO, UJJWAL GUPTA, The Pennsylvania State University, J. ULISES REVESLES, Virginia Commonwealth University, JONATHAN D’EMIDIO, The Pennsylvania State University, SHIV KHANNA, Virginia Commonwealth University, A.W. CASTLEMAN, The Pennsylvania State University. DEPARTMENT OF PHYSICS, VIRGINIA COMMONWEALTH UNIVERSITY COLLABORATION, DEPARTMENTS OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY COLLABORATION — Anionic and neutral Pb$_n$In$_y$ clusters containing up to 5 Pb and up to 7 In atoms have been investigated using negative ion photodetachment spectroscopy along with first-principles electronic structure studies within a gradient corrected density functional approach function. The stability and electronic properties of these clusters have been characterized through studies of the detachment energies, gaps in the electronic spectrum, variations in binding energy, and nature of the electronic states. Particularly stable clusters have been grouped into two families of stable species. Pb$_n$In$_y$, Pb$_2$In$_2$, and Pb$_3$In$_2$ exhibit enhanced stability compared to their neighbors and the stability is linked to the aromatic character identified in their molecular orbitals. On the other hand, Pb$_n$In$_y$, and Pb$_3$In$_2$ exhibit enhanced stability associated with filled electronic shells within a confined nearly free electron gas.

4:54PM D41.00011 Influence of Nanoparticles on Fragility and Collective Particle Motion in Polymer Glass-Formation, JACK DOUGLAS, Polymers Division, NIST, FRANCIS STARR, Department of Physics, Wesleyan University — We investigate the impact of nanoparticles (NP) on glass formation in polymer melts by molecular dynamics simulation. The NP cause significant changes in both fragility and the average length of string-like cooperative motion, where the extent of the effect depends on the NP-polymer interaction and NP concentration. These dynamical changes can be interpreted via the Adam-Gibbs (AG) theory if we assume the strings represent the abstract cooperatively rearranging regions (CRR) of the AG model, whose basic assumptions are reviewed. Molecular additives are also effective at altering the fragility of glass formation and extent of string-like cooperative motion so the modulation of fragility and cooperative motion with additives seems to be a general effect. We find that the fragility of glass formation is mainly controlled mainly by the differential change of L with respect to T near the glass transition rather than the actual size L of the collective motion. We also find a near proportionality between m and the glass transition temperature in our nanocomposite system, which greatly simplifies the T dependence of structural. The classical entropy theory of glass-formation is considered as a complementary tool to gain analytic insights into these additive effects on polymer glass formation.

5:18PM D41.00013 Structural Analysis of Bonding in Au-Ge Clusters, DANIELLE MCDERMOTT, KATHIE NEWMAN, University of Notre Dame — The study of Gold-Germanium clusters is important in understanding systems such as gold catalyzed nanowire growth. Of particular concern is the bonding behavior between the two chemical elements, one tending to form metallic bonds, the other covalent. DFT calculations and Conjugate Gradient relaxations were performed on clusters ranging in size from 50 to 150 atoms using the SIESTA code to find the geometries of metastable states. Emphasis has been placed on developing accurate and dependable bases to be used to study nano-sized systems. The binding energy, coordination number, bond lengths and bond angles are studied as a function of the size and composition of Ge-Au clusters. We will discuss a nanoscale “phase diagram” for gold and germanium and will also discuss the topology of the bonding network.

Tuesday, March 22, 2011 8:00AM - 10:48AM — Session H38 DCP DBP: Focus Session: Quantum Coherence in Biology I
8:00AM H38.00001 Indicators of quantum coherence in light-harvesting dynamics . ALEXANDRA OLAYA-CASTRO, Department of Physics and Astronomy, University College London — Characterizing quantum dynamics of electronic excitations in a variety of light-harvesting systems is currently of much interest [1]. In particular, it is important to identify measures that appropriately quantify the strength of coherent dynamics and its impact on different time scales of the light-harvesting process. In this talk I will discuss quantum transport performance measures that are defined based on the probability for the dynamics to successfully distinguish different initial photo-excitation conditions. I will also discuss how initial state distinguishability can provide information on spatially correlated phonon fluctuations as well as on the non-markovian character of the quantum dynamics. The prototype systems considered here are cryptophyte light-harvesting antennae isolated from marine algae [2, 3]. Experimental quantification of state distinguishability can be realized by monitoring the evolution of selected off-diagonal density matrix elements and therefore it could be achieved with current two-dimensional spectroscopy techniques.


8:36AM H38.00002 Phonon-mediated path-interference in electronic energy transfer . HODA HOSSEIN-EJAD, University of Toronto, ALEXANDRA OLAYA-CASTRO, University College London, GREGORY D. SCHOLES, University of Toronto — Motivated by the recent observations of quantum coherence in light-harvesting antennae, we present a formalism to quantify the contribution of path-interference in phonon-mediated electronic energy transfer. The transfer rate between two molecules is computed by considering the quantum mechanical amplitudes associated with pathways connecting the initial and final sites. This includes contributions from classical pathways, but also terms arising from their interference. By treating the vibrational modes of the molecules as a non-Markovian harmonic oscillator bath, we compute the first-order path-interference correction to the classical transfer rate. We show that the correction due to path-interference may have either a vibrational or an electronic character, and may exceed the contribution of the indirect classical pathways.

8:48AM H38.00003 Efficiency of the energy transfer in the FMO complex using hierarchical equations on Graphics Processing Units . TOBIAS KRAMER, CHRISTOPH KREISBECK, University of Regensburg, Germany, MIRTA RODRIGUEZ, IEM CSIC, Madrid, Spain, BIRGIT HEIN, University of Regensburg, Germany — We study the efficiency of the energy transfer in the Fenna-Matthews-Olson complex solving the non-Markovian hierarchical equations (HE) proposed by Ishizaki and Fleming in 2009, which include properly the reorganization process. We compare this to the Markovian approach and find that the Markovian dynamics overestimates the thermalization rate, yielding higher efficiencies than the HE. Using the high-performance of graphics processing units (GPU) we cover a large range of reorganization energies and temperatures and find that initial quantum beatings are important for the energy distribution, but of limited influence to the efficiency. Our efficient GPU implementation of the HE allows us to calculate nonlinear spectra of the FMO complex. References see www.quantumdynamics.de

9:00AM H38.00004 Efficient GPU calculation of 2D-echo spectra of excitonic energy-transfer in systems with large reorganization energy . BIRGIT HEIN, CHRISTOPH KREISBECK, TOBIAS KRAMER, University of Regensburg, Germany, MIRTA RODRIGUEZ, IEM CSIC, Madrid, Spain — Using the Fenna-Matthews-Olson light harvesting complex as example, we calculate the two dimensional echo spectra (2D echo) of a multi-site system coupled to phonon baths using the propagation scheme suggested by Ishizaki and Fleming in 2009 which works for large system-bath couplings. We study the anti-correlations in the shapes of the 2D spectrum peaks which are seen as evidence for exciton energy transfer. This computationally demanding calculation uses 2.6 h GPU (graphics processing unit) time compared to 2.8 weeks time on a high performance conventional CPU cluster. The efficient implementation of the exact hierarchical equations obliterates the need for approximative methods and facilitates the interpretation and comparison of theory and experiment for systems with large reorganization energies. References see www.quantumdynamics.de

9:12AM H38.00005 Simulation of dissipative quantum dynamics in the presence of strongly-interacting and structured environments: a many-body approach to memory effects . ALEX CHIN, Ulm University, JAVIER PRIOR, Universidad Politécnica de Cartagena, SUSANA F. HUELGA, MARTIN B. PLENIO, Ulm University — Quantum systems which interact strongly with complex and structured environments are receiving increasing attention due to their importance in contexts such as solid-state quantum information processing and bio-molecular quantum dynamics. Unfortunately, these systems are difficult to simulate as the system-bath interactions cannot be treated perturbatively, and standard approaches are invalid or inefficient. Here we combine time-dependent density matrix renormalization group methods with techniques from the theory of orthogonal polynomials to provide an efficient method for simulating open quantum systems at zero and finite temperatures. Using this technique we demonstrate a number of novel dynamical effects which result from long bath memories induced by either sharp spectral structures or strong coupling, and comment on how these can be exploited to drive efficient transport in small networks. We also show how our technique can be used to find the equilibrium properties of excitations in strongly-renormalizing environments, and present some results on the quantum phase transition in the sub-Ohmian spin-boson model.

9:24AM H38.00006 Optimal Excitation energy transfer dynamics in light-harvesting systems1. JIANLAN WU2, JIANSHU CAO, ROBERT SILBAY, Chemistry Department, MIT — With the facilitation of surrounding protein environments, excitation energy transfer (EET) in photosynthetic systems is highly efficient and robust. This talk compares different descriptions of dissipative exciton dynamics, discusses the generic mechanism of optimal energy transfer, and explores its implications for light-harvesting systems. (i) The generalized Bloch-Redfield equation provides an accurate description of exciton dynamics over a broad range of parameter space. (ii) The generic mechanism of optimal efficiency allows us to examine the interplay of quantum coherence, dynamics noise, and static disorder in a unified conceptual framework. (iii) The topological symmetry and network structures in photosynthetic systems reveal useful insights for the optimal design of artificial energy transfer systems.

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1This work was supported by the MIT Energy Initiative (MITEI) Seed Grant, the MIT Center for Excitonics funded by DOE (Grant Number DE-SC0001088), and ARO DOD (Grant Number W911NF-091-04880).

2Physics Department, Zhejiang University, PR China

9:36AM H38.00007 A quantum landscape study of energy transfer efficiency in light-harvesting complexes . ALIREZA SHABANI, Princeton, MASoud MOHSENI, MIT, HERSCHEL RABITZ, Princeton, SETH LLOYD, MIT — Over billion years of evolution some photosynthetic complexes have turned into highly efficient light energy harvesting systems. In this work, we demonstrate optimality and robustness of energy transfer in the Fenna-Matthews-Olson (FMO) protein complex with respect to all the relevant parameters of system and environmental interactions. To this end we developed an efficient technique for studying the dynamics of energy transfer in a non-Markovian and non-perturbative regime. For the FMO protein of green sulfur bacteria we find that all the relevant natural parameters to lay within the optimal and robust regimes of energy transfer process. This suggests a peculiar interplay of internal and external forces in order to have a system that functions optimally while being robust under physiological conditions.
Fast and efficient excitation transfer across disordered molecular networks

10:00AM H38.00009 Regenerative quantum coherence in photosynthesis under natural conditions

10:12AM H38.00010 Enhanced exciton diffusion length via cooperative quantum transport

10:24AM H38.00011 Concatenated quantum codes in biological systems

10:36AM H38.00012 A possible mechanism for quantum coherence assisted ion transport in ion channels

Tuesday, March 22, 2011 11:15AM - 2:15PM – Session J21 DMP GIMS DCP: Focus Session: Imaging and Modifying Materials at the Limits of Space and Time Resolution I
The effect of Au condensation in laser desorption/ionization of organic materials

Atomic-level simulations of structural transformations in layered Au-Cu and Ag-Cu metal targets irradiated by a femtosecond laser pulse

Optical Antennas for Enhanced Light Absorption and Emission

Laser dynamics of laser excited self-assembly gold nanocrystals by time resolved X-ray diffraction

Ultrafast Laser Matter Interaction and Pump-probe Imaging of Transient Electric Fields
of the evolving valence charge density in chemical reactions. Ultrafast pump-probe studies of photoinduced dynamics can also be studied. We have carried out experiments in coherent diffraction from protein nanocrystals, including Photosystem I membrane protein, at the Linac Coherent Light Source (LCLS) at SLAC. The crystals are filtered to sizes less than 2 microns, and are delivered to the pulsed X-ray beam in a continuously flowing liquid jet. Millions of diffraction patterns were recorded at the LCLS repetition rate of 60 Hz. Tens of thousands of the single-shot diffraction patterns have been indexed, and combined into a single crystal diffraction pattern, which can be phased for structure determination and analyzed for the effects of pulse duration and fluence. Experimental data collection was carried out as part of a large collaboration involving CFEL DESY, Arizona State University, Max Plank Institute for Medical Research, University of Upsala, SLAC, LBNL, LLNL, using the XAMP apparatus which was designed and built by the Max Planck Advanced Study Group at CFEL.

The LCLS is operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences.

1:39PM J21.00009 Plans for an Upgrade of the Advanced Photon Source1, DENNIS MILLS, Argonne National Laboratory, APS-U PROJECT TEAM — We are presently developing plans for an upgrade of the Advanced Photon Source facility. Science has formally issued Critical Decision 0 and approved the Mission Need Statement in April of 2010, authorizing the APS to develop a conceptual design for the APS Upgrade (APS-U) project. The proposed upgrade will include enhancements to the accelerator, beamlines, and facility infrastructure. The high brilliance x-ray beams at high photon energy (e.g. > 25 keV) provided by the APSUpgrade will have strong impact on research in energy, the environment, new or improved materials, and biological studies. High-energy x-rays can penetrate into a wide range of realistic and/or extreme environments and allow imaging of structures and processes in unprecedented detail on picosecond time scales and nanometer length scales. The presentation will include some of the essential goals of the APS-U and proposed strategies to attain those goals.

1The Advanced Photon Source at Argonne National Laboratory is supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

1:51PM J21.00010 The Jefferson Lab VUV-FEL at 10 eV and above1, GWYN WILLIAMS, Jefferson Lab, FEL TEAM — We will present details of the vacuum ultraviolet performance of the Jefferson Lab Free Electron Laser. The JLab FEL is oscillator-based [1] and uses a superconducting energy recovered linac for CW RF operation at up to 75 MHz. Lasing at a fundamental wavelength of 372 nm, the third harmonic is at 124 nm, corresponding to a photon energy of 10 eV. The energy per pulse in the fundamental is 20 microjoules, which at 9 MHz yields an average power of 180 Watts. The pulses have a FWHM of order 300 fs, which essentially determines the optical bandwidth. The third harmonic, which is a 0.1 - 1% fraction of this, is considerably brighter than any other source in the region. Further, being an FEL, there is a wide range of tunability in the 1 eV to 15 eV range. Additional reach is possible with increased electron beam energy, and some options will be discussed in the talk.


2:03PM J21.00011 Ultrafast optical fiber microbeam for in-depth fabrication, trapping and fluorescence excitation , MERVYN PINTO, UT Arlington, YOGESHWAR MISHRA, CUSAT, NINAD INGLE, SAMARENDRA MOHANTY, UT Arlington — Micro-focused laser beam is finding widespread application in two-photon polymerization (TPP), microsurgery, two-photon fluorescence microscopy and optical trapping of microscale objects. However, limited by short working distance of the microscope objective, it is essential to develop fiber based laser microbeam for in-depth applications. While fiber-optic two-photon fluorescence excitation (TPE) has been explored in past for endoscopic imaging, only recently we demonstrated optical trapping and microsurgery using single fiber optical microbeam. Here, we present use of ultrafast laser coupled to microfabricated single mode optical fiber for in-depth fabrication of microstructures by TPP as well as TPE and manipulation of microscopic objects by fiber optical microbeam tweezers. The microfabrication of fiber optic axicon tip was optimized so as to perform all the four functions, namely fabrication, excitation, manipulation and collection of fluorescence from the trapped object. Owing to the propagation distance of Bessel-like beam emerging from the axicon-fiber tip, relatively longer streak of fluorescence was observed over the microsphere length. Stable trapping of the fluorescent objects was observed due to reduced scattering force as compared to axial gradient force. These results using multifunctional optical fiber will be presented.

Tuesday, March 22, 2011 11:15AM - 1:39PM –
Session J38 DCP: Focus Session: Ultrafast Dynamics and Imaging II A130/131

11:15AM J38.00001 Probing Ultrafast Solution-Phase Chemistry in the X-ray Water Window and beyond via Soft X-ray Spectroscopy1, NILS HUSE2, Chemical Sciences Division, Lawrence Berkeley National Laboratory — A prerequisite for a microscopic understanding of chemical reactions is knowledge of the ultrafast interplay of valence charge distributions, spin states, and nuclear degrees of freedom. These degrees of freedom are often intricately coupled, leading to very complex dynamics. Femtosecond core-level spectroscopy is very well suited to study such dynamics via x-ray absorption near-edge structure (for information on changes in valence charge distribution / spin-state) and via the extended x-ray absorption fine structure (for information in nuclear arrangements) due to the very localized nature of the initial states of well-defined symmetry and the high chemical specificity of core-level excitations. We have employed femtosecond core-level spectroscopy to study metal-ligand interactions in solution of transistional metal ions as well as synthesized complexes of model systems to demonstrate the feasibility and merit of ultrafast solution-phase soft X-ray spectroscopy. Laser-induced charge transfer reactions on sub-100 fs time scales trigger structural dynamics in first-row transition-metal complexes that display multiple spin-state changes within 300 fs upon photo-excitation. The combined analysis of vibrational, optical, and core-level spectroscopy reveals a complex interplay of nuclear, electronic, and spin degrees of freedom in these systems that leads to detailed insights into the underlying reaction mechanisms. These are prototypic in nature for a variety of organometallic systems. The combined applicability of theoretical and experimental methods is demonstrated here.

1This work was supported by the Department of Energy under Contract No. DE-AC02-05CH11231.
11:51AM J38.00002 Ultrafast Dynamics in Helium Nanodroplets Probed by Femtosecond Time-Resolved EUV Photoelectron and Ion Imaging. OLEG KORNILOV, Max-Born-Institut, OLIVER BÜNERMANN, Georg-August-University, ALI EFTETKAHI-BAFROOEI, Lawrence Berkeley National Laboratory, STEPHEN R. LEONE, DANIEL M. NEUMARK, University of California-Berkeley, OLIVER GESSNER, Lawrence Berkeley National Laboratory — Femtosecond time-resolved EUV photoelectron and ion imaging are employed to study the relaxation dynamics of electronically excited helium nanodroplets. Excitation into a broad droplet absorption band (∼3.8 eV) is followed by ionization with a delayed IR pulse. The transient photoelectron spectra and angular distributions indicate that electronically excited helium atoms are predominantly emitted in either an aligned 1s4p Rydberg state within less than ∼100 fs or in a non-aligned 1s3d state within ∼200 fs. The transient ion imaging results suggest that different Rydberg atoms are emitted with significantly different kinetic energy distributions that closely resemble Maxwell-Boltzmann distributions with temperatures of 2700 K (1s3d) and 490 K (1s4p). The results are interpreted in terms of a dynamic model that is based on the local density dependent blue shift of atomic Rydberg states in the droplet environment.

12:03PM J38.00003 “Molecular spectrometers” in the condensed phase: local THz-FIR response from femtosecond fluorescence. NIKOLAUS ERNSTING. Humboldt University Berlin — We examine dye molecules whose color depends on the polarity of the environment. Following fast optical excitation, their fluorescence band typically red-shifts by 0.5 eV on femtosecond to nanosecond time scales. This “dynamic Stokes shift” reflects the joint molecular and environmental reorganisation of the system. Solvation dynamics has been studied for decades in this way that the dynamics of the environment itself can be extracted. We contribute with two research lines: (1) development of rigid polar solvation probes whose vibrational response is removed from that of water, for example, and (2) fluorescence techniques which measure the dynamic Stokes shifts more precisely. Two results will be shown. The frequency-dependent permittivity ε(ω) of water surrounding N-Methyl-6-Quinolone is extracted up to about 100 cm⁻¹ from the time-resolved fluorescence shift R(t). The key consists in an analytical connection ε(ω) → R(t) which is needed for data fitting. Measurements with the cryptoprotectant saccharide trehalose in water serve to establish the method. Its unique feature is locality, i.e. the possibility to measure ε(ω) around a supramolecular structure with a covalently connected or embedded probe. THz vibrational activity of a biopolymer is thus measured locally, on the effective length scale for polar solvation, with an embedded molecular probe. For this purpose 2-hydroxy-7-nitro-fluorene was linked into a 13mer duplex opposite an abasic site. The NMR solution structure shows that the fluorene moiety occupies a well-defined position in place of a base-pair. The dynamic Stokes shifts for solution in H₂O and D₂O are quantified. Their difference is much larger than expected for free water, suggesting that only bound water is observed. A weak 26 cm⁻¹ spectral oscillation of the emission band is observed which is not present when the probe is free in solution, and is therefore caused by the supramolecular structure (DNA and hydration water).

12:39PM J38.00004 Tunable acoustic terahertz generation in InGaN quantum wells effected by metal nanocrystals. MEG MAHAT, ANTONIO LIOPIS, Department of Physics, University of North Texas, Denton, TX, 76201, USA, SERGIO PÉRIERA, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal, IAN WATSON,Instutes of Photonics, SUPA, University of Strathclyde, Glasgow, G4W, UK, TAE CHOI, Departments of Mechanical Engineering, University of North Texas, Denton, TX, 76203, USA, ARKADII KROKHIN, ARUP NEOGI, Department of Physics, University of North Texas, Denton, TX, 76201, USA — The strained semiconductor multiple quantum wells have the capability to generate acoustic terahertz emission via coherent acoustic phonon oscillations. The frequency of the THz emission is usually limited by the periodicity of the quantum wells or superlattice structures. We propose a novel technique to modify the frequency and amplitude of THz oscillations by the inclusion of the metal nanocrystals (NCs) within InGaN/GaN multiple quantum wells via the self-assembled inverted hexagonal pits. Time resolved differential transmission measurements demonstrate a four-five folds decrease in the THz frequency under band edge excitation conditions. A theoretical model predicts a strong dependence of the amplitude and period of the oscillations on the radius of the metal NCs.

12:51PM J38.00005 “Making the Molecular Movie”: First Frames. R.J. DWAYNE MILLER, Max Plank Research Group for Atomically Resolved Dynamics, University of Hamburg, CFEL/DESY and University of Toronto — Femtosecond Electron Diffraction has enabled atomic resolution to structural changes as they occur, essentially watching atoms move in real time—directly observe transition states. This experiment has been referred to as “making the molecular movie” and has been previously discussed in the context of a gedanken experiment. With the recent development of femtosecond electron pulses with sufficient number density to execute single shot structure determinations, this experiment has been finally realized. A new concept in electron pulse generation was developed based on a solution to the N-body electron propagation problem involving up to 10,000 interacting electrons that has led to a new generation of extremely bright electron pulsed sources that minimizes space charge broadening effects. Previously thought impossible to generate acoustic terahertz emission via coherent acoustic phonon oscillations, the new type of femtosecond electron sources have been developed to create extremely bright, coherent electron pulses that can be used to image the atomic structure of molecules with atomic resolution. The transient photoelectron spectra and angular distributions indicate that electronically excited helium atoms are predominantly emitted in either an aligned 1s4p Rydberg state within less than ∼100 fs or in a non-aligned 1s3d state within ∼200 fs. The transient ion imaging results suggest that different Rydberg atoms are emitted with significantly different kinetic energy distributions that closely resemble Maxwell-Boltzmann distributions with temperatures of 2700 K (1s3d) and 490 K (1s4p). The results are interpreted in terms of a dynamic model that is based on the local density dependent blue shift of atomic Rydberg states in the droplet environment.

1:27PM J38.00006 Two-dimensional dynamical reconstruction of the valence exciton in LiF. XIAOQIAN M. CHEN, YU GAN, PETER ABBAMONTE, University of Illinois at Urbana-Champaign, CHEN-LIN YEH, Tamkang University, Taiwan, DIEGO M. CASA, Argonne National Laboratory, WEI KU, Brookhaven National Laboratory — The structure and dynamics of excitons are interesting because excitons are model many-body excitations with technological relevance, e.g. to the behavior of photocells. In a previous study, we used inelastic X-ray scattering, together with inversion techniques, to reconstruct one-dimensional projection images of exciton propagation in LiF in real space and time, and showed that the exciton in LiF is of the Frenkel type. Here we generalize our previous work to a two-dimensional plane in LiF. Our new images of exciton propagation show intricate shape changes arising from scattering off of the crystal lattice. Our results are compared to model Wannier function calculations for a more detailed test of the Frenkel model.

3This work was supported by the U.S. Department of Energy under grants DE-FG02-07ER46459 and DE-FG02-07ER46453.

Tuesday, March 22, 2011 11:15AM - 2:15PM
Session J40 DCP: Theory of Clusters and Nanoscale Systems A122/123
11:15AM J40.00001 Nanomaterials synthesized by electrochemical discharges: qualitative and quantitative performance, ANIS ALLAGUI, ROLF WUTHRICH, Concordia University — During the electrochemical discharges in aqueous solutions, the electronic avalanches induce several reactions of dimerization and recombination of the hydrated electrons and H⁺ and OH⁻ radicals, generated by the radiation of water molecules. With the introduction of metallic ions M⁺, the successful manufacture of nanoparticles is controlled by the continuous competition of reduction of M⁺, by the powerful reducing agents e⁻ and H⁺ to lower levels of valency, and the back reaction of oxidation by OH⁻. With the assumption that the concentration of metal ions is high enough when compared to those of species e⁻, H⁺ and OH⁻, the differential yield G between the formation and consumption of M⁺ in a given finite volume around the electron-emitting electrode is modeled by homogeneous kinetics. It is found G to be proportional to the concentration of metal ions, the speed and penetration depth of the electrons, and the ratio of rate constants of reactions of nucleation and polymerization, which are supported by previous contributions on the dynamics and stability of the phenomenon.

11:27AM J40.00002 ABSTRACT WITHDRAWN —

11:39AM J40.00003 Structural Oscillation in Pd₁₃ During Oxidation/Reduction, D.R. ROY, J. ULISES REVELES, S. VINCENT ONG, S.N. KHANNA, Virginia Commonwealth University, A.M. KÖSTER, P. CALAMINICI, CINVESTAV, DEPARTMENT OF PHYSICS, VIRGINIA COMMONWEALTH UNIVERSITY COLLABORATION, DEPARTAMENTO DE QUÍMICA, CINVESTAV COLLABORATION — First principles electronic structure calculations within a gradient corrected density functional formalism have been carried out to investigate the electronic structure and magnetic properties of bare and oxidized Pd₁₃ clusters. It is shown that the ground state of neutral Pd₁₃ is a bilayer structure that can be regarded as a fragment of the bulk, while a compact icosahedron is higher in energy. The addition of an electron, however, reverses the ordering of structures and Pd₁₃ becomes a nonmagnetic icosahedral ground state. Similar reordering of structure occurs as an O₂ molecule is added to the neutral cluster. The talk will focus on the oscillations between the two structures during catalysis process.

1We gratefully acknowledge support from the Air Force Office of Scientific Research through a grant FA9550-08-1-0400.

11:51AM J40.00004 Computational Studies on the Energy Landscape of Pt-Pd nanoparticles, ALVARO POSADA-AMARILLAS, Dept. de Inv. en Física, Unisón, RAFAEL PACHECO-CONTRERAS, Dept. de Química, Cineast, DORA J. BORBÓN-GONZÁLEZ, LAURO OLIVER PAZ-BORBÓN, Fritz Haber Institut, ROY L. JOHNSTON, School of Chemistry, University of Birmingham, J. CHRISTIAN SCHÖN, Max Planck Institute for Solid State Research — Bimetallic nanoparticle such as Pt-Pd are currently the subject of intense research mainly due to their important catalytic properties. Clusters structure, composition and degree of mixing or segregation all play important roles in determining their chemical activity. It is presented here an exhaustive study of the structure of Pt-Pd nanoparticles, obtained by a Genetic Algorithm (GA) which incorporates the Gupta potential to mimic interaction for bimetallic atoms. This procedure provided an icosahedral structure as the lowest in energy. The threshold method (TM) is used to analyze the energy landscape of 13-atom Pt@Pd₁₃ nanoparticle, as well as the transition probabilities for those structures with pentagonal symmetry found by the TM. Disconnectivity graphs are obtained for both a vast exploration of the potential energy surface (PES) and the exploration around the lowest energy structure. We found low interconversion transition rates for the putative global minimum provided by the GA code, which was confirmed by the TM algorithm.

1:03PM J40.00005 Negative ions of transition metal-halogen clusters, KALPATARU PRADHAN, Department of Physics, VCU, Richmond, VA, 23284, USA, GENNADY L. GUTSEV, Department of Physics, Florida A&M University, FL 32307, USA, PURUSOTTAM JENA, Department of Physics, VCU, Richmond, VA, 23284, USA — A systematic density functional theory based study of the structure and spectroscopic properties of neutral and negatively charged MXₙ clusters formed by a transition metal atom M (M=Sc, Ti, V) and up to seven halogen atoms X (X=F, Cl, Br) has revealed a number of interesting features: (1) Halogen atoms are bound chemically to Sc, Ti, and V for n<max, where the maximal valence n_max equals to 3, 4, and 5 for Sc, Ti, and V, respectively. For n>n_max, two halogen atoms became dimerized in the neutral species, while dimerization begins at n=5, 6, and 7 for negatively charged clusters containing Sc, Ti, and V. (2) Magnetic moments of the transition metal atoms depend strongly on the number of halogen atoms in a cluster and the cluster charge. (3) The number of halogen atoms that can be attached to a metal atom exceeds the maximal formal valence of the metal atom. (4) The electron affinities of the neutral clusters abruptly rise at n=n_max, reaching values as high as 7 eV. The corresponding anions could be used in the synthesis of new salts, once appropriate counterions are identified.

We acknowledge the DTRA grant.

12:15PM J40.00006 Crystal Field Splitting and Stabilization of CuMgx- Clusters, VICTOR M. MEDEL, J. ULISES REVELES, A.C. REBER, M.C. QIAN, S.N. KHANNA, Virginia Commonwealth University, DEPARTMENT OF PHYSICS, VIRGINIA COMMONWEALTH UNIVERSITY TEAM — The electronic states in clusters group into shells much in the same way as in atoms. Clusters with filled electronic shells exhibit enhanced stability as manifested through observed magic numbers in metal clusters. An important issue is if stable species can be attained at sub-shell fillings. In this work we have carried out first principles electronic structure calculations on CuAl₆⁻ and CuMg₆⁻ clusters to demonstrate this intriguing effect. It is shown that the ionic cores in the clusters can order to generate internal electric fields that lead to splitting of the supershells, much in the same way as the crystal field splitting of atomic states in crystals. The studies offer a new approach to forming magic species though control of the composition and the arrangement of atoms. The talk will highlight these effects and how they can be seen in experiments.

We gratefully acknowledge support from the Air Force Office of Scientific Research through a grant FA9550-09-1-0371.

12:27PM J40.00007 Ab initio study of dimer and one-dimensional chain structures of M@Au₁₂ (M = W, Mo) clusters, SORA PARK, GUNN KIM, YOUNG-KYUN KWON, Kyung Hee University — Using density functional theory, we investigate the structural and electronic properties of the dimer and one-dimensional (1D) chain structures composed of metal-encapsulated Au₁₂ nanoclusters (M@Au₁₂, M = W, Mo) with icosahedral (I₅) and cuboctahedral (O₁) symmetries. We consider various dimer configurations with different compounds and symmetries to find the most stable dimer structure in each case. We find that during dimerization (either homogeneous or heterogeneous dimer), Au atoms in the one cluster tend to form triangular bonds with counterpart Au atoms in the other. By maximizing the number of Au-Au bonds by dimerization, any cluster is stabilized by about 3 eV. We further find their stable 1D chain structures by considering various 1D chain configurations with different compounds and symmetries. Our results demonstrate that the spin-orbit coupling effects are significant on the electronic and magnetic properties as well as the structural stability due to 5d electrons in transition metal atom M of the M@Au₁₂ nanocluster. We also present interesting differences in electronic and magnetic properties between I₅- and O₁-symmetric 1D polymerized M@Au₁₂ chain structures.
12:39PM J40.00008 Interpretation of Cp(*) - protected Aluminum Clusters as Superatom Complexes, P. ANDRE CLAYBORNE, OLGA LOPEZ-ACEVEDO, Department of Chemistry, USC, University of Jyväskylä, ROBERT WHETTEN, University of Jyväskylä and Georgia Institute of Technology, HENRIK GRÖNSECK, Competence Centre for Catalysis and Department of Applied Physics, Chalmers University of Technology, HANNU HÄÄKINEN, Department of Chemistry and Department of Physics, USC, University of Jyväskylä — Metal clusters stabilized by a surface ligand shell represent an interesting intermediate state of matter between pure metal and a metalloid. Such “metalloid” particles are characterized by the balance between metal-metal bonds in the core and metal-ligand bonds at the exterior of the cluster. In previous studies, the electronic stability observed for selected ligand-protected aluminum clusters is not fully understood. By density functional theory calculations, we illustrate here that the electronic stability of various experimentally isolated Cp(*) – protected aluminum clusters can be explained using the electron shell model for the aluminum core, coupled with an ionic Al-Cp(*) interaction at the surface. Thus, one may classify ligand-protected aluminum clusters as “superatom complexes” similar to the ligand-protected gold clusters.

12:51PM J40.00009 Probing the existence of energetically degenerate cluster isomers by chemical tagging, QIAN WANG, Virginia Commonwealth University, QIANG SUN, PURU JENA — Current methods for identifying the ground state geometry of a cluster require synergy between theory and experiment. However, this becomes a difficult problem when the accuracy of the theoretical methods is not sufficient to distinguish between nearly degenerate isomers. Using density functional theory based calculations we show that the near degeneracy between the planar and cage structures can be lifted by tagging these with halogens and superhalogens moieties such as Cl and BO2. The energy of the planar Au16-isomer is lowered from 0.15 eV before tagging to 0.51 ~ 0.55 eV after tagging, thus providing a way to probe its coexistence.

1:03PM J40.00010 Gold clusters at finite temperature: influence of fluxionality on ligand adsorption, LUCA M. GHIRINGHELLI, ELIZABETH C. BERET, JÖRG MEYER, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG, Berlin, Germany — Metal clusters, in particular in relation with their catalytic properties, have been the object of intensive experimental and theoretical studies, in the recent years. A great deal of effort has been devoted by many theoretical groups to understanding the zero kelvin properties of such clusters. Here, by focusing on small gas phase AuNi clusters (3 ≤ N ≤ 20) and their interaction with CO and O2 as a showcase, we illustrate a methodology for the study of small clusters and their interaction with atoms and molecules at finite temperature. We combine all-electron density functional theory, including xc-f-electron dependent van-der-Waals tail corrections, with finite temperature sampling techniques, like Biased MD and Parallel Tempered MD. We find an unusual flexibility of the clusters, at room and lower temperature. At certain sizes, AuN clusters at room temperature are liquid droplets. This has an important implication, when accounting for the dynamics of ligand adsorption. One has to consider that the energy released by an exothermic ligand adsorption heats up the newly formed complex, and the equilibration with the environment is much longer than the typical timescale for conformational rearrangement. In this respect, the very concept of a preferred adsorption site in the bare cluster might be meaningless.

1:15PM J40.00011 Pseudohalogenos as Building Blocks of Hyperhalogens: A Case Study with Au(CN)2 Complexes, DEVELLENA SAMANTA, Virginia Commonwealth University, MIAO MIAO WU, Peking University, China, PURUSOTTAM JENA, Virginia Commonwealth University, VIRGINIA COMMONWEALTH UNIVERSITY TEAM, PEKING UNIVERSITY, CHINA COLLABORATION — Electron affinity (EA) is one of the major factors that govern reactivity. Halogen atoms possess the highest electron affinities among the elements in the periodic table since it takes only one electron to close their shell. Pseudohalogens also require one electron to close their shell and thus mimic the properties of halogens. A typical example is the CN moiety whose electron affinity (3.8 eV) is slightly larger than that of Cl. Using calculations based on density functional theory we show that when a Au atom is surrounded by CN moieties, the electron affinity of Au(CN)2 complexes rise above that of CN for x≥2 and reach a value as high as 8.4 eV, thus forming hyperhalogen. Electron affinities also show odd even alternation with the clusters with even x having higher EA values. Equilibrium geometries, electronic structure and spectroscopic properties of these complexes will be presented and results will be compared with available experimental data.

1:27PM J40.00012 Chirality in Metallic Clusters, IGNACIO L. GARZON, LUIS A. PEREZ, Universidad Nacional Autonoma de Mexico — In this work, we present a theoretical study on the structural, vibrational, electronic, and optical properties of chiral bare gold clusters. We consider the case of the Au34 cluster for which extensive experimental studies on its structural and electronic behavior had been published recently. Our results show that the lowest-energy isomers of the Au34 cluster correspond to two chiral structures with C1 and C3 point symmetry groups, being the C3 isomer slightly more stable than the C1 one. The calculated structure factors, which have been measured using trapped ion electron diffraction, indicate that these isomers are almost indistinguishable. On the other hand, their electronic DOS show different features around the HOMO-LUMO energy gap, which may be detected through optical spectroscopies. In fact, our calculated absorption and circular dichroism spectra show clear differences in the optical behavior of these chiral clusters. Another important property that distinguishes the C1 and C3 isomers is the different spatial distribution of the atomic coordination on the cluster surface, which would generate distinct enantiomeric adsorption patterns with chiral molecules. These results confirm the existence of intrinsically chiral bare gold clusters.

1:39PM J40.00013 Free gold clusters in CO and O2 atmosphere: an ab initio study, ELIZABETH C. BERET, LUCA M. GHIRINGHELLI, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG, Berlin — The marked catalytic activity of gold nanoparticles has inspired a large number of scientific contributions from different fields. However, many questions still lack a satisfying answer, for example what are the structures and stoichiometries of the gold particles in the presence of the reactive gases, and how do their catalytic properties depend on the particle size [1]. We answer these questions for neutral gold clusters modeled in a gas phase atmosphere containing CO and O2 in variable compositions, and in a temperature range between 100 and 600 K. To this aim, DFT (PBE)–based ab initio atomistic thermodynamics technique [2] is applied, including full account of the vibrational contribution to the free energy. As a result, the preferred cluster+adsorbate structures for different environmental conditions are obtained and interpreted as candidate intermediates in the catalytic CO oxidation reaction.


1:51PM J40.00014 Structure-specific spectroscopy of plasmon-supporting nanoparticles, KEN-NETH KNAPPENBERGER, Florida State University — Recent advances in the development of sensitive ultrashort laser-based spectroscopic probes to investigate dynamics of high surface-to-volume metal and alloy nanostructures will be discussed. Electronic relaxation and interparticle electromagnetic coupling processes in hollow gold nanospheres (HGNs) and HGN aggregates were studied using femtosecond pump–surface plasmon probe and second harmonic generation spectroscopies, including single-particle measurements. In the case of HGNs, an unexpected, but systematic, blue shift of the spectral position of the surface plasmon resonance was observed upon nanoparticle aggregation. Femtosecond time-resolved measurements, high-resolution TEM, and Finite-Difference Time-Domain calculations demonstrate that this blue shift results from interparticle cavity coupling, an effect not possible for solid nanospheres. The efficiency of this coupling was tailored by controlling HGN aspect ratio over a vast range of sizes (20 nm to 80 nm outer diameters). This effect may be applied to developing more efficient optical and electronic devices, including photovoltaics.

Financial support by the Academy of Finland. The computational resources were provided by the CSC - the Finnish IT Center for Science in Espoo.
optical experiments on SWNTs, revealing novel properties of high-density 1-D excitons as well as coherent lattice vibrations. We have carried out a series of ultrafast and nonlinear optical experiments on SWNTs, revealing novel properties of high-density 1-D excitons as well as coherent lattice vibrations. We have shown that there exists an upper limit on the density of 1-D excitons in SWNTs, which results in photoluminescence saturation. Using a model based on diffusion-limited exciton-exciton annihilation, we provided realistic estimates for the exciton densities in the saturation regime. We also predicted and demonstrated that there is an optimum temperature at which the exciton density can be maximized, due to the existence of a dark exciton state. Using ultrashort pulses, we have also investigated the dynamics of coherent phonons (CPs) in SWNTs, including both the low frequency radial breathing mode and high frequency G-mode phonons. Pulse shaping techniques allowed us to generate and detect CPs in SWNTs in a chirality-selective manner, which provided insight into the chirality dependence of light absorption, phonon generation, and phonon-induced band-structure modulations. Finally, we observed novel large-amplitude CPs through near-band-edge excitations as well as strongly polarization-dependent CP signals in highly-aligned SWNTs.

This work was performed in collaboration with Y. Murakami, A. Srivastava, T. A. Searles, L. G. Booshehri, E. H. Hårold, D. T. Morris, J.-H. Kim, K.-J. Yee, Y.-S. Lim, G. D. Sanders, C. J. Stanton, and R. Saito.


3:06PM L1.00002 Femtosecond magnetism and spin manipulation on a time-scale of the exchange interaction

ALEXEY KIMEL, Radboud University Nijmegen — The dynamics of phase transformations on the time-scale pertinent to atomic, orbital and spin motion is a rather unexplored field in physics. This is also a particularly interesting problem of modern magnetism, a study of which may have tremendous consequences for future development of magnetic recording technology. However, generation of magnetic field pulses much shorter than 100 ps and strong enough to reverse magnetization (more than 1T) is an extremely challenging technical problem. As a result the dynamics of the magnetic phase transitions at the sub-100 ps time-scale remains to be one of the most intriguing areas of modern magnetism [1,2]. Recently it has been observed that a 40 fs laser pulse influences spins in a magnet as an equally short pulse of effective magnetic field with a strength up to 20 T [3,4]. In my talk I will discuss how these opto-magnetic pulses can be used to excite a magnet on a time-scale of the exchange interaction between the spins [5-7]. Novel insights into the physics of non-equilibrium magnetism will be provided, showing that two exchange-coupled magnetic sublattices of a ferrimagnet may have totally different spin dynamics [8]. As a result, ultrafast spin reversal of two antiferromagnetically coupled magnetic sub-lattices appears to proceed via a novel ferromagnet-like transient state.


3:42PM L1.00003 Theory of ultrafast pump-probe phenomena in high-temperature superconductors

JIAN-XIN ZHU, Los Alamos National Laboratory, Los Alamos, NM 87545 — The physics underlying the pairing mechanism for high-temperature superconductors remains a topic of current interest. The complexity lies with the existence of competing interactions in these strongly correlated electronic materials. The ultra-fast pump-probe technique can make a stride to untangle the competing degrees of freedom (DOF). In this talk, the theoretical underpinning for this technique will be reviewed. In particular, we have developed a three-temperature model [1] to simulate the real time dependence of the electron and phonon temperatures in high-temperature superconductors. The model considers anisotropic electron-phonon coupling [2]. Based on this model, we have calculated the time-resolved spectral function, which exhibits interesting features with time delay. It has been found that the excitation of phononic DOF can provide a defining signature for the existence of electron-vibration mode coupling [1]. In addition, the time-resolved optical conductivity and Raman spectra will also be discussed within the same model [3]

1. Jianmin Tao and Jian-Xin Zhu, Phys. Rev. B 81, 224506 (2010);

This work was supported by the National Nuclear Security Administration of the U.S. DOE at LANL under Contract No. DE-AC52-06NA25396.
Tuesday, March 22, 2011 2:30PM - 5:30PM – Session L21 DMP GIMS DCP: Focus Session: Imaging and Modifying Materials at the Limits of Space and Time Resolution II

2:30PM L21.00001 Nanoscale phase transitions within single ion tracks. WILLIAM WEBER, University of Tennessee, RAM DEVANATHAN, Pacific Northwest National Laboratory, PEDRO MOREIRA, Universidade Estadual de Campinas — The dynamics of track development due to the passage of energetic ions through solids is a long-standing issue relevant to nuclear materials, age-dating of minerals, space exploration, and nanoscale fabrication of novel devices. We have integrated computer simulation and experimental approaches to investigate nanoscale phase transitions under the extreme conditions created within single tracks of energetic ions in the Gd

4:18PM L1.00004 Ultrafast Optical Excitation in YBa$_2$Cu$_3$O$_{6.5}$: Tracing the Optical Phonons

ALEXEI PASHKIN, University of Konstanz — The time-resolved spectroscopy of nonequilibrium states proved to be a powerful tool for observation of the electron-phonon scattering dynamics and the recombination of photoexcited quasiparticles (QP), particularly in high-temperature cuprate superconductors. However, most of the reported experiments monitor only the electronic subsystem [1-5]. Thus, a detailed dynamics of the various phonon modes during an initial non-thermal regime has been beyond reach. Here we utilize the field-resolved ultrabroadband THz spectroscopy to resonantly track ultrafast phonon and QP dynamics of optimally doped single crystals of YBa$_2$Cu$_3$O$_{6.5}$ [6]. The superconducting state is perturbed by 12-fs optical pump pulses, and the induced changes in the mid-infrared optical conductivity are probed by THz transients. Thus, we simultaneously observe the dynamics of nonequilibrium QPs and two specific phonon modes with a time resolution of 40 fs. A quantitative line shape analysis of the apex oxygen vibration allows us to separately follow its transient occupation and coupling to the Josephson plasma resonance. A strong phonon population and the maximum QP density are reached within the same time scale of 150 fs demonstrating that the lattice absorbs a major portion of the pump energy before the QPs are thermalized. Our results indicate substantial electron-phonon scattering in YBa$_2$Cu$_3$O$_{6.5}$ and introduce a powerful approach for characterizing transient phonon dynamics in a broad variety of solids.

1 S. G. Han et al., Phys. Rev. Lett. 65, 2708 (1990);
2 R. A. Kaindl et al., Science 287, 470 (2000);
3 D. Averitt et al., Phys. Rev. B 63, 140502 (2001);
5 R. P. Saichu et al., Phys. Rev. Lett. 102, 177004 (2009);

2:42PM L21.00002 Exploring electron beam induced heat and mass transport at the atomic scale$^1$, CHRISTIAN KISIELOWSKI, Lawrence Berkeley National Laboratory — In recent years the performance of mid-voltage electron microscopes was significantly boosted to reach deep sub-Ångstrom resolution around 0.5 Å at 300 kV in broad beam (TEM) and focused probe (STEM) modes. Atomic resolution microscopy at voltages as low as 50 kV (and possibly below) was fostered. As a result the detection of single atoms across the Periodic Table of Elements is now possible even if light atoms are considered. After decades of striving for resolution enhancement, electron microscopy has now reached a limit that is given at a fundamental level by the Coulomb scattering process itself and by beam-sample interactions, which set a maximum dose limit that can be easily reached for soft and hard materials with the developed high-brightness electron guns. Consequently, new frontiers for electron microscopy emerge and this contribution addresses dynamic processes at the single atom level that can now be captured in time series of images at frequencies below 1 Hz reaching towards kHz. In this frequency range much of the observed atom dynamics is electron beam induced and the control of beam-sample interaction imposes constraints as well as opportunities. In this contribution it is shown that it seems feasible to exploit beam sample interactions to gain better insight into heat and mass transport in soft and hard matter at atomic resolution.

$^1$This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

3:06PM L21.00004 Surface characterization at the spatial resolution limit with Individual Cluster Impacts$^1$, FRANCISCO FERNANDEZ-LIMA, MICHAEL J. ELLER, JOHN D. DEBORD, STANISLAV V. VERKHOTUROV, Texas A&M University, SERGE DELLA-NEGRA, IPN, Orsay, EMILE A. SCHWEIKERT, Texas A&M University — The use of cluster bombardment (e.g. Cu$_{60}$ and Au$_{400}$) for surface analysis and characterization has shown significant advantages due to enhanced emission of molecular ions, low damage cross section, and reduced molecular fragmentation. At temporally and spatially discrete cluster impacts, the small impacted volume ($10^3$ nm$^3$) and ionized ejecta are ideal candidates for surface molecule interrogation. In the present talk, recent measurements of co-emitted photons, electrons and secondary ions from individual cluster impacts for several projectile-target combinations will be presented. Inspection of the photon and electron emissions show that the emission profiles are correlated with the target structure/composition at the nanometer level, with the particularity that co-emitted photons, electrons and secondary ion pairs can be used as indicators of the surface content and homogeneity. Examples of surface mapping of intact molecules via electron emission microscopy combined with secondary ion detection will be shown.

$^1$This work was supported by the National Science Foundation (Grant CHE-0750377). F. A. F-L acknowledges the National Institute of Health support (Grant No. 1K99RR030188-01).
3:18PM L21.00005 Electronic response of dielectric covered metal surfaces to highly charged ions

R.E. LAKE, Clemson University, J.M. POMEROY, National Institute of Standards and Technology, C.E. SOSOLIK, Clemson University — The strong Coulombic perturbation on a solid target from a highly charged ion (HCI) initiates a complex many-body response from target electrons that can produce novel effects such as potential energy sputtering, nanofeature formation and huge secondary electron yields. Far above the surface, HClS reach a critical electron capture distance and neutralization proceeds via resonant charge transfer over the vacuum barrier [1]. Motivated by recent experiments [2], we detail the onset of charge transfer between a HCl and a metal covered with a dielectric thin film (Co with 1.5 nm Al2O3) to determine the film’s effect on the critical distance. Surprisingly, we find that the first captured electrons are pulled through the exposed dielectric and come from the underlying metal. Additionally, the Al2O3 film lowers the effective work function of the target and extends the critical distance compared to a clean metal. I will discuss how the experimental parameters (thin film material/thickness and ion charge state/velocity) can be tuned to allow the ion to interact with electrons in either the metal or thin film.


We acknowledge support from NIST and NSF-CHE-0548111.

3:30PM L21.00006 Extraordinary sensitivity of nanoscale infrared spectroscopy demonstrated on Graphene and thin SiO2

GREG ANDREEV, Z. FEI, UCSD, W. BAO, Z. ZHAO, C.N. LAU, UC Riverside, L.M. ZHANG, Boston U. M. FOGLER, G. DOMINGUEZ, M. THIEMENS, UCSD, F. KEILMANN, Max Planck, Garching, D. BASOV, UCSD — Infrared Spectroscopy is a powerful tool for characterizing materials by their vibrational mode fingerprint and/or electron conductivity. Its application to nanoscale resolved studies is highly desirable but remained challenging mainly for two reasons: a suitable source of intense, broadband infrared illumination was not widely available and the spatial resolution of conventional microscopes was limited by diffraction. We have resolved both issues by utilizing tunable External Cavity Quantum Cascade Lasers (EC-QCLs) as an intense illumination source for a scattering Scanning Near Field Optical Microscope (s-SNOM), capable of <10nm spatial resolution. With this combination of EC-QCLs + s-SNOM, we demonstrate strong bottom and top infrared absorbance in thin oxide layers (SiO2) as thin as 2nm and even single atomic layers of Carbon (Graphene). The spectra register contrasts for volumes as small as 20x20x1nm3 = 400 yolkotiles of SiO2, and about 70 yl of Graphene over a broad spectral range: 1065-2250 cm-1. We explain the origins of this extraordinary sensitivity with an improved theoretical framework for calculating the near field response of a multilayer system.

3:42PM L21.00007 Mesoscopic metal-insulator transitions at twin domain walls in improper ferroelastic VO2

ALEXANDER TSELEV, Oak Ridge National Laboratory — Appearance of unusual phenomena at interfaces of different materials due to symmetry breaking and atomic, electronic, or spin reconstructions is well established area of intensive research. Domain walls in ferroic materials also can show unusual behavior due to symmetry discontinuities. VO2 is a strongly-correlated-electron material, which exhibits a metal-insulator phase transition with a structural, lattice symmetry-lowering transformation making this material an improper ferroelastic. We observe mesoscopic metal-insulator transitions at the ferroelastic domain walls in the lower-symmetry phase of VO2 that occur at temperatures as much as 10-12 ºC below the bulk transition, resulting in the formation of metallic channels in the semiconducting material. The experiments are made using AFM-based scanning near-field microwave microscopy, which allows simultaneous accurate imaging of topography and the low-frequency dielectric function with a special resolution as high as 50 nm. The latter is possible due to a relatively high frequency used (in a few GHz range), when the sample-probe capacitive coupling becomes sufficiently strong and the electric current path is complete by displacement currents between the sample, probe tip, and the probe shield electrode. Density functional calculations indicate that ferroelastic domain walls of this type possess metallic character at low temperatures, which can be ascribed to elevated structural symmetry at the domain walls. The observed behavior, linked as well to the strain inhomogeneity inherent to ferroelastic materials, is generally relevant to symmetry-lowering phase transitions in other material systems.

4:18PM L21.00008 Simulation of Non-contact Atomic Force Microscopy for Structural Analysis

JAMES CHELIKOWSKY, TZU-LIANG CHAN, University of Texas at Austin, C.Z. WANG, KAI-MING HO, Ames Laboratory of US DOE, Iowa State University — A powerful probe of materials centers on the use of atomic force microscopy (AFM). However, an analysis of AFM images can be complex and challenging. We present an efficient scheme to simulate non-contact AFM images by employing a first-principles self-consistent potential from the sample as the essential input. This scheme does not require an explicit modeling of the AFM tip. Our method will be illustrated by applying it to various types of semiconductor surfaces including Si(111) (7x7), TiO2 (110) (1x1), Ag/Si(111)- (√3 x √3) R30o and Ge/Si(105) (1x2) surfaces. We obtain good agreement with experimental results and previous theoretical studies by using this scheme. The method can quickly and efficiently aid in identifying different models for surface structures.

4:30PM L21.00009 Synchrotron X-ray Enhanced Scanning Tunneling Microscopy

VOLKER ROSE, JOHN FREELAND, Argonne National Laboratory — Proper understanding of complex phenomena occurring in nanostructures requires tools with both the ability to resolve the nanometer scale as well as provide detailed information about chemical, electronic, and magnetic structure. Scanning tunneling microscopy (STM) achieves the requisite high spatial resolution; however, direct elemental determination is not easily accomplished. X-ray microscopies, on the other hand, provide elemental selectivity, but currently have spatial resolution only of tens of nanometers. We present a novel and radically different concept that employs detection of local synchrotron x-ray interactions utilizing a STM that provides spatial resolution, and x-ray absorption directly yields chemical, electronic, and magnetic sensitivity. If during tunneling the sample is simultaneously illuminated with monochromatic x-rays, characteristic absorption will arise. Electrons that are excited into unoccupied levels close to the Fermi level modulate the tunneling current giving rise to elemental contrast.

This work was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

4:42PM L21.00010 Frequency comb generation in a tunneling junction by intermode mixing of ultrastark laser pulses

MARK HAGMANN, NewPath Research L.L.C., DZMITRY YAROTSKI, ANATOLY EFIMOV, ANTOINETTE TAYLOR, Los Alamos National Laboratory — Nonlinear interaction of electromagnetic radiation with tunneling electrons results in a number of peculiar physical phenomena, such as frequency mixing and imaging of insulating surfaces with scanning tunneling microscopy (STM). Arguably, the most promising among them is coupling of femtosecond laser pulses to the STm for materials dynamics observation at nm/ps scales. However, the underlying physics is still poorly understood and the majority of existing studies of nonlinear mixing have been restricted to the use of CW lasers in a narrow range. Here, we present a new method for the hyper-spectral characterization of the nonlinear effects in tunneling junction. We use a 10-fs laser pulses at a nominal repetition rate of 74.25 MHz to generate a frequency comb in the tunneling current with frequencies up to 1 GHz. The typical output power at the fundamental (repetition) frequency is -120 dBm, and decreases for higher harmonics. The observed magnitude and square-law dependence of the signal power on the tunneling current and incident laser power are in good agreement with theoretical predictions.
4:54PM L21.00011 First principles computation of dynamical structure factor in real and momentum space in cuprates, YUNG JUI WANG, B. BARBIELLINI, HSIN LIN, TANMOY DAS, SUSMITA BASAK, Northeastern Univ. (NU), P. E. MUNARENS, Delft Univ. of Tech. and NU, S. KAPRZYK, NU and AGH (Poland), R. S. MARKIEWICZ, A. BANSIL, NU — We present a method for efficient, accurate first-principles calculations of the dynamical structure factor $S(q, \omega)$ in periodic systems, using products of real space Green functions and fast Fourier transforms (FFT). We further invert $S(q, \omega)$ via Fourier transformation [1] to reconstruct the propagator of electron density $X(x, t)$ in real space and time domain, thereby visualising spatially the dynamics of an electron doped cuprate system in real time. The present method is useful for many-body perturbation theories of excitations based on Density Function Theory (DFT) and modeling of various highly resolved spectroscopies going beyond the standard LDA [2-5]. Some illustrative examples will be presented. Work supported by the US DOE.


5:06PM L21.00012 Beam self-focusing in the near field emission scanning electron microscopy, FUXIANG LI, ARTEM ABANOV — Recent experiment on the near field emission scanning electron microscopy shows an unexpectedly high lateral and vertical resolution. We show that these effects can be explained by the beams self-focusing. We derive the equations for the beam propagation and solve them numerically. Our results are in a very good agreement with the experiment.

5:18PM L21.00013 Enhancing the spatial resolution in PEEM beyond 30nm using diamondoid surface coating, HITOSHI IISHIWATA, Stanford University, HENDRIK OHLDAG, Stanford Synchrotron Radiation Lightsource, ZHI-XUN SHEN, NICK MELOSH, Stanford University, ANDREAS SCHOLL, Advanced Light Source — The spatial resolution in Photoemission Electron Microscopy typically does not allow imaging features smaller than 30nm. PEEM resolution is limited by chromatic and spherical aberrations of the electrostatic lenses in the microscope column in combination with a wide angular and energy distribution of the secondary electrons to make these aberrations significant. Diamondoids have recently been shown to act as a monochromator for secondary electrons, thus reducing chromatic aberration in PEEM. In addition to improving the resolution of the microscope the diamondoid coating will also enhance the image intensity since now more secondary electrons will be accepted by the aperture. At 10kV the spatial resolution of PEEM is of the order of 150-200nm so that the magnetic domains can hardly be recognized anymore without the diamondoid coating. However, they become visible on the sample that was coated with diamondoids, indicating that the coating improved the spatial resolution by monochromatizing the secondary electrons. We also find that the image intensity is enhanced by a factor of 2-3 with the diamondoid coating. These initial findings on samples with relatively large domains of 150nm are very encouraging and we are therefore convinced that we can push the resolution limit below 30nm studying samples with smaller domains at higher acceleration voltages of 20kV.

Tuesday, March 22, 2011 2:30PM - 4:42PM — Session L38 DCP DBP: Focus Session: Quantum Coherence in Biology II A130/131

2:30PM L38.00001 The role of quantum coherence in excitonic energy transfer: quantum process tomography, molecular dynamics and efficiency measures, ALAN ASPURU-GUZIK, Department of Chemistry and Chemical Biology, Harvard University — Long-lived electronic coherence in various photosynthetic complexes at cryogenic and room temperature have generated vigorous efforts both in theory and experiment to understand their origins and explore their potential role to biological function. The ultrafast signals resulting from the experiments that show evidence for these coherences result from many contributions to the molecular polarization. Quantum process tomography (QPT) is a technique whose goal is that of obtaining the time-evolution of all the density matrix elements based on a designed set of experiments with different preparation and measurements. The QPT procedure was conceived in the context of quantum information processing to characterize and understand general quantum evolution of controllable quantum systems, for example while carrying out quantum computational tasks. We introduce our QPT method for ultrafast experiments, and as an illustrative example, apply it to a simulation of a two-chromophore subsystem of the FMO photosynthetic complex, which was recently shown to have long-lived quantum coherences. Our FMO model is constructed using an atomistic approach to extract relevant parameters for the simulation of photosynthetic complexes that consists of a quantum mechanics/molecular mechanics approach combined with molecular dynamics and the use of state-of-the-art quantum master equation approaches. We provide a set of methods that allow for quantifying the role of quantum coherence, dephasing, relaxation and other elementary processes in energy transfer efficiency in photosynthetic complexes, based on the information obtained from the atomistic simulations, or, using QPT, directly from the experiment. The possible presence or absence of effects due to correlated protein motion is discussed. The role of non-Markovianity will be discussed. The ultimate goal of the combination of this diverse set of methodologies is to provide a reliable way of quantifying the role of long-lived quantum coherences and obtain atomicistic insight of their causes.

1 Supported by DARPA Quantum Effects in Biological Environments and MIT/Harvard/BNL DOE Center for Excitonicics.

3:06PM L38.00002 Multidimensional electronic spectroscopy of phycobiliproteins from cryptophyte algae, DANIEL TURNER, University of Toronto — We describe new spectroscopic measurements which reveal additional information regarding the observed quantum coherences in proteins extracted from photosynthetic algae. The QPT procedure was conceived in the context of quantum information processing to characterize and understand general quantum evolution of controllable quantum systems, for example while carrying out quantum computational tasks. We introduce our QPT method for ultrafast experiments, and as an illustrative example, apply it to a simulation of a two-chromophore subsystem of the FMO photosynthetic complex, which was recently shown to have long-lived quantum coherences. Our FMO model is constructed using an atomistic approach to extract relevant parameters for the simulation of photosynthetic complexes that consists of a quantum mechanics/molecular mechanics approach combined with molecular dynamics and the use of state-of-the-art quantum master equation approaches. We provide a set of methods that allow for quantifying the role of quantum coherence, dephasing, relaxation and other elementary processes in energy transfer efficiency in photosynthetic complexes, based on the information obtained from the atomistic simulations, or, using QPT, directly from the experiment. The possible presence or absence of effects due to correlated protein motion is discussed. The role of non-Markovianity will be discussed. The ultimate goal of the combination of this diverse set of methodologies is to provide a reliable way of quantifying the role of long-lived quantum coherences and obtain atomicistic insight of their causes.

3:42PM L38.00003 Simulation study of 2D spectrum of molecular aggregates coupled to correlated vibrations, DARIUS ABRAMAVICIUS, VYTAUTAS BUTKUS, LEONAS VALKUNAS, Physics Dept. Vilnius University, SHAUL MUKAMEL, Chemistry Dept. University of California Irvine — Oscillatory dynamics of two-dimensional (2D) spectra of photosynthetic pigment-protein complexes raise the questions of how to disentangle various origins of these oscillations, which may include quantum beats, quantum transport, or molecular vibrations. We study the effects of correlated overdamped fluctuations and under-damped vibrations on the 2D spectra of Fenna-Matthews-Olson (FMO) aggregate, which has well-resolved exciton resonances, and a circular porphyrophyrin aggregate (P6), whose absorption shows vibrational progression. We use a generic exciton Hamiltonian coupled to a bath, characterized by a spectral density. Fluctuations have smooth, while vibrations have $\delta$-type spectral densities. We show how various scenarios of correlated molecular fluctuations lead to some highly oscillatory cross-peaks. Molecular vibrations cause progression of diagonal peaks in the 2D spectrum and make their corresponding cross-peaks highly oscillatory. We, thus, demonstrate that bath fluctuations and molecular vibrations of realistic molecular aggregates are highly entangled in 2D spectroscopy.

1 DA acknowledges grant VP1-3.1-SMM-07-V, SM - the grants CHE0745892 (NSF), DRPA BAA-10-40 QUBE.
3:54PM L38.00004 Coherent Control of Single Molecules at Room Temp, NIEK VAN HULST, DAAN BRINKS, RICHARD HILDNER, ICFO - the Institute of Photonic Sciences (Barcelona) Spain — Electronic coherence plays a key role in natural processes like ultrafast energy transfer and charge separation. Coherent control has proven powerful, however in complex biosystems with different conformations and environments, the intrinsic inhomogeneity of the synchronized subset severely limits the achievable degree of control. The ultimate solution to overcome intrinsic inhomogeneities is the investigation of the behavior of one molecule at a time. Here we report the observation and manipulation of vibrational wave-packet interference and electronic coherence in individual molecules at ambient conditions. Adapting time and phase distribution of the optical excitation field to the dynamics of each molecule we achieve a superior degree of control. The time-phase maps show distinct diversity between different, yet chemically identical, molecules. We induce Rabi-oscillations and control the coherent superposition state in a single molecule. Broadly distributed coherence decay times are found for different individual molecules giving direct insight into the structural heterogeneity of the local surroundings. Our approach allows single-molecule coherent control in a variety of complex inhomogeneous systems and thus to study the role of coherence in energy transfer of single biocomplexes under natural conditions. D.Brink et al. Nature 465, 905 (2010); R.Hildner et al. Nat. Physics doi:10.1038/nphys1858 (2010).

4:06PM L38.00005 Shaped ultrafast pulses for coherent control of energy flow in light harvesting complexes, MOHAN SAROVAR, K. BIRGITTA WHALEY, University of California, Berkeley — We report on preliminary investigations of the use of evolutionary algorithms for the design of shaped femtosecond laser pulses to control energy flow in the Fenna-Matthews-Olson (FMO) light harvesting complex. We shape the experimentally accessible phase degrees of freedom of pulses of various duration and assess the ability to control (i) the exciton population on distinct chromophores, and (ii) the purity of the FMO complex state at short times. We assess the experimental feasibility of the designed pulses and sketch directions for future improvement of the pulse design technique.

We acknowledge support from DARPA under the QuEST program.

4:18PM L38.00006 Towards experimental verifications of the transport mechanisms in light-harvesting dynamics, F. CARUSO, S. MONTANGERO, T. CALARCO, S.F. HUELGA, M.B. PLENIO, Ulm Univ. — Recently, we identified the key mechanisms explaining the very high efficiency and robustness of excitation energy transfer in bacterial photosynthesis, finding that dephasing noise may remarkably enhance the capability of transmitting energy (classical/quantum information) in light-harvesting systems (in communication complex networks [Caruso et al., PRL 2010]), by opening up additional transport pathways and suppressing the ineffective ones. To verify the relevance of such mechanisms in the actual bio-molecular systems, we propose how to gain control over the light-harvesting dynamics by using quantum optimal control tools. In this way, by means of optimally shaped and robust laser pulses, we can: i) faithfully prepare the photosystem in some specific initial state (local site or coherent superposition, e.g. quasi-dark and -bright states), and ii) probe efficiently the dynamics, under realistic experimental conditions, i.e. sample of randomly oriented light-harvesting complexes and extra laser constraints related to an experiment in progress. These results could allow us to more easily discriminate the different transport pathways, to characterize the environmental properties, and so enhance our comprehension of coherent processes in biological complexes.

1 EU Marie-Curie Fellowship

4:30PM L38.00007 Photobiomodulation (PBM) Applications in Ophthalmology, ROBERT DOTSON, Private Medical Practice — In a very real sense, we are all creatures of light. This fact is just now beginning to impact medicine, as quantum theory begins to spread outside the confines of physics and into the life sciences. No longer can living organisms simply be viewed as retorts for biochemical reactions. They also demonstrate an energy component that will prove to be the unifying force of life in all its varied forms. With the advent of this shift in the life sciences, light is becoming an increasingly important diagnostic and therapeutic tool within medicine. Ophthalmologists have long been concerned with light and its application and, consequently, have an interest in the coming scientific revolution, photomedicine. A brief history of the use of low energy light for healing, a review of some of the established cellular effects will be presented. Finally, brief clinical studies will be presented illustrating the benefits of PBM – specifically regarding: corneal healing, glaucoma, and dry age-related macular degeneration. The purpose of this talk is to introduce the emerging field of PBM to the physics community at large.

Tuesday, March 22, 2011 2:30PM - 5:18PM —

2:30PM L39.00001 High-resolution laser-based detection for magnetic tweezers, KEIR NEUMAN, National Institutes of Health — Magnetic tweezers are a versatile and powerful single-molecule manipulation technique capable of applying force and torque on single bio-molecules. They afford several unique advantages over other single-molecule manipulation techniques such as optical tweezers or atomic force microscopy. The hallmark of magnetic tweezers is the ability to twist bio-molecules without the need for complex optical instrumentation. Perhaps less known but of equal significance, magnetic tweezers rely on a slowly decaying magnetic field gradient (1 mm) to impose force so they are intrinsically configured in a passive force clamp mode. These features make magnetic tweezers particularly well suited for the study of nucleic acid structure, DNA topology, and protein-nucleic acid interactions. The one downside to most magnetic tweezers to date is that they rely on video tracking methods to determine the position of the particle. Despite recent progress, the spatial and temporal resolution and accuracy are fundamentally limited by image tracking techniques. I will describe recent improvements utilizing laser-based detection to overcome these limitations. We implemented back-scattered laser-based detection combined with video image tracking to achieve high-resolution, high-bandwidth, three-dimensional position tracking.

3:06PM L39.00002 Massively Parallel Single-Molecule Manipulation Using Centrifugal Force, WESLEY WONG, KEN HALVORSEN, Harvard University — Precise manipulation of single molecules has led to remarkable insights in physics, chemistry, biology, and medicine. However, two impediments have impeded the widespread adoption of these techniques are equipment cost and the laborious nature of making measurements one molecule at a time. To meet these challenges, we have developed an approach that enables massively parallel single-molecule force measurements using centrifugal force [1]. This approach is realized in the centrifuge force microscope, an instrument in which objects in an orbiting sample are subjected to a calibration-free, macroscopically uniform force-field while their micro-to-nanoscopic motions are observed. We demonstrate high-throughput single-molecule force spectroscopy with this technique by performing thousands of rupture experiments in parallel, characterizing force-dependent unbinding kinetics of an antibody-antigen pair in minutes rather than days. Currently, we are taking steps to integrate high-resolution detection, fluorescence, temperature control and a greater dynamic range in force. With significant benefits in efficiency, cost, simplicity, and versatility, single-molecule centrifugation has the potential to expand single-molecule experimentation to a wider range of researchers and experimental systems.

and Manipulation, HAGAR ZOHAR, CRAIG HETHERINGTON, CARLOS BUSTAMANTE, SUSAN MULLER, University of California, Berkeley

We show that single-molecule elasticity enters a linear power-law regime, and then a high-force asymptotic regime well described by the Marko-Siggia wormlike chain model. All told, we observe two transitions between three elastic regimes. We show that the transition forces can be used to determine the polymer's Kuhn length, excluded volume, and entanglement number. Measurements of the distribution of the time to unfold a single-molecule of a given protein under an externally applied force have emerged as an important tool with which to study the mechanical stability and energy landscape of a protein. In such an experiment the protein is potentially subject both to internal fluctuations in structure as well as external fluctuations in temperature and applied force. We report on a theoretical exploration of the effects that each kind of fluctuation may have on the measured lifetime distribution. We show that it is extremely difficult to distinguish internal fluctuations from external fluctuations in the lifetime distribution. We find that the rate distribution has higher sensitivity to the origins of fluctuations. Therefore, we propose an experimental protocol to estimate the approximate magnitude of internal fluctuations by intentionally adding increasing amounts of external fluctuations and measuring the skewness of the resulting rate distribution.

Onset of excluded volume in poly(ethylene oxide) elasticity measurements, ANDREW DITTMORE, Materials Dept., UCSB, DUSTIN B. MCINTOSH, Physics, UCSB, OMAR A. SALEH, Materials Dept., UCSB — We use magnetic tweezers to control tension in an 80 KDa poly(ethylene oxide) (PEG) chain. In good solvent, force effectively transforms the swollen coil into a series of smaller polymers ("tension blobs") and progressively diminishes self-avoidance interactions between distant parts of the chain. Excluded volume effects dominate the low-strain elasticity, where the extension follows a 2/3 power law in force according to scaling predictions. These effects disappear as the polymer first enters a linear power-law regime, and then a high-force asymptotic regime well described by the Marko-Siggia wormlike chain model. All told, we observe two transitions between three elastic regimes. We show that the transition forces can be used to determine the polymer's Kuhn length, excluded volume, and thermal blob size, and find that PEG requires roughly 30 Kuhn lengths before self-avoidance becomes significant. Thus, we show that single-molecule elasticity can quantify the onset of a polymer's excluded volume, a problem that has eluded bulk measurement techniques.

Peptide Nucleic Acids as Tools for Single-Molecule Sequence Detection and Manipulation, HAGAR ZOHAR, CRAIG HETHERINGTON, CARLOS BUSTAMANTE, SUSAN MULLER, University of California, Berkeley — The ability to strongly and sequence-specifically attach modifications such as fluorophores and haptons to individual double-stranded (ds) DNA molecules is critical to a variety of single-molecule experiments. We propose using modified peptide nucleic acids (PNAs) for this purpose and implement them in two model single-molecule experiments where individual DNA molecules are manipulated via microfluidic flow and optical tweezers, respectively. We demonstrate that PNAs are versatile and robust sequence-specific tethers.

Resolving Single Molecule Lysozyme Dynamics with a Carbon Nanotube Electronic Circuit, YONGKI CHOI, ISSA S. MOODY, ISRAEL PEREZ, TATYANA SHEPS, GREGORY A. WEISS, PHILIP G. COLLINS, Depts. of Physics and Astronomy, Chemistry, and Molecular Biology, Univ. of California at Irvine, Irvine, CA 92697 — High resolution, real-time monitoring of a single lysozyme molecule is demonstrated by fabricating nanoscale electronic devices based on single-walled carbon nanotubes (SWCNT). In this sensor platform, a biomolecule of interest is attached to a single SWCNT device. The electrical conductance transduces chemical events with single molecule sensitivity and 10 microsecond resolution. In this work, enzymatic turnover by lysozyme is investigated, because the mechanistic details for its processivity and dynamics remain incompletely understood. Stochastically distributed binding events between a lysozyme and its binding substrate, peptidoglycan, are monitored via the sensor conductance. Furthermore, the magnitude and repetition rate of these events vary with pH and the presence of inhibitors or denaturant agents. Changes in the conductance signal are analyzed in terms of lysozyme's internal hinge motion, binding events, and enzymatic processing.

Mechanical properties of NRR domain from human Notch 1 studied by single molecule AFM force spectroscopy, ROBERT SZOSKIEWICZ, ASHIM DEY, Dept. of Physics, Kansas State University — For proteins in living cells, forces are present from macroscopic to single molecule levels. Single molecule atomic force microscopy in force extension (FX-AFM) mode measures forces at which proteins undergo major conformational transitions with <10 pN force sensitivity (FX-AFM). Here, we present the results of the FX-AFM experiments on a construct comprising the NRR domain from human Notch 1. It is believed that understanding the mechanical properties of Notch at the single molecule level can help to understand its role in triggering some breast cancers. The experimental results on the Notch construct and further analysis revealed several conformational transitions of this molecule under force. These results opened a path for further investigations of Notch constructs at various physiologically relevant conditions.

Non-Perturbative Tracking of Processive DNA Synthesis with Single-Molecule Fluorescence, EVERTT LIPMAN, CHARLES WICKERSHAM† — We have demonstrated recently that double-stranded DNA labeled with a periodic series of fluorescent dyes can be used to track a single helicase. Here we describe how this technique can be modified to follow DNA synthesis. By means of a stepwise loss of fluorescence during strand displacement, we monitor processive motion of a single φ29 DNA polymerase without labeling or altering the enzyme or the template strand, and without applying any force. We observe a wide range of speeds, with the highest exceeding by several times that observed in other single-molecule experiments. Because this method enables repeated observations of the same polymerase traversing identical segments of DNA, it should prove useful for studying sequence-specific effects in DNA replication and transcription.

Present address: California Institute for Quantitative Biomedical Research, UC Berkeley
4:42PM L39.00010 Single molecule studies reveal new mechanisms for microtubule severing¹, JENNIFER ROSS, JUAN DANIEL DIAZ-VALENCIA, MARGARET MORELLI, UMass Amherst, DONG ZHANG, DAVID SHARP, AECOM — Microtubule-severing enzymes are hexameric complexes made from monomeric enzyme subunits that remove tubulin dimers from the microtubule lattice. Severing proteins are known to remodel the cytoskeleton during interphase and mitosis, and are required in proper axon morphology and mammalian bone and cartilage development. We have performed the first single molecule imaging to determine where and how severing enzymes act to cut microtubules. We have focused on the original member of the group, katanin, and the newest member, fidgetin to compare their biophysical activities in vitro. We find that, as expected, severing proteins localize to areas of activity. Interestingly, the association is very brief: they do not stay bound nor do they bind cooperatively at active sites. The association duration changes with the nucleotide content, implying that the state in the catalytic cycle dictates binding affinity with the microtubule. We also discovered that, at lower concentrations, both katanin and fidgetin can depolymerize taxol-stabilized microtubules by removing terminal dimers. These studies reveal the physical regulation schemes to control severing activity in cells, and ultimately regulate cytoskeletal architecture.

1This work is supported by the March of Dimes Grant #5-FY09-46.

4:54PM L39.00011 Polymer Nanocomposites as a Facile Method for Engineering Acto-Myosin Networks at the Interface, MATTHEW CAPORIZZO, University of Pennsylvania Department of Materials Science and Engineering, YUJIE SUN, YALE GOLDMAN, University of Pennsylvania Department of Physiology, RUSSELL COMPOSTO, University of Pennsylvania Department of Materials Science and Engineering. NANO-BIO INTERFACE CENTER COLLABORATION — Filamentous actin acts as the rails for the molecular motor myosin in muscle contraction and intercellular mass transport. Consequently, understanding the process by which actin organizes, polymerizes, and binds is fundamental for the design of myosin based actuators capable of responding to external stimuli. Starting with atomically smooth, freshly cleaved mica optically coupled to glass slides, a random copolymer nanoparticle composite is engineered for in situ single molecule TIRF/AFM studies with controlled roughness, electrostatic binding strength, and binding site density. Four distinct regimes of actin binding are observed: no attachment, end-on attachment, weak side-on attachment, and side-on immobilization. Transitions between regimes are likely to mark competition between the affinity to charged nanoparticles and the inherent resistance of the semi-rigid filaments to bending. Surface conditions optimal for actin immobilization are identified, and Myosin V stepping kinetics are studied on the artificially immobilized filaments, confirming filament support of motility. Supported by NSF grant DMR-0425780.

5:06PM L39.00012 Electrostatic Effects on the Elasticity of Single ssDNA Molecules, DUSTIN B. MCINTOSH, OMAR A. SALEH, University of California Santa Barbara — Nucleic acids are highly-charged polyelectrolytes whose structure and function strongly depend on the concentration and type of salt ions in solution. We have created a simple experimental system for studying nucleic acid/ion interactions, based on magnetic-tweezer measurements of the elasticity of single denatured ssDNA molecules in solutions with a known salt concentration. Using this system, we were able to reconcile single-molecule force-extension data with scaling theories of self-avoiding polymers, and we found that the Kuhn length of ssDNA scales with the Debye length in NaCl solutions. (Saleh et al., PRL 102, 068301 (2009)). Here, we use the system to investigate interactions of ssDNA with multivalent salts. We find that, in divalent salt, ssDNA elasticity is qualitatively similar to that in monovalent salt, but with significant quantitative differences. Notably, at low ionic strength, ssDNA in divalent salt maintains the same low-force scaling behavior (“Pinus blob” regime) as seen in monovalent salts. However, there are differences in the elastic behavior at high forces (> a few pN). In addition, analysis of the low-force scaling behavior indicates it requires ~100 fold smaller concentrations of divalent salt to condense ssDNA. We discuss the data in the context of electrostatic theories, including Debye-Huckel, as well as bulk experiments on similar systems.

Tuesday, March 22, 2011 2:30PM - 5:30PM — Session L41 DCP: Condensed Phase Dynamics and Structure A115/117

2:30PM L41.00001 Temperature and Lengthscale Dependence of Solvophobic Solvation in a Water-like Liquid, JOHN DOWDLE, PETER ROSSKY, University of Texas at Austin — Temperature and lengthscale dependence of the solvation of cavity solutes is investigated along the saturation curve of the Jagla liquid, a simple liquid consisting of particles that interact via a spherically symmetric potential combining hard and soft core interactions. The results are compared with an identical calculation for a model of a typical atomic liquid, the Lennard-Jones potential, and with predictions for cavity solubilities in water made by the recently developed cavity equation of state. We find that the Jagla liquid captures the qualitative thermodynamic behavior of hydrophobic hydration as a function of temperature for both small and large lengthscale solutes. The results suggest that a competition between two length scales that favors low-density open structures at temperature is decreased is an essential interaction of a liquid that models hydrophobic hydration.

2:42PM L41.00002 Effects of Physical Confinement on the Hysteresis between Melting and Freezing Temperatures of Decanol¹, SAMUEL AMANUEL, JARGALSAIKHAN DULMAA, AMER KHRAISAT, Department of Physics and Astronomy, Union College, Schenectady, NY 12308 — There is substantial evidence that physical confinement alters melting and freezing temperatures of materials. These have been qualitatively explained using free energy considerations. However, it is not clear how physical confinement influences melting and freezing when the bulk material itself exhibits substantial supercooling. Bulk 2-decanol, for instance, exhibits substantial hysteresis between its melting (approximately -23°C) and freezing (-3°C) temperatures. Evidently, both its melting and freezing temperatures are influenced by physical size. However, the hysteresis between the freezing and melting temperatures seems less sensitive to physical size. This may be the result of differences in homogeneous versus heterogeneous nucleation in physically confined 2-decanol.

¹This work has been supported by Faculty Research Fund, Union College.

2:54PM L41.00003 Evaluating the Liquid Liquid Phase Transition Hypothesis of Supercooled Water, DAVID LIMMER, DAVID CHANDLER, University of California, Berkeley — To explain the anomalous behavior of supercooled water it has been conjectured that buried within an experimentally inaccessible region of liquid water’s phase diagram there exists a second critical point, which is the terminus of a first order transition line between two distinct liquid phases. The so-called liquid-liquid phase transition (LLPT) has since generated much study, though to date there is no consensus on its existence. In this talk, we will discuss our efforts to systematically study the metastable phase diagram of supercooled water through computer simulation. By employing importance-sampling techniques, we have calculated free energies as a function of the density and long-range order to determine unambiguously if two distinct liquid phases exist. We will argue that, contrary to the LLPT hypothesis, the observed phenomenology can be understood as a consequence of the limit of stability of the liquid far away from coexistence. Our results suggest that homogeneous nucleation is the cause of the increased fluctuations present upon supercooling. Further we will show how this understanding can be extended to explain experimental observations of hysteresis in confined supercooled water systems.
3:06PM L41.00004 Anomalous lattice parameter isotope-shift in hexagonal ice Ih from first principle calculations1, BETÜL PAMUK, MARIVI FERNANDEZ-SERRA, PHILIP ALLEN, Stony Brook University — The lattice parameters of light (H2O) and heavy (D2O) ice Ih differ by 0.09% [1]. The larger lattice constant is that of the heavier isotope, contrary to normal expectations. This isotope shift of the lattice constant is linked to the zero point energy of phonons in ice. In particular, it can be linked to the anti-correlation of the O-H stretch frequency and the O-O distance in H-bonded materials. In order to determine which phonons give the anomaly, we calculate Grünewald parameters of H2O and D2O ice using first principles density functional theory, within the frozen phonon approximation. Our results show a strong dependence on the density functional chosen. We analyze these differences and make connections to experiment. These results indicate that not only H-bond effects but also van der Waals interactions are necessary to reproduce the correct lattice constant zero-point shifts in ice.


This work is supported by DOE award numbers DE-FG02-08ER46550 and DE-SC0003871.

3:18PM L41.00005 Local effects in the X-ray absorption spectrum of salt water, ERIC SCHWEGLER, Lawrence Livermore National Laboratory, HEATHER KULIK, Stanford University, NICOLA MARZARI, University of Oxford, ALFREDO CORREA, Lawrence Livermore National Laboratory, DAVID PRENDERGAST, Lawrence Berkeley National Laboratory, GIULIA GALLI, UC Davis — We have used first principles molecular dynamics and theoretical X-ray absorption spectroscopy (XAS) to investigate the aqueous solution of cations in MgCl2, CaCl2, and NaCl solutions. We focus our discussion on the species-specific effects that Mg2+, Ca2+, and Na+ have on the X-ray absorption spectrum of the respective solutions. For the divalent cations, we find that the water molecules form a rigid first solvation shell around Mg2+ and a more flexible solvation shell around Ca2+ also exhibit differing hydrogen bonding characteristics. Acceptor hydrogen bonds present in the water surrounding Ca2+ enhance a post-edge peak near 540 eV in the XAS spectrum, while the absence of such hydrogen bonding features for the first shell surrounding Mg2+ corresponds to a diminished intensity at the post-edge peak. For Na+, we find that a broad tilt angle distribution results in broadened post-edge features, despite donor-and-acceptor populations comparable to Ca2+. We present re-averaged spectra of the MgCl2, CaCl2, and NaCl solutions that provide an explanation of concentration-dependent features that have been found in corresponding experimental measurements.

3:30PM L41.00006 Nuclear momentum distribution and potential energy surface in hexagonal ice1, LIN LIN, Princeton University, JOSEPH MORMONE, Columbia University, ROBERTO CAR, Princeton University, MICHELE PARRINELLO, ETH Zurich — The proton momentum distribution in ice Ih has been recently measured by deep inelastic neutron scattering and calculated from open path integral Car-Parrinello simulation. Here we report a detailed investigation of the relation between momentum distribution and potential energy surface based on both experiment and simulation results. The potential experienced by the proton is largely harmonic and characterized by 3 principal frequencies, which can be associated to weighted averages of phonon frequencies via lattice dynamics calculations. This approach also allows us to examine the importance of quantum effects on the dynamics of the oxygen nuclei close to the melting temperature. Finally we quantify the anharmonicity that is present in the potential acting on the protons.

This work is supported by NSF and by DOE.

3:42PM L41.00007 The quantum nature of the hydrogen bond: insight from path-integral molecular dynamics, BREN T WALKER, XIN-ZHENG LI, ANGELOS MICHAELIDES, London Centre for Nanotechnology and Department of Chemistry, University College London, London WC1E 6BT, U.K — Hydrogen (H) bonds are weak, generally intermolecular bonds, that hold together much of soft matter, the condensed phases of water, network liquids, and many ferroelectric crystals. The small mass of H means H-bonds are inherently quantum mechanical; effects such as zero point motion and tunneling should be considered, although often are not. In particular, a consistent picture of quantum nuclear effects on the strength of H-bonds and consequently the structure of H-bonded systems is still absent. Here, we report ab initio path-integral molecular dynamics studies on the quantum nature of the H-bond. Systematic examination of a range of H-bonded systems shows that quantum nuclei weaken weak H-bonds but strengthen relatively strong ones. This correlation arises from a competition between anharmonic intermolecular bond bending and intramolecular bond stretching. A simple rule of thumb enables predictions to be made for H-bonded bonded materials in general with merely classical knowledge (e.g. H-bond strength or H-bond length). Our work rationalizes the contrasting influence of quantum nuclear dynamics on a wide variety of materials, including liquid water and HF, and highlights the need for flexible molecules in force-field based studies of quantum nuclear dynamics.

3:54PM L41.00008 Hydration phase diagram for BaO terminated BaTiO3, JOHN MARK MARTIREZ, Department of Chemistry, University of Pennsylvania, WISSAM AL-SAIDI, Department of Chemical and Petroleum Engineering, University of Pittsburgh, ANDREW RAPPE, Department of Chemistry, University of Pennsylvania — This study reveals geometries H2O adopts upon adsorption on BaO terminated BaTiO3(BTO) at low to high saturation. A hydration phase diagram for the aforementioned termination is presented, for moderate temperatures, and moderate to ultra high vacuum H2O pressures. Calculations suggest a very stable H2O adsorption for wide range of pressures, including high vacuum conditions (pH2O 10^-12 bar). This opens venues for mechanistic studies and hopefully will serve as a guide to condition that might suppress H2O adsorption on BTO for applications where it is undesired.

The authors acknowledge support from the AFOSR under Grant FA9550-07-1-0397, from the DOE under Grant DE-FG02-08ER15920, and computational support from the HPCMO.

4:06PM L41.00009 ABSTRACT WITHDRAWN —

4:18PM L41.00010 Topological reaction coordinates to explore the structure of atomic clusters and organic molecule isomers from first principles, FABIO PIETRUCCI, CECAM EPF Lausanne (CH), WANDA ANDREONI, CECAM and Institut de Théorie des Phénomènes Physique EPF Lausanne (CH) — We introduce a simple reaction coordinate based on spectral graph theory which describes the topology of the network of chemical bonds around a given atom. We employ the reaction coordinate in combination with DFT-based first-principles metadynamics to systematically explore the possible structures of silicon and carbon clusters (including fullerene-like cages) for sizes of tens of atoms. From our extensive exploration we are able to estimate the fractal dimension of the configuration space, which both for silicon and carbon clusters turns out to be quite low. Using the same approach we simulate the interconversion among a large number of chemically relevant organic molecules which are isomers of the C4H8N formula unit, and we demonstrate the possibility of automatically exploring isomerisation, association, and decomposition reactions without prior knowledge of the products involved.
Transport through a quantum dot with excitonic dot-lead coupling

ELSTE, DAVID R. REICHMAN, ANDREW J. MILLIS, Columbia University — We study the effect of a Coulombic dot-lead interaction on transport through a quantum dot hybridized to two Luttinger-liquid leads. A bosonization approach is applied to treat the interaction between charge fluctuations on the dot and the dynamically generated image charge in the leads. The nonequilibrium distribution function of the dot and the tunneling current are computed within a master-equation approach. Particular attention is paid to two situations: (i) a quantum dot placed between two leads such that it cuts the Luttinger liquid into two semi-infinite quantum wires; (ii) a quantum dot side-hybridized to two parallel infinite quantum wires. The presence of the excitonic dot-lead coupling is found to enhance transport in the vicinity of the Coulomb-blockade threshold. This behavior is in contrast to the usual power-law suppression of electronic tunneling which is found if this interaction is ignored.

AJM acknowledges support from NSF-DMR-0705847 and FE from the Deutsche Forschungsgemeinschaft.


Spectroscopic and Theoretical Investigations of the Potential Energy Surfaces of Molecules with Intramolecular \( \pi \)-type Hydrogen Bonding

OCOLA, HEE-WON SHIN, AB-DULAZIZ AL-SAADI, JAAN LAANE, Texas A&M University — Spectroscopic methods and theoretical calculations have been utilized to investigate the conformations of several cyclic organic molecules. The laser induced fluorescence (LIF) spectra of 2-indanol show the presence of four conformations. The one with intramolecular hydrogen bonding between the –OH group and the benzene ring is of lowest energy. The potential energy surface (PES) in terms of the ring puckering and internal rotational vibrations, which govern the conformational changes, was determined. 3-Cyclopeten-1-ol presents a similar PES as established from its infrared and Raman spectra and theoretical calculations. This PES also shows the presence of four conformations. The \( \pi \)-bonding conformer lies at lowest energy. LIF has been used to study the conformational energies of 2-hydroxytetralin, and 2-cyclohexenol has been investigated by infrared and Raman techniques. The analyses of the hydrogen bonding in these molecules as well as in a dozen others were supported by both \textit{ab initio} and DFT calculations.

Supported by R.A. Welch grant A-0396.

Raman Spectra and the Potential Energy Function for the Internal Rotation of 1,3-Butadiene and its Isotopomers

LAANE, PRAVEENKUMAR BOOPALACHANDRAN, Texas A&M University, NORMAN CRAIG, Oberlin College — The gas-phase Raman spectra of 1,3-butadiene-\( d_0 \), 2,3-\( d_2 \), 1,1,4,4-\( d_4 \), and \( d_6 \) have been collected with CCD detection with numerous scans of ten hours or more. For each isotopomer eight Raman transitions in the 240-330 cm\(^{-1} \) region corresponding to double quantum jumps of the \( A_u \) internal rotation (\( \nu_{13} \)) were observed for the \( \text{trans} \) conformer. Weaker bands in the 170-260 cm\(^{-1} \) region were assigned to the \( \text{gauche} \) conformation, which lies at higher electronic energy. A potential function for the internal rotation, which fits the data for all the isotopomers, was determined. This function shows the \( \text{gauche} \) form to be 966 cm\(^{-1} \) higher in energy and the barrier between the \( \text{trans} \) and \( \text{gauche} \) structures to be 2055 cm\(^{-1} \). The \( \text{cis} \) structure has an energy 408 cm\(^{-1} \) higher than the \( \text{gauche} \). Fourteen combination band or hot band series involving \( \nu_{13} \) for the \( \text{trans} \) conformer were also observed, and these allow the internal rotation levels in various excited vibrational states to be determined.

Supported by R.A. Welch grant A-0396.

Transition and Excited States of 1,1'-azo-bis-1,2,3-triazole

GONCHAROV, VLADIMIR, Vanderbilt University, OLGA GONCHAROVA, Vertex Pharmaceuticals Inc., KALMAN VARGA, Vanderbilt University — A novel photochromic molecule has been recently synthesized. The photoinduced trans-azo-bis-1,2,3-triazole molecule is efficiently controlled by a xenon flash lamp suggesting a potential in photonic and molecular mechanics applications. We perform a synergistic quantum molecular dynamics (QMD), real-time dependent density functional theory (TDDFT) and TDDFT- perturbation theory study to capture and elucidate the transition state, excitation energies and optical properties of the molecule. We also use it to perform test of recently developed real-time TDDFT method to calculate hyperpolarizabilities and compare results with the Sternheimer method.

Yu-Chuan Li et al. J. Am. Chem. Soc., 2010, 132, 12172


Importance of Electronic Relaxation for Inter-Coulombic Decay in Aquous Systems

PRENDERGAST, DAVID, Molecular Foundry, Lawrence Berkeley National Laboratory (LBNL), CRAIG P. SCHWARTZ, RICHARD J. SAYKALLY, Chemistry Dept., University of California, Berkeley and Chemical Sciences, LBNL, SHEHRIN FATEHI, Kenneth S. Pitzer Center for Theoretical Chemistry, University of California, KEITH V. LAWLER, Chemical Sciences, LBNL, C. WILLIAM MCCURDY, Chemical Sciences, LBNL and Departments of Applied Science and Chemistry, University of California, Davis — Inspired by recent photoelectron spectroscopy experiments on hydroxide solutions, we have examined the conditions necessary for enhanced (and, in the case of solutions, detectable) intermolecular Coulombic decay (ICD) – Auger emission from an atomic site other than that originally excited. We present general guidelines, based on energetic and spatial overlap of molecular orbitals, for this enhancement of ICD-based energy transfer in solutions. These guidelines indicate that this decay process should be exhibited by broad classes of biomolecules and suggest a design criterion for targeted radiooncology protocols. Our findings indicate that ICD processes in hydroxide solutions are not dependent on hydroxide hydrogen bond donation.

Supported by DOE BES Contract No. DE-AC02-05CH11231.

Wednesday, March 23, 2011 8:00AM - 10:48AM – Session P38 DCP DBP: Focus Session: Quantum Coherence in Biology III A130/131
8:00AM P38.00001 Barrier compression and tunneling in enzyme catalysed reactions. NIGEL SCRUTTON, University of Manchester — Nuclear quantum mechanical tunneling is important in enzyme-catalysed H-transfer reactions. This viewpoint has arisen after a number of experimental studies have described enzymatic reactions with kinetic isotope effects that are significantly larger than the semi-classical limit. Other experimental evidence for tunneling, and the potential role of promoting vibrations that transiently compress the reaction barrier, is more indirect, being derived from the interpretation of e.g. mutational analyses of enzyme systems and temperature perturbation studies of reaction rates/kinetic isotope effects. Computational simulations have, in some cases, determined excited kinetic isotope effects and tunneling contributions, and identified putative promoting vibrations. In this presentation, we present the available evidence – both experimental and computational – for environmentally-coupled H-tunneling in several enzyme systems, from our recent work on redox enzyme systems. We then consider the relative importance of tunneling contributions to these reactions. We find that the tunneling contribution to these reactions confers a rate enhancement of approx. 1000-fold. Without tunneling, a 1000-fold reduction in activity would seriously impair cellular metabolism. We infer that tunneling is crucial to host organism viability thereby emphasising the general importance of tunneling in biology.

8:36AM P38.00002 The control of electron transfer pathways in biomolecular systems: the role of fluctuations. SPIROS SKOURTIS, Department of Physics, University of Cyprus — Electron transfer reactions are ubiquitous in biology. They are observed in both protein and DNA systems. Biological electron transfer mechanisms range from tunnelling to thermally activated hopping. Due to the floppiness of biomolecules, molecular motion is an important determinant of the electron transfer rate. The electronic couplings that enable electron transfer in biomolecular systems can be understood in terms of competing and interfering electron transfer pathways that are controlled by structure, dynamics, and initial state preparation. We review recent theoretical progress on the effects of conformational distributions, excited-state polarization, and electron-nuclear dynamics on tunneling electron transfer reactions in different biomolecular systems. We discuss how highly fluctuating-transfer-rate control can be achieved in the presence of a highly fluctuating environment.


9:12AM P38.00003 A molecular breakwater enhances electron transfer between proteins. NATHAN S. BABCOCK, University of Calgary, AURÉLIEN DE LA LANDE, Universite Paris-Sud, JAN REZÁČ, Academy of Sciences of the Czech Republic, BARRY C. SANDERS, DENNIS R. SALAHUB, University of Calgary — Does natural selection optimize molecular biomachinery at the quantum level? We present statistical characterizations of molecular dynamics at an interprotein electron transfer (ET) interface. In simulations of the wild-type protein complex, we find that the most frequently occurring molecular configurations afford superior electronic coupling due to the consistent presence of a single water molecule hydrogen-bonded between the donor and acceptor sites. We attribute the persistence of this water bridge to a "molecular breakwater" composed of several hydrophobic residues surrounding the acceptor site. The breakwater supports the function of solvent-organizing residues by limiting the exchange of water molecules between the sterically constrained ET region and the surrounding bulk. When the breakwater is affected by a mutation, bulk solvent molecules disrupt the water bridge, resulting in reduced electronic coupling. These results suggest that protein surface residues may stabilize interprotein solvent dynamics to enable coherent ET along a single molecular pathway.

9:24AM P38.00004 Mixed quantum classical simulations of vibrational energy transport in alpha-helices\textsuperscript{3}. ANNE GOJ, ERIC BITTNER, University of Houston — We use mixed classical/quantum simulations to study the time dependence of an excitation of a C=O vibration on a 3-10 helix of \textalpha-Aminoisobutyric acid (AIB), a system which represents a test case for the formation of self-trapped vibrational excitation states on protein helices. Due to the inherent disorder in the system caused by the finite temperature and fluctuations in hydrogen bonding, the excitation tunnels randomly among C=O sites along the helix. Quantum forces are insufficient to establish a coherent relationship between the location of the excitation and the contraction of hydrogen bonds around this site. Our simulations indicate that the excitation frequently becomes localized on the end of the helix due to the defect in helical structure caused by unwinding. Our results generally do not support the existence of Davydov type solitons in biological helix systems under physiological conditions.

\textsuperscript{3}This work was funded by the National Science Foundation (CHE-1011894) and the Robert Welch Foundation (E-1334).


\textsuperscript{1}With many thanks to the Wellcome Trust

10:12AM P38.00006 Recent developments in the physics of your sense of smell\textsuperscript{2}. ANDREW HORSFIELD, Imperial College London. LUCA TURIN, MIT, YEONG-AH SOH, Imperial College London, MARION SOURIBES, MARSHALL STONEHAM, LIANHENG TONG, PAUL WARBURTON, UCL — A radical proposal in 1996 [L. Turin, Chem. Senses 21, 773 (1996)] was that human olfactory receptors use phonon assisted electron tunnelling to probe the vibrational spectrum of odorants in order to determine their chemical identity. A development of this model [J. C. Brookes et al., Phys. Rev. Lett., 98, 038101 (2007)] showed that this Turin mechanism is indeed physically possible, even robust, but left a number of questions open. One such question is: between which sites does the tunnelling electron pass? Our recent calculations support a particular pair of likely sites. Because of the complexity of biological environments, probing the receptor is difficult. Thus we have begun to investigate the properties of a semiconductor nanowire device that mimics the key processes [A. P. Horsfield et al., J. Appl. Phys., 108, 014511 (2010)]. We will present the latest findings of this study.

\textsuperscript{2}This work is supported by DARPA (Grant N66001-10-1-4062), EPSRC (Grant No. EP/H005544/1) and AFOSR (Grant No. FA8655-08-1-3082).
Depending on the direction of non-radiative processes, such optoelectronic structures could work both in photovoltaic as well as in light emitting modes.

The carrier multiplication (CM) is the process of production of two or more electron-hole pairs (excitons) per single absorbed photon. Detailed understanding of the mechanisms of this process is of importance for developing novel cheap and efficient photovoltaic devices.

The coupling between two receptor subunits and allosterically modulate the response to GABA. If this idea is correct, benzodiazepines should not only be regarded as keys fitting into a lock, but also as one-electron chemical field-effect transistors fitting into an electronic circuit.

This research was supported by the Department of Energy, Office of Basic Energy Sciences and the National Science Foundation.

Wednesday, March 23, 2011 8:00AM - 11:00AM — Session P41 DCP: Focus Session: Fundamental Issues in Interfacial Charge Transport for Energy Applications I A115/117

8:00AM P41.00001 Excitons at Interfaces , XIAOYANG ZHU, University of Texas at Austin — Solar photovoltaics based on molecular and nano materials commonly involve excitons. This results from strong Coulomb attraction between an electron and a hole due to the low dielectric constants of molecules or quantum confinement of nano materials. In this lecture, I will address the question of how excitons dissociate at donor/acceptor interfaces. The first example deals with charge separation in organic photovoltaics. Due to the low dielectric constant of organic materials, an electron-hole pair across an organic donor/acceptor interface is bound by the Coulomb potential. This gives rise to a set of H-atom like states called charge-transfer excitons, as observed experimentally. The lowest energy charge transfer exciton state has a binding energy much higher than kT at room temperature. This leads to the conclusion that hot charge transfer exciton states must be involved in charge separation in organic photovoltaics.

8:36AM P41.00002 The Effect of Photoexcitation and Population Relaxation on Carrier Multiplication Efficiency in Semiconductor Nanocrystals and Bulk , ANDREI PIRYATINSKI, KIRILL VELIZHANIN, Los Alamos National Laboratory — The carrier multiplication (CM) is the process of production of two or more electron-hole pairs (excitons) per single absorbed photon. Detailed understanding of the mechanisms of this process is of importance for developing novel cheap and efficient photovoltaic devices. To model the CM dynamics, we have developed an exciton scattering model which accurately treats the contributions of different multi-exciton generation pathways on the CM rate. Furthermore, the model allows one to study CM in nanocrystalline and bulk semiconductor materials. Using this model, we performed a numerical study of photogeneration and population relaxation processes contributing to CM in PbSe nanocrystals and bulk. It is found that the photogeneration provides small contribution to the total quantum efficiency compared to the population relaxation process. The resonant incoherent bie exciton production is found to be the main mechanism of CM in both cases of direct bie exciton photogeneration and during the population relaxation. Comparison to the published experimental data shows that the calculations reproduce experimentally observed trends providing insight into the mechanisms of CM.

9:00AM P41.00004 Non-radiative Energy Transfer in Colloidal Nanocrystals/Silicon Hybrid Structures , HUE MINH NGUYEN, The University of Texas at Dallas, Department of Physics, OLIVER SEITZ, DAMIEN AUREAU, AMANDEEP SRA, YVES CHABAL, The University of Texas at Dallas, Department of Materials Science, ANTON Malko, The University of Texas at Dallas, Department of Physics — The integration of organic and inorganic materials at the nanoscale offers the possibility of developing new photonic devices that could potentially combine the advantages of both classes of materials. Such optoelectronic structures could work both in photovoltaic as well as in light emitting modes depending on the direction of non-radiative exciton energy transfer (NRET). In present work, we studied hybrid structures consisting of a monolayer of the colloidal nanocrystal quantum dots (NQDs) grafted on hydrogenated Si surface via amine modified carboxy-alkyl chains linkers. Such approach allowed us to passivate Si surface to suppress non-radiative surface state defects ($N_{SS} < 10^{11}$ cm$^{-2}$) and provided with the controllable spacer lengths between NQDs and Si. We performed systematic measurements of NRET via time-resolved and steady-state photoluminescence (PL) in the range of 10K to 300K and as a function of spacer lengths and quantified NRET rates. Local field effects due to the acceptor surface (Si) are discussed.

1Supported by the Office of Basic Energy Sciences of the US Department of Energy
9:36AM P41.00005 Ab initio theory of impact ionization applied to silicon nanocrystals1. MARTON VOROS, Budapest University of Technology and Economics, ADAM GALLI, Hungarian Academy of Sciences, Research Institute for Solid State Physics and Optics, DARIO ROCCA, GERGELY ZIMANYI, GIULIA GALLI, UC Davis — Abstract. We present a multi-exciton formation (MEG) in semiconducting nanocrystals may lead to overcome the well-known Shockley-Queisser limit when building semiconductor-based solar cells. A thorough, theoretical understanding of the experiments that reported MEG in e.g. Si and PbSe nanocrystals, is still missing and could significantly contribute to clarify the several controversial results in the field.

9:48AM P41.00006 Optical properties of crystalline and amorphous silicon slabs with adsorbed metal clusters and with dopants: A combined ab-initio electronic structure and density matrix treatment1. DIMITRI KILIN, University of South Dakota, DAVID MICHA, JESSICA RAMIREZ, University of Florida — Abstract. The optical absorbance and surface photovoltage of slabs of Si with varying number of layers have been calculated starting from their atomic structure. Results have been obtained for nanostructured surfaces with adsorbed metal clusters and for group III and V dopants, from ab initio DFT with periodic boundary conditions for extended systems, and from time-dependent DFT for supercells. Density matrix equations of motion (EOM) have been parametrized in a basis set of Kohn-Sham orbitals, for both crystalline and amorphous Si slabs [1]. Results for properties and from electronic charge distributions provide insight on slab confinement effects for electronically excited states and for particle-hole creation. In addition, the integrodifferential EOMs have been solved for an initial femtosecond pulse excitation [2] to analyze the nature of electron transfer at the surfaces, relevant to photovoltaics.

1Support from Grant NSF DMR-1035468 is acknowledged.

10:00AM P41.00007 Ultrafast Single and Multiple Exciton Dissociation in CdSe and PbS Quantum Dots1. TIANQUAN LIAN, Emory University — Abstract. Charge transfer to and from quantum dots (QDs) is of intense interest because of its important roles in QD-based devices, such as solar cells and light emitting diodes. Recent reports of multiple exciton generation (MEG) by one absorbed photon in some QDs offer an exciting new approach to improve the efficiency of QD-based solar cells and to design novel multi-electron/hole photocatalysts. However, two main challenges remain. First, the efficiency of MEG process remains controversial and may need to be significantly improved for practical applications. Second, the utilization of the MEG process requires ultrafast exciton dissociation prior to the exciton-exciton annihilation process, which occurs on the 10 s to 100 s ps time scale. In this presentation we report a series of studies of exciton dissociation dynamics in quantum dots by electron transfer to adsorbed electron acceptors. We show that excitons in CdSe can be dissociated on the a few picosecond timescale to various adsorbates. As a proof of principle, we demonstrated that multiple excitons (generated by multiple photons) per QD can be dissociated by electron transfer to adsorbed acceptors (J. Am. Chem. Soc. 2010, 132, 4858-4864). We will discuss the dependence of these rates on the size and the nature of the quantum dots and possible approaches to optimize the multiple exciton dissociation efficiency.

1This work is supported by the NSF and by the Dreyfus Foundation to DM.

10:36AM P41.00008 Short time evolution of electronic charge transfer and separation, and quantum coherences, at photoexcited crystalline and amorphous Si surfaces: Adsorbate and dopant effects1. DAVID MICHA, ANDREW LEATHERS, University of Florida, DMITRI KILIN, University of South Dakota — Abstract. The short time evolution of populations of electronic states and their quantum coherence at nanostructured surfaces of semiconductors provide insight on mechanisms of electronic charge transfer and separation. Starting from atomic structure, density matrix (DM) equations of motion (EOM) have been generated from a general formulation of dissipative quantum dynamics and have been parametrized in a basis set of Kohn-Sham orbitals, for both crystalline and amorphous Si slabs [1] with metal cluster adsorbates and with group III and V dopants. Integrodifferential EOMs have been solved for an initial ground state excited by femtosecond light pulses [2] to provide the time evolution of direct and indirect electron transfer at the surfaces. Results show that one of the transfer mechanisms can lead to long term separation of electronic charge, and what material properties contribute to large charge transfer and separation.

1This work is supported by the NSF Chemistry Division and by the Dreyfus Foundation to DM.

10:48AM P41.00009 Investigation of electron-hole recombination in multi-layered quantum dots using explicitly correlated wavefunction based methods1. ARINDAM CHAKRABORTY, Syracuse University — Abstract. Electron-hole pairs are generated by photoexcitation of electrons to excited electronic states. Accurate calculations of electron-hole binding energies and recombination probabilities can give important insights into the photovoltaic properties of semiconductor quantum dots. In the present work, the challenge of accurate treatment of electron-hole correlation is addressed by developing explicitly correlated electron-hole wavefunction that depends on electron-hole interparticle distance. The explicitly correlated ansatz for the electron-hole wavefunction is used to calculate eigenvalues and eigenfunction of the electron-hole Hamiltonian in multi-layered quantum dots using self-consistent field (SCF) and configuration interaction (CI) techniques. These methods are applied to investigate influence of the core/shell structure and chemical composition on electron-hole binding energies and recombination probabilities. The calculations indicate that for a given chemical composition there exists a optimum core/shell structure that minimizes electron-hole recombination. Comparison with experimental studies on similar system show good agreement between the experimental and computed results.
11:15AM Q7.00001 Does Tumor Development Follow a Programmed Path?1, ROBERT AUSTIN, Princeton University — The initiation and progression of a tumor is a complex process, resembling the growth of a embryo in terms of the stages of development and increasing differentiation and somatic evolution of constituent cells in the community of cells that constitute the tumor. Typically we view cancer cells as rogue individuals violating the rules of the games played within an organism, but I would suggest that what we see is a programmed and algorithmic process. I will then question if tumor progression is dominated by the random acquisition of successive survival traits, or by a systematic and sequential unpacking of "weapons" from a pre-adapted "toolkit" of genetic and epigenetic potentialities? Can we then address this hypothesis by data mining solid tumors layer by layer?

1Support of the NSF and the NCI is gratefully acknowledged.

11:51AM Q7.00002 Adaptation Driven by Spatial Heterogeneities1, RUTGER HERMSEN, Center for Theoretical Biological Physics, University of California, San Diego, CA, USA — Biological evolution and ecology are intimately linked, because the reproductive success or "fitness" of an organism depends crucially on its ecosystem. Yet, most models of evolution (or population genetics) consider homogeneous, fixed-size populations subjected to a constant selection pressure. To move one step beyond such "mean field" descriptions, we discuss stochastic models of evolution driven by spatial heterogeneity. We imagine a population whose range is spatially varying environmental parameter, such as a temperature or the concentration of an antibiotic drug. Individuals in the population replicate, die and migrate stochastically. Also, by mutation, they can adapt to the environmental stress and expand their local range. Thus, the framework explicitly demonstrates a profound connection to many fundamental concepts in physics, as such stochastic processes are testable. In this talk, I will present a positive answer to this calling. I will explain on our construction of endogenous network theory based on molecular-cellular and other genetic/genomic effects and to environmental factors. Furthermore, such framework can be made quantitative and with predictions experimentally testable. Naturally questions have been asked that whether it is possible to develop alternative frameworks such that they can connect both to mutations and Progression: beyond "cancer as diseases of genome"

References:

1This work was supported by the Center for Theoretical Biological Physics sponsored by the National Science Foundation (NSF) (Grant PHYS-0822283).

12:27PM Q7.00003 Experimental Ignition of Evolution on Fitness Landscapes, KRISTELLE ROBIN, Institute for Advanced Studies, HKUST — Microbiologist are starting to revise the single cell centered view of evolution to a multicellular view, considering it at entire population scale, and even whole ecosystem. Indeed, as Darwin recognized on the Galapagos Island, evolution of a community of bacteria is strongly influenced by the global spatial stress and depends of the neighboring communities. This collective dynamical process can be studied using micro-nanofabricated landscape to create stressed conditions. Our microfluidic device consists of interconnected chambers in 2D hexagonal geometries. The design of our ecology enable to combine gradients of antibiotic and nutrient, thus generating population gradient and motion of bacteria across them. We study here evolution of resistance to the antibiotic ciprofloxacin in highly-stressed conditions. Non-random mutations are induced in the collectivity to develop resistance to the antibiotic. Channels between microhabitats allow motion of bacteria between different islands, and once evolution is ignited in a local metapopulation, a very fast spread through the collectivity happens. In such environments, evolution is observed in typical time scales of few hours. Knowing the complexity of natural world, we believe that our approach provide a model to understand the rapid emergence of resistance to antibiotic and its spread in the entire population.

References:

1Supported by USA NIH and China NSF.

1:03PM Q7.00004 Towards a Quantitative Endogenous Network Theory of Cancer Genesis and Progression: beyond "cancer as diseases of genome"1, PING AO, Shanghai Jiaotong University — There has been a tremendous progress in cancer research. However, it appears the current dominant cancer research framework of regarding cancer as diseases of genome leads impasse. Naturally questions have been asked that whether it is possible to develop alternative frameworks such that they can connect both to mutations and other genetic/genomic effects and to environmental factors. Furthermore, such framework can be made quantitative and with predictions experimentally testable. In this talk, I will present a positive answer to this calling. I will explain on our construction of endogenous network theory based on molecular-cellular agencies as dynamical variable. Such cancer theory explicitly demonstrates a profound connection to many fundamental concepts in physics, as such stochastic processes are testable. Naturally questions have been asked that whether it is possible to develop alternative frameworks such that they can connect both to mutations and Progression: beyond "cancer as diseases of genome"

References:

1Supported by USA NIH and China NSF.

1:39PM Q7.00005 Understanding the distribution of fitness effects of mutations by a biophysical-organismal approach, SHIMON BERSHTEIN, Harvard University — The distribution of fitness effects of mutations is central to many questions in evolutionary biology. However, it remains poorly understood, primarily due to the fact that a fundamental connection that exists between the fitness of organisms and molecular properties of proteins encoded by their genomes is largely overlooked by traditional research approaches. Past efforts to breach this gap followed the “evolution first” paradigm, whereby populations were subjected to selection under certain conditions, and mutations which emerged in adapted populations were analyzed using genomic approaches. The results obtained in the framework of this approach, while often useful, are not easily interpretable because mutations get fixed due to a convolution of multiple causes. We have undertaken a conceptually opposite strategy: Mutations with known biophysical and biochemical effects on E. coli’s essential proteins (based on computational analysis and in vitro measurements) were introduced into the organism’s chromosome and the resulted fitness effects were monitored. Studying the distribution of fitness effects of such fully controlled replacements revealed a very complex fitness landscape, where impact of the microscopic properties of the mutated proteins (folding, stability, and function) is modulated on a macroscopic, whole genome level. Furthermore, the magnitude of the cellular response to the introduced mutations seems to depend on the thermodynamic status of the mutant.


11:15AM Q40.00001 Primordial Particles; Collisions of Inelastic Particles, GEORGE SAGI, George S. Sag Research — Three-dimensional matter is not defined by Euclidian or Cartesian geometries. Newton’s and Einstein’s laws are related to the motions of elastic masses. The study of collisions of inelastic particles opens up new vistas in physics. The present article reveals how such particles create clusters composed of various number of particles. The probability of each formation, diplets, triplets, etc. can be calculated. The particles are held together by a binding force, and depending upon the angles of collisions they may also rotate around their center of geometry. Because of these unique properties such inelastic particles are referred to as primordial particles, Pp. When a given density of Pp per cubic space is given, then random collisions create a field. The calculation of the properties of such primordial field is very complex and beyond the present study. However, the angles of collisions are infinite in principle, but the probabilities of various cluster sizes are quantum dependent. Consequently, field calculations will require new complex mathematical methods to be discovered yet.
11:27AM Q40.00002 Aggregation of Thermal Particles in Simulation1, IAT NENG CHAN, University of Macau — Based on the Schrödinger Equation, energy levels are evaluated for charged particle or atom surrounded by few atoms imitated to atomic cavity situations under multipole or Lennard-Jones interactions. To examine the states of corresponding eigenvalues, the associated wave functions from simulation are plotted in three-dimension to elucidate the space distribution of particles. In cases for testing on effect of different adjacent atomic structures, concentration region of distribution is revealed from a series of results. The range of localization shown also is affected by the type and strength of interactions between particles and atoms, besides the number and position of surrounding atoms. The thermal effect considered in the computation is modeled by average over results from random fluctuation of atom positions for a given heating grade. Moreover, analysis with fuzzy conditions is applied to reduce the complicated and time-consumption approach, also for the training in science education. Even the investigation is limited and tentative, qualitative studies on different parameters and structures can provide the influence of factors and approximate information to compare with the experience evidences.

1Supported by UM grant No. RG062/09-10S/CIN/FST.

11:39AM Q40.00003 Many Body Density Matrix Theory2, C.J. TYMCZAK, Texas Southern University — One fundamental limitation of quantum chemical methods is the accuracy of the approximate many-body theoretical framework. Accurate many-body formalisms for quantum chemical methods do exist, but these methods are computationally very expensive. Methods also exist that are much less computationally expensive such as Hartree-Fock, Density Functional and the Hybrid Functional theories, but at a reduced representation of the exact many-body ground state. This severely limits either the system size that can be addressed accurately, or the accuracy of the representation. What is needed is a method that represents the many-body ground states accurately, but with a low computational cost. Recently, a method for determining the response, to any order of the perturbation, within the density matrix formalism has been discovered. This method opens up the possibility of computing the variational many-body ground states to unprecedented accuracy within a simplified computational approach. We report on the theoretical development of this methodology, which we refer to as Many Body Density Matrix Theory. This theory has many significant advantages over existing methods. One, its computational cost is equivalent to Hartree-Fock or Density Functional Theory. Two it is a variational upper bound to the exact many-body ground state energy. Three, like Hartree-Fock, it has no self-interaction. And four, it is size extensive.

2Funded by Welch Foundation Grant J-1675

11:51AM Q40.00004 Probing the Surface-to-Bulk Transition: A Closed-Form, Constant-Scaling Algorithm for Computing Subsurface Green Functions, MATTHEW REUTER, Department of Chemistry, Northwestern University, TAMAR SEIDEMAN, MARK RATNER — A closed-form algorithm for computing subsurface Green functions—the blocks of a material’s Green function between the surface and the bulk—is presented, where we assume the system satisfies a common principal layer approximation. By exploiting the block tridiagonal and nearly block Toeplitz structure of the Hamiltonian and overlap matrices, this method scales independently of the system size (constant scaling), allowing studies of large systems. As a proof-of-concept example, we investigate the decay of surface effects in an armchair graphene nanoribbon, demonstrating the persistence of surface effects hundreds of atomic layers (~0.5 μm) away from a surface. We finally compare the surface-to-bulk transitions of finite and semi-infinite systems, finding that finite systems exhibit amplified surface effects.

12:03PM Q40.00005 Projecting the phase-space trajectory of multidimensional non-equilibrium systems onto a discrete set of states: a Projective Dynamics approach, KATJA SCHAEFER, M.A. NOVOTNY, Department of Physics and Astronomy, Mississippi State University — Phase-space trajectories, which are either continuous or possess small discontinuities, can be projected onto a discrete set of states with nearest neighbor coupling. The pointwise projection leads for non-equilibrium systems to a non-Markovian process, even if the dynamics of the original system is Markovian. However, using time-averaged transition-rates a Markov process can be obtained, which has the same overall properties as the original dynamics of the system. The projected process defines a new dynamics, which only in the limit \( t \to \infty \) obtains the property on the time-scale of the averaging procedure. We demonstrate the Projective Dynamics method in theory and applications to absorption processes, which in general are not describable through equilibrium or steady-state models. We show the discrete set of states \( \{\zeta_i\} \) can be chosen arbitrarily (with slight restrictions) for all systems.

12:15PM Q40.00006 Finding lowest saddle point, QING LU, Department of Mechanical Engineering and Division of Materials Science and Engineering, Boston University, MINGHAI LI, Gustaf H. Carlson School of Chemistry and Biochemistry, Clark University, AKIHIRO KUSHIMA, Department of Materials Science and Engineering, University of Pennsylvania, XI LIN, Department of Mechanical Engineering and Division of Materials Science and Engineering, Boston University — A history-penalized basin filling algorithm is presented in this work which identifies the lowest saddle point starting from any given initial state on any given potential energy hypersurface. The natural analogy of this algorithm is filling a barrel with water; by monitoring the location where leakage occurs one identifies the lowest opening on the wall of the barrel. The successful implementation of this algorithm relies on insightful choices of the penalty function, penalty function combination, and peak refinement. Several types of penalty functions are implemented to study the interactions of two classical systems, the ad-cluster surface diffusion and supercooled binary Lennard-Jones liquid. The results have shown that the ad-cluster prefers non-Markovian behavior. One the other hand, the supercooled binary Lennard-Jones liquid prefers Markovian behavior.

12:27PM Q40.00007 The Reaction of Carbon Dioxide with Water Clusters: an Ab Initio Metadynamics Study, GREGOIRE GALLET, FABIO PIETRucci, CECAM EPF Lausanne (CH), WANDA ANDREONI, CECAM and Institut de Théorie des Phénomènes Physique EPF Lausanne (CH) — Simulations are often invoked as aid to understand and optimize carbon capture and sequestration processes. The hydration of carbon dioxide (CO2) offers an excellent test case for assessing the reliability of computational schemes. We present a density-functional-theory study of the reaction of CO2 with water clusters. The first step was to validate DFT results in different approximations of the exchange and correlation functional with respect to quantum chemical methods for the structure, binding energies and vibrational frequencies of several isomers. Next, simulations of the reactions leading to the formation of carbonic acid were performed using metadynamics as accelerating procedure. This method allows us both to identify the reaction mechanisms and to obtain an estimate of the free energy barriers via the reconstruction of the free energy profiles. Comparisons were drawn with previous static calculations of the barriers. As reference, a similar calculation in liquid water will be presented.

12:39PM Q40.00008 Triplet Pairing and Odd-Electron Densities in Constrained-Pairing Mean-Field Theory, JASON K. ELLIS, Department of Physics and Astronomy and Department of Chemistry, Rice University, CARLOS A. JIMENEZ-HOYOS, Department of Chemistry, Rice University, GUSTAVO E. SCUSERIA, Department of Chemistry and Department of Physics and Astronomy, Rice University — Describing strong (also known as static or non-dynamical) correlation caused by degenerate or nearly degenerate orbitals near the Fermi level remains a theoretical challenge, particularly in molecular systems. Constrained-pairing mean-field theory (CPMFT) has been quite successful capturing the effects of static correlation in bond formation and breaking in closed- shell molecular systems. This method uses singlet electron entanglement to model static correlation at mean field cost. The present work extends the previous formalism to include triplet pairing, allowing a description of same-spin correlation and open-shell species. Additionally, a spin-orbital extension of the “odd-electron” formalism of Yamaguchi and co-workers is presented as a method for understanding triplet radical character in molecules. Results from representative systems are presented.
12:51PM Q40.00009 Dynamical Mean-Field Theory for Quantum Chemistry¹. NAN LIN, Department of Physics, Columbia University, 538 West 120th Street, New York, NY 10027, USA, CHRISTIAN MARIANETTI, Department of Applied Physics, Columbia University, New York, NY 10027, USA, ANDREW MILLIS, Department of Physics, Columbia University, 538 West 120th Street, New York, NY 10027, USA, DAVID REICHMAN, Department of Chemistry, Columbia University, 3000 Broadway, New York, NY 10027, USA — The dynamical mean-field concept of approximating an unsolvable many-body problem in terms of the solution of an auxiliary quantum impurity problem, introduced to study bulk materials with a continuous energy spectrum, is here extended to molecules, i.e., finite system with a discrete energy spectrum. Application to chains and small clusters of hydrogen atoms yields ground state energies which are competitive with leading quantum chemical approaches at intermediate and large interatomic distances, and provides good approximations to the excitation spectrum. The method is a promising approach to the strong correlation problems of quantum chemistry.

¹This work is supported by NSF-DMR-075847, NSF-CHE-0641523 and NYSTAR.

1:03PM Q40.00010 Constrained Active Space Unrestricted Mean-Field Approaches for Controlling Spin-Contamination. TAKASHI TSUCHIMOCHI, GUSTAVO E. SCUSERIA, Department of Chemistry, Rice University — We have recently shown that unrestricted Hartree-Fock (UHF) variationally reduces to high-spin restricted open-shell Hartree-Fock when constraints are imposed on the eigenvalues of the spin density matrix [T. Tsuchimochi and G. E. Scuseria, J. Chem. Phys. 133, 141102 (2010)]. We here generalize these ideas and propose to control spin-contamination in UHF by releasing the constraints in an active space while imposing them elsewhere. If the active space is properly chosen, our constrained UHF (CUHF) method greatly benefits from a controlled broken-symmetry effect while avoiding the massive spin contamination arising in the traditional UHF. We apply Löwdin’s projection operator to CUHF and obtain multireference wave functions with moderate computational cost. We report results on singlet-triplet energy gaps to show that our constrained scheme outperforms fully unrestricted methods. This constrained approach can be readily used in Kohn-Sham (KS) density functional theory with similar favorable effects, provided that spin-contamination is given by the KS orbitals as in UHF.

1:15PM Q40.00011 Nuclear quantum effects using selective mode excitation in water. SRIRAM GANESHAN, MARIVI FERNANDEZ-SERRA, Stony Brook university — Recently, Ceriotti et al. [1] introduced a comprehensive framework to use a custom-tailored Langevin equation with correlated-noise in the context of MD simulations. One of the interesting applications of these thermostats is that, such a framework can be used to selectively excite normal modes whose frequency falls within a prescribed, narrow range [2]. The general idea of this work is to understand whether the selective excitation of modes in some systems like water is enough to reproduce the necessary nuclear quantum effects at a given temperature. Ceriotti et al. has also implemented their colored noise thermostat (Langevin) to the PIMD of TIP4P/F model [3]. In this work we study how the TIP4P/F responds to the selective mode excitation using the delta-thermostats. We apply this delta thermostat to the molecular dynamics of TIP4P/F [4] water force field, a model explicitly fitted with the lack of zero point ionic vibrations. TIP4P/F provides us an ideal platform to study the effect of selective mode excitation on water. We address the question of whether selective mode excitations are enough to generate the nuclear quantum effects in water. This work will also provide a way to identify the dominant modes for which the quantum effects are important. [1] Chem. Theory Comput. 6, 1170 (2010) [2] Proc. Comp. Sci. 1, 1601 (2010), [3] J. Chem. Phys. 131, 024501 (2009), [4] J. Chem. Phys. 133, 124104 (2010).

1:27PM Q40.00012 Ab Initio Composite Methods. ANGELA WILSON, WANYI JIANG, GBENGA OYEDEPO, MARIE LAURY, University of North Texas — In this brief presentation, we highlight recent developments of the ab initio composite method, the correlation consistent Composite Approach (ccCA). Recent work has enabled ccCA to be utilized for 3d transition metals, as well as for species for which a multireference wavefunction is required. We overview the development, as well as applications of the method to the prediction of spectroscopic and thermodynamic properties of molecules.

1:39PM Q40.00013 Distortion of scanning-tunnelling-spectroscopy images of isolated molecules induced by electron correlation. MASSIMO RONTANI, DIMITRIOS TOROZ, STEFANO CORNI, CNR-NANO S3, Modena, Italy — Scanning tunnelling spectroscopy (STS) visualizes electron states in both extended systems and nano-objects, as quantum dots and molecules. Whereas bulk quantum states are insensitive to electron number fluctuations, an energy gap opens each time a new electron is injected into the STS tip into a sufficiently small system. This gap originates from the interaction of the next incoming electron with the others already present in the system. In this Coulomb blockade regime a fundamental question is whether the wave function of the “quasi-particle” added to the system -imaged by the STS tip- is sensitive to electron-electron interaction. Here we show that the STS images of single planar molecules with metal centres predicted by ab initio many-body calculations differ qualitatively from their uncorrelated counterparts. We find in the maps resolved at the Fermi energy that correlation significantly removes spectral weight from the metal atom, as well as the overall weight is remarkably reduced. This change may be measured and compared with STS images of molecules without the metal center, whose many-body and uncorrelated versions are alike.

1:51PM Q40.00014 Maximizing the hyperpolarizability poorly determines the potential. ROLFE PETSCHEK, TIMOTHY ATHERTON, JOSEPH LESNIEWSKY, GREG WIGGERS, Case Western Reserve University — Increasing the non-linear response of materials to an electric field, characterized by quantities such as the first hyperpolarizability, is a matter of importance for applications. We optimized the zero frequency β of a one-dimensional potential well containing a single electron by freely adjusting the shape of that potential. It was shown that with careful optimization the maximum hyperpolarizability converges quickly with increasing numbers of parameters in the potential to approximately 0.708951 of the proven upper bound. The Hessian of β at the maximum makes it clear that there is a very wide range of nearby, nearly optimal potentials: with several measures of differences between potentials, this Hessian has only two large eigenvalues with the others diminishing quickly. The optimum potentials are substantially different and more affected by small eigenvectors than the wavefunctions. Thus, wavefunctions are superior for describing the conditions that optimize the hyperpolarizability. Prospects for a concise description of the two important constraints on near-optimum potentials and wavefunctions are discussed.


11:15AM Q41.00001 First principles simulations of materials and processes in photo- and electro-catalysis. ANABELLA SELLONI, Princeton University — I shall discuss applications of electronic structure calculations and molecular dynamics simulations to understand materials properties and reaction mechanisms in photo- and electro-catalysis. Examples will include studies of the interface between water and titanium dioxide (TiO2), a widely used photocatalyst capable of splitting water in O2 + H2, and the cycle of H2 production from water by the active site of an enzyme of hydrogen-producing bacteria, the di-iron hydrogenase, linked to a pyrite electrode.
11:51AM Q41.00002 Theoretical studies on a new pattern of laser-driven systems: towards elucidation of direct photo-injection in dye-sensitized solar cells. KENJI MISHIMA, KOICHI YAMASHITA, The University of Tokyo — We theoretically and numerically investigated a new type of analytically solvable laser-driven systems inspired by electron-injection dynamics in dye-sensitized solar cells. The simple analytical expressions were found to be useful for understanding the difference between dye excitation and direct photo-injection occurring between dye molecule and semiconductor nanoparticles. More importantly, we propose a method for discriminating experimentally dye excitation and direct photo-injection by using time-dependent fluorescence. We found that dye excitation shows no significant quantum beat whereas the direct photo-injection shows a significant quantum beat.

2This work was supported by Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST) “Development of Organic Photovoltaics toward a Low-Carbon Society,” Cabinet Office, Japan.

12:03PM Q41.00003 Investigation of the Potential Difference between C60 and TiOPc on Ag(111) by Local Probe Techniques. KRISTEN BURSON, YINYING WEI, WILLIAM CULLEN, JANICE REUTT-ROBEY, University of Maryland-College Park — One challenge for increasing efficiency of organic photovoltaics is to understand the barrier to exciton separation that exists at the interface between organic molecules. Here we report a local probe measurement of the potential barrier at the interface between monolayer C60, a good electron acceptor, and honeycomb phase TiOPc, an organic with high hole mobility, on Ag(111). We employ UHV AFM (atomic force microscopy) and KPFM (Kelvin probe force microscopy) to obtain simultaneous images of the potential and topographic landscapes. This technique allows for high spatial resolution of both the potential and the topography. In addition to reporting the work function difference between C60 and TiOPc, we investigate the work function for C60 on Ag(111).

12:15PM Q41.00004 Ultrafast proton coupled charge transfer dynamics in photocatalysis. HRVJ OE PETEK, University of Pittsburgh — In this talk I will present our experimental and theoretical studies on the nature of electron and hole acceptor states and their dynamics for protic solvent molecule (H\textsubscript{2}O, CH\textsubscript{3}OH) covered TiO\textsubscript{2} surfaces. Electron-hole pair generation by band gap excitation can introduce charges into protic solvent/TiO\textsubscript{2} interface, which can drive photocatalytic processes. By time resolved two-photon photoemission and DFT electronic structure calculations we identify the partially solvated or "wet" electron acceptor states, and their proton-coupled electron transfer (PCET) dynamics. Because holes are through to be the primary reagents for photocatalysis on TiO\textsubscript{2}, we also explore possible hole driven PCET dynamic pathways.

12:51PM Q41.00005 First-principles study on Ru(4,4',4"-tricarboxy-2,2':6',2"-terpyridine)(NCS)\textsubscript{3} sensitizer on TiO\textsubscript{2} anatase(101) surface: Adsorbed structures and electronic states for dye-sensitized solar cells. KEITARO SODEYAMA, MASATO SUMITA, YOSHITAKA TATEYAMA, National Institute for Materials Science MANA — Dye-sensitized solar cells are expected as a cost effective solar-to-electricity energy conversion devices. The efficiency of the power conversion is greater than 10% when Ru(II) poly-pyridyl sensitizers are used. For further improvement of the efficiency, we need to understand the adsorbed structures at atomic level in detail. In this study, we investigated the adsorbed structures of Ru(4,4',4"-tricarboxy-2,2':6',2"-terpyridine)(NCS)\textsubscript{3} sensitizer on TiO\textsubscript{2} anatase(101) surface. For four possible adsorbed structures (two candidates have one adsorbed carboxy group(one-leg) and the others have two adsorbed groups(two-leg)), we found the adsorption energies are quite similar within 0.4 eV. This is attributed to the presence of the hydrogen bond between the hydrogen of carboxyl group and the oxygen of the surface in the one-leg structure. We also calculated the excited states of the four structures of the sensitizer by TDDFT and found that the UV spectrum shift depending on the structure differences.

1This work is supported by JST-CREST, PRESTO, and KAKENHI.

1:03PM Q41.00006 Reverse-engineering the atomic-scale structure of the TiO/2/N3 interface in dye-sensitized solar cells using O1s core-level shifts. CHRISTOPHER PATRICK, FELICIANO GIUSTINO, Department of Materials, University of Oxford — Dye-sensitized solar cells employing mesoporous titania films sensitized with ruthenium-based dyes have attracted considerable attention in recent years due their central role in technologies for solar energy conversion, including dye-sensitized solar cells (DSSCs) and solar photocatalysis. However, the mechanisms of interfacial electron transfer and subsequent electron transport induced by photoexcitation of the molecular adsorbates remain only partially understood. We report recent progress in studies of nanoporous TiO\textsubscript{2} thin-films functionalized with molecular adsorbates, with emphasis on interfacial electron injection, molecular rectification and the mechanism of electron transport through sintered TiO\textsubscript{2} nanoparticles in thin-films relevant to photocatalysis. However, the mechanisms of interfacial electron transfer and subsequent electron transport induced by photoexcitation of the molecular adsorbates remain only partially understood. We report recent progress in studies of nanoporous TiO\textsubscript{2} thin-films functionalized with molecular adsorbates, with emphasis on interfacial electron injection, molecular rectification and the mechanism of electron transport through sintered TiO\textsubscript{2} nanoparticles in thin-films relevant to photocatalysis.

1:15PM Q41.00007 Studies of Interfacial Electronic Processes in Nanoporous TiO\textsubscript{2} Thin-Films. VICTOR BATISTA, Yale University — Metal-oxide nanoparticles sensitized to visible light by covalent attachment of molecular adsorbates have attracted considerable attention in recent years due their central role in technologies for solar energy conversion, including dye-sensitized solar cells (DSSCs) and solar photocatalysis. However, the mechanisms of interfacial electron transfer and subsequent electron transport induced by photoexcitation of the molecular adsorbates remain only partially understood. We report recent progress in studies of nanoporous TiO\textsubscript{2} thin-films functionalized with molecular adsorbates, with emphasis on interfacial electron injection, molecular rectification and the mechanism of electron transport through sintered TiO\textsubscript{2} nanoparticles in thin-films relevant to DSSCs.

3The author acknowledges support from DOE (grants DE-FG02-07ER15909 and ANSER EFRC Award Number DE-PS02-08ER15944) and NSF (grants ECCS-0404191 and CHE (911520).

1:51PM Q41.00008 Efficient adsorbate transport by electron wind: The role of resonant photoexcitation. KIRILL VELIZHANIN, DMITRY SOLENOV, Los Alamos National Laboratory — We study the surface electromigration force acting on an organic molecule at a conducting (metal) surface. The dominant contribution to the force comes from the scattering of metallic electrons off the molecule, as they tunnel to and from nearby molecular orbitals. When metal carries non-zero current, the net force is directed with the current flow. This force, however, is often too small for efficient transport of adsorbed molecules and only reveals itself through a contribution to the metal resistivity. We show that surface-molecule electron wind force can be substantially enhanced and controlled by exploiting appropriate resonances between molecular and metallic states activated by coherent light. This effect opens a path to new surface-molecule functionality, including high resolution spatially controlled force patterns, controlled molecule motion, etc.
by birds or other animals, optimal design features could be used to manufacture biologically inspired, but man-made magnetic compass systems. Regardless of whether or not a radical pair mechanism is indeed used to affect a radical-pair based mechanism in birds and discuss the approach and its limitations. Theoretically, we will focus on the question of how one should physics of the radical pair mechanism and the current state of evidence supporting it. Experimentally, we will focus on the use radio-frequency magnetic fields compass of animals surmises that the magnetic field is perceived by its effect on the coherent spin evolution within a non-equilibrium photochemical radical role?

THORSTEN RITZ, Dept of Physics and Astronomy, University of California, Irvine — One hypothesis of the process underlying the magnetic

A115/117

2:03PM Q41.00009 Real-time observation of bond-by-bond interface formation during oxidation of H-terminated (111)Si by second-harmonic generation, BILAL GOKCE, North Carolina State University, ERIC J. ADLES, Johns Hopkins University, DAVID E. ASPNES, KENAN GUNDOGDU, North Carolina State University — Structure of solids is typically determined at the atomic level by techniques such as X-ray and electron diffraction, which are sensitive to positions of atomic nuclei. However, structure is determined by bonds between atoms, which are difficult to measure directly. We combine second-harmonic generation and the bond-charge model of nonlinear optics to probe, in real time, the dynamics of bond-by-bond chemical changes during the oxidation of H-terminated (111)Si, a surface that has been well characterized by static methods. Oxidation is activated by applied macroscopic strain, and exhibits anisotropic kinetics with one of the three equivalent back-bonds of on-axis samples reacting differently from the other two. This also leads to transient changes in bond directions. Strain is known to increase oxidation rate of Si for thermal oxides, however its affects at the microscopic scale has not been studied at the bond level. By comparing results for surfaces strained in different directions, we show that in-plane control of surface chemistry is possible. The use of nonlinear optics as a bond-specific characterization tool is readily adaptable for studying structural and chemical dynamics in many other condensed-matter systems.

Wednesday, March 23, 2011 2:30PM - 4:06PM –
Session T38 DCP DBP: Focus Session: Quantum Coherence in Biology IV A130/131

2:30PM T38.00001 Biophysics of Magnetic Orientation: Radical Pairs, Biogenic Magnetite, or both? , JOE KIRSCHVINK, California Institute of Technology — Two major biophysical mechanisms for magnetoreception in terrestrial animals, one based on biogenic magnetite and another on radical-pair biochemical reactions, have been the subject of experiment and debate for the past 30 years. The magnetite hypothesis has stood the test of time: biogenic magnetite is synthesized biochemically in Bacteria, Protists, and numerous Animal phyla, as well as in some plants. Chains of single-domain crystals have been detected by clean-lab based SQUID magnetometry in animal tissues in all major phyla, followed by high-resolution TEM in selected model organisms, as well as by electrophysiological studies demonstrating the role of the ophthalmic branch of the trigeminal nerve in the magnetoreceptive process. Pulse-remagnetization - configured to uniquely flip the polarity of single-domain ferromagnets - has dramatic effects on the behavior of many birds, honeybees, mole rats, turtles, and bats, to cite a growing list. Magnetite-containing cells in the vicinity of these neurons in fish are now the subject of intense study by our consortium. The existence of a specialized class of magnetite-containing magnetoreceptor cells in animal tissues is no longer controversial. In contrast, less success has been achieved in gaining experimental support across a range of taxa for the radical-pair hypothesis. Although this mechanism was proposed to explain an early observation that birds would not respond to complete inversion of the magnetic vector, many organisms (even some birds) do indeed respond to the field polarity. We also note that few, if any, of these critical experiments have been done using fully double-blind methods. This is joint work with: M. M. Walker (University of Auckland, New Zealand) and M. Winklhofer (LMU Munich, Germany).

3:06PM T38.00002 Magnetic compasses in biological systems: Does quantum physics play a role? , THORSTEN RITZ, Dept of Physics and Astronomy, University of California, Irvine — One hypothesis of the process underlying the magnetic compass of animals surmises that the magnetic field is perceived by its effect on the coherent spin evolution within a non-equilibrium photochemical radical pair reaction. If this hypothesis were proven, it would be a dramatic demonstration of a quantum process with clear biological significance. We will review the physics of the radical pair mechanism and the current state of evidence supporting it. Experimentally, we will focus on the use radio-frequency magnetic fields to affect a radical-pair based mechanism in birds and discuss the approach and its limitations. Theoretically, we will focus on the question of how one should design a radical pair to be optimally sensitive to the direction of a weak magnetic field. Regardless of whether or not a radical pair mechanism is indeed used by birds or other animals, optimal design features could be used to manufacture biologically inspired, but man-made magnetic compass systems.

3:42PM T38.00003 Quantum Control and Entanglement in a Chemical Compass , GIAN GIACOMO GUERRESCHI, JIANMING CAI, HANS J. BRIEGER, University of Innsbruck, Institute for Quantum Optics and Quantum Information (IQOQI) of the Austrian Academy of Science — The radical-pair mechanism is one of the two main hypotheses to explain the navigability of animals in weak magnetic fields, enabling, e.g., birds to see Earth’s magnetic field. It also plays an essential role in spin chemistry. Here, we show how quantum control can be used to either enhance or reduce the performance of such a chemical compass, providing a new route to further study the radical-pair mechanism and its applications. We study the role of radical-pair entanglement in this mechanism, and demonstrate its intriguing connections with the magnetic-field sensitivity of the compass. Beyond their immediate application to the radical-pair mechanism, these results also demonstrate how state-of-the-art quantum technologies could potentially be used to probe and control biological functions.

3:54PM T38.00004 A Biochemical Double Slit , IANNIS KOMINIS, University of Crete - Physics Department — Radical-ion-pair reactions, fundamental in photosynthesis and at the basis of the avian magnetic compass mechanism, have been recently shown to offer a rich playground for applying methods and concepts from quantum measurement/quantum information science. We will demonstrate that radical-ion-pair reactions are almost the exact analog of the optical double slit experiment, i.e. Nature has already engineered biochemical reactions performing the act of quantum interference. We will further elaborate on the non-trivial quantum effects pertaining in these reactions and the recent debate on their fundamental theoretical description that these effects have sparked.

Wednesday, March 23, 2011 2:30PM - 5:30PM –
Session T41 DCP: Focus Session: The Role of Water in Energy Production and Utilization I A115/117
2:30PM T41.00001 Deciphering the morphology of ice films on metal surfaces1, KONRAD THÜRMER, Sandia National Laboratories, CA — Although extensive research has been aimed at the structure of ice films [1], questions regarding basic processes that govern film evolution remain. Recently we discovered how ice films as many as 30 molecular layers thick can be imaged with STM [2]. The observed morphology yields new insights about water-solid interactions and how they affect the structure of ice films. This talk gives an overview of this progress for crystalline ice films on Pt(111) [2-5]. STM reveals a first molecular water layer very different from bulk ice: besides the usual hexagons it also contains pentagons and heptagons [3]. Slightly thicker films (∼1nm, at T=120K) are comprised of ∼3nm-high crystallites, surrounded by the one-molecule-thick wetting layer. These crystals develop by nucleating layers on their top facets [4]. Measurements of the nucleation rate as a function of crystal height provide estimates of the energy of the ice-Pt interface. For T=115K surface diffusion is fast enough that surface smoothing and 2D-island ripening is observable [5]. By quantifying the T-dependent ripening of island arrays we determined the activation energy for surface self-diffusion. The shape of these 2D islands varies strongly with film thickness. We attribute this to a transition from polarized ice at the substrate towards proton disorder at larger film thicknesses. Despite fast surface diffusion ice multilayers are often far from equilibrium. For example, ice grows between ∼120 and ∼160 K in its cubic variant rather than in its equilibrium hexagonal form. We found this to be a consequence of the mismatch in the atomic Pt-step height and the ice-bilayer separation and propose a mechanism of cubic-ice formation via growth spirals around screw dislocations [2].


3:06PM T41.00002 A Priori Method for First Principles Study of Aqueous Electrochemistry: Application to Biofuels and Catalysis, KENDRA LETCHWORTH WEAVER, RAVISHANKAR SUNDARARAMAN, TOMAS ARIAS, Cornell University — We present a novel description of water which will allow the first a priori studies of catalysis of biofuels in aqueous electrochemical environments. Our method offers a computationally efficient alternative to the thermal sampling required by molecular dynamics yet provides a more realistic description of bulk water than including explicit frozen water or traditional continuum solvation models. Into Joint Density Functional Theory (JDFT), which joins an electron density-functional for the solute with classical density-functional theories for liquid water into a single variational principle for the free energy of the combined system, we introduce the innovation of an a priori form of the coupling functional between the quantum-mechanical system and liquid water based on a local density approximation to the Hohenberg-Kohn density-only functional. Without any fits to solvation data whatsoever, this new method predicts solvation energies of small organic molecules well compared to state-of-the art empirical quantum-chemical cavity approaches. The site interaction potentials produced closely resemble the widely used TIP3P site potentials for water without requiring any empirical parameters.

3:18PM T41.00003 A priori classical density functional methods of water: toward first principles exploration of aqueous based energy systems, RAVISHANKAR SUNDARARAMAN, KENDRA LETCHWORTH WEAVER, TOMAS ARIAS, Cornell University — The microscopic structure of inhomogeneous water plays a critical role in the properties of a wide variety of important energy systems including fuel cells and photoelectrochemical cells. Joint density functional theory has proven to be an efficient tool for the quantum-mechanical modeling of systems such as Pt electrodes in the presence of water, but requires theories for water which go beyond semi-empirical continuum solvation models, and accurate models for the coupling between water and electronic systems. Toward this end, we present a new density-functional description of liquid water capable of predicting interatomic correlation functions, the linear and nonlinear dielectric response, and solvation energies without empirical fit parameters. The functional itself is built upon the site-potential representation of the ideal gas, a hard sphere reference fluid for the repulsive correlations, and an equation of state that reproduces the bulk properties of water over the entire extent of its liquid phase. Hydrogen bonding, the local tetrahedral structure and orientational correlations are captured a priori by a density-functional reformulation of the Kirkwood model for the dielectric constant.

4:18PM T41.00006 Ordering of confined water between metallic surfaces1, ADRIEN POISSIER, MARIA V. FERNANDEZ-SERRA, Stony Brook University — It has been pointed out (PCCP 2010, Poissier et al.) that the hydrogen bonding type interaction occurring at water/metal interface makes the two type of interfacial water orderings (hydrophobic or hydrophilic overlayers) very close in energy. The most stable, hydrophobic, overlayers has very small net dipole moment perpendicular to the surface, while the least stable (in vacuum) hydrophilic interface has a large (≈ 1.8D) net dipole moment. First principles molecular dynamics simulations of liquid water confined between two Pd surfaces have been performed and structural and electronic water properties have been studied in detail. We show that water confinement in this situation results in a spontaneous symmetry breaking of the system, inducing an electric field across the liquid water slab. We discuss the origin of this spontaneous polarization and show its dependence with the confinement distance along the direction perpendicular to the planes of the surfaces.

1 This work is supported by DOE award number DE-SC0003871
4:30PM T41.00007 Exploring hydration at the nanoscale. PETER ROSSKY, University of Texas at Austin — It is widely appreciated that water molecules contribute a critical element to the forces governing chemical processes in an aqueous environment, and the purported differences in water structure induced by the presence of confining surfaces are correspondingly likely to play a role in interfacial chemistry. The development of a detailed understanding of the organization of fluid water at the interface with real materials is therefore of great interest. In this presentation, results obtained from fully atomistic computer simulations of water in the presence of confining interfaces will be discussed, with the goal of elucidating the molecular level influence of surface character on water structure and energetics. Further, we emphasize the expansion of studies to temperatures and pressures well outside the conventional realm of the ambient solvent thermodynamic state. The interface examples to be considered in this presentation emphasize systematic studies designed to elucidate guiding principles. These include extended and nanoscale hydrophobic and hydrophilic crystalline surfaces and interfaces with systematically patterned hydrophobicity.

This work is the result of support for Collaborative Research by the US National Science Foundation.

5:06PM T41.00008 ABSTRACT WITHDRAWN

5:18PM T41.00009 Energy transport during sessile-water-droplet evaporation. HADI GHASEMI, University of Toronto, CHARLES WARD, University of Toronto — Energy transport mechanisms for a steadily evaporating water droplet maintained on Cu or Au(111) surfaces are compared. In the absence of buoyancy-driven convection, thermal conduction and thermocapillary convection are the active modes of energy transport. The dominant mode varies along the liquid-vapor interface. Although thermal conduction is the dominant mode in regions far from the contact line, thermocapillary convection is by far the larger mode of energy transport near the three-phase contact line. The latter region is where most of the droplet evaporation occurs. Evaporation experiments on both Cu and Au(111) suggest that the thermocapillary convection provides more than 92% of the total energy required for the evaporation.

We gratefully acknowledge the support Natural Sciences and Engineering Council of Canada and the Canadian Space Agency


2:30PM T42.00001 Insights into protein evolution landscapes from folding models. EUGENE KOONIN, National Center for Biotechnology Information, National Library of Medicine, National Institutes of Health — Off-lattice models of protein folding were employed to investigate the origins of the evolutionary rate distributions and fitness landscapes. For each robust folder, the network of sequences that share its native structure is identified. The fitness of a sequence is a simple function of the number of misfolded molecules produced to reach a characteristic protein abundance. Fixation probabilities of mutants are computed under a simple population dynamics model, and the fold-averaged evolution rate is computed using a Markov chain on the fold network. The distribution of the logarithm of the evolution rates exhibits a peak with a long tail on the low rate side and resembles the universal empirical distribution of the evolutionary rates more closely than either distribution resembles the log-normal distribution. We next addressed the question of the extent of determinism in protein evolution. Limited empirical studies suggest that the fitness landscapes of protein evolution are significantly smoother, or more additive, than random landscapes. However, widespread sign epistasis seems to restrict evolution to a small fraction of available trajectories, thus making the evolutionary process substantially deterministic. Access to complete fitness landscapes within the model framework enables exhaustive analysis of evolutionary trajectories. The model landscapes were compared to a continuum of artificial landscapes of varying smoothness. In maximally smooth, fully additive landscapes, evolution cannot be predicted because all paths are accessible. However, a small amount of noise can make most paths inaccessible while preserving the overall structure of the landscape. Although the model landscapes are almost additive, most paths are non-monotonic with respect to fitness, so evolutionary trajectories can be approximately predicted. Thus, protein folding physics seems to dictate the universal distribution of the evolutionary rates of protein-coding genes and the quasi-deterministic character of evolution.

3:06PM T42.00002 A mechanism for the evolution of allosteric control in proteins. KIMBERLY REYNOLDS, RAMA RANGANATHAN, Green Center for Systems Biology, and Department of Pharmacology, University of Texas Southwestern Medical Center — Co-evolution analysis indicates a general architecture for natural proteins in which sparse networks of physically contiguous amino acids underlie basic aspects of structure and function. These networks, termed sectors, are spatially organized such that active sites are linked to many surface sites distributed throughout the protein structure. Here, we propose that sectors represent an evolutionarily conserved “wiring” mechanism that effectively functionalizes a large but non-random fraction of the protein surface - that is, perturbation at sector-connected surface positions should preferentially yield coupling to the active site. To test this premise, we conducted a comprehensive “domain insertion scan,” and show that sector-connected surface sites are statistically significant locations for the emergence of allosteric control in vivo. This finding suggests practical guidelines for the engineering of new allosteric systems, and permits description of a plausible model for the evolution of intermolecular communication and regulation.

3:18PM T42.00003 Biophysical Aspects of Spindle Evolution. REZA FARHADIFAR, Harvard University, CHARLIE BAER, University of Florida, DANIEL NEEDLEMAN, Harvard University — The continual propagation of genetic material from one generation to the next is one of the most basic characteristics of all organisms. In eukaryotes, DNA is segregated into the two daughter cells by a highly dynamic, self-organizing structure called the mitotic spindle. Mitotic spindles can show remarkable variability between tissues and organisms, but there is currently little understanding of the biophysical and evolutionary basis of this diversity. We are studying how spontaneous mutations modify cell division during nematode development. By comparing the mutational variation - the raw material of evolution - with the variation present in nature, we are investigating how the mitotic spindle is shaped over the course of evolution. This combination of quantitative genetics and cellular biophysics gives insight into how the structure and dynamics of the spindle is formed through selection, drift, and biophysical constraints.

3:30PM T42.00004 The relationship between relative solvent accessibility and evolutionary rate in protein evolution. CLAUS WILKE, The University of Texas at Austin — Recent work with the yeast Saccharomyces cerevisiae shows a linear relationship between the evolutionary rate of sites and the relative solvent accessibility (RSA) of the corresponding residues in the folded protein. Here, we aim to develop a mathematical model that can reproduce this linear relationship. We first demonstrate that two models that both seem reasonable choices (a simple model in which selection strength correlates with RSA and a more complex model based on RSA-dependent amino-acid distributions) fail to reproduce the observed relationship. We then develop a model based on observed site-specific amino-acid distributions and show that this model behaves appropriately. We conclude that evolutionary rates are directly linked to the distribution of amino acids at individual sites. Because of this link, any future insight into the biophysical mechanisms that determine amino-acid distributions will improve our understanding of evolutionary rates.
and is encoded in the sequence in an idiosyncratic manner in the PDZ family. Correlations, and strikingly, even in the absence of a native state. Thus, we suggest that native-state stability is not a fundamental requirement for function, and function is captured by sectors? Using simulated-annealing Monte Carlo, we introduce variation in the sequence of a single member of the PDZ family in a manner that either preserves or disrupts sector correlations. Experimentally we show that function is specifically retained in designed proteins that obey sector base substitutions at G-C and G-C sites. This introduces a quantum Darwinian evolution model which (a) simulates incidence of cancer data and (b) implies insight into quantum origins of evolutionary extinction. Data identify an inherited "genetic space," s, which is initially mutation-free and satisfies the inequality, \( s = 0.97 \). When accumulated stochastic mutations cause s-values to approach their evolutionarily allowed threshold limit, s = 0.97 + e, age-related degenerative disease is manifested. This implies a gain in evolutionary advantage which protects the gene pool against unsafe levels of mutation. Data requiring coherent states imply that classical duplex DNA contains an embedded microphysical subset of electron lone-pairs and hydrogen bonded protons that govern time-dependent genetic specificity in terms of quantum probability laws.

Thursday, March 24, 2011 8:00AM - 11:00AM
Session V38 DCP DBP: Focus Session: The Physics of Evolution II A130/131

8:00AM V38.00001 Natural Selection in Large Populations, MICHAEL DESAI, Harvard University. I will discuss theoretical and experimental approaches to the evolutionary dynamics and population genetics of natural selection in large populations. In these populations, many mutations are often present simultaneously, and because recombination is limited, selection cannot act on them all independently. Rather, it can only affect whole combinations of mutations linked together on the same chromosome. Methods common in theoretical population genetics have been of limited utility in analyzing this coupling between the fates of different mutations. In the past few years it has become increasingly clear that this is a crucial gap in our understanding, as sequence data has begun to show that selection appears to act pervasively on many linked sites in a wide range of populations, including viruses, microbes, Drosophila, and humans. I will describe approaches that combine analytical tools drawn from statistical physics and dynamical systems with traditional methods in theoretical population genetics to address this problem, and describe how experiments in budding yeast can help us directly observe these evolutionary dynamics.

8:36AM V38.00002 Understanding Biological Fitness From First Principles, EUGENE SHAKHNOVICH, Harvard University — This abstract not available.

9:12AM V38.00003 Geometry Genetics and Evolution, ERIC SIGGIA, Rockefeller University — Darwin argued that highly perfected organs such as the vertebrate eye could evolve by a series of small changes, each of which conferred a selective advantage. In the context of gene nets, this idea can be recast into a predictive algorithm, namely find networks that can be built by incremental adaptation (gradient search) to perform some task. It embodies a "kinetic" view of evolution where a solution that is quick to evolve is preferred over a global optimum. Examples of biochemical kinetic networks were evolved for temporal adaptation, temperature compensated entrainable clocks, explore-exploit trade off in signal discrimination, will be presented as well as networks that model the spatially periodic somites (vertebrae) and HOX gene expression in the vertebrate embryo. These models appear complex by the criterion of 19th century applied mathematics since there is no separation of time or spatial scales, yet they are all derivable by gradient optimization of simple functions (several in the Pareto evolution) often based on the Shannon entropy of the time or spatial response. Joint work with P. Francois, Physics Dept. McGill University.

3With P. Francois, Physics Dept. McGill University

9:48AM V38.00004 TBD, TANJA KORTEMME, UCSF — This abstract not available.

10:24AM V38.00005 Dynamical Mueller’s Ratchet: Population Size Dependence of Evolutionary Paths in Bacteria, DIRK LORENZ, Department of Physics and Astronomy, Rice University, JEONG-MAN PARK, Department of Physics, The Catholic University of Korea, MICHAEL DEEM, Departments of Physics and Astronomy and Bioengineering, Rice University, MICHAEL DEEM TEAM — Experimental evolution has recently enabled the complete quantitative description of small-dimensional fitness landscapes. Quasispecies theory allows the mathematical modeling of evolution on such a landscape. Typically, analytic solutions for these models are only exactly solvable for the case of an infinite population. Here we use a functional integral representation of population dynamics and solve it using the Schwinger Boson method. This allows us to compute the first-order correction to the average fitness for finite populations. We will use these results to explain the experimental observations of dynamics of evolution in finite populations.

10:36AM V38.00006 At the crossroads of biophysics and evolution: protein robustness and evolvability, WOUTER HOFF, MASATO KUMAUCHI, Department of Microbiology and Molecular Genetics, Oklahoma State University — Proteins consist of only 20 different amino acids with modest chemical reactivity, but perform a breathtaking range of functions. How do proteins achieve such functional versatility? Novel insights are emerging from research at the interface of protein biophysics and molecular evolution. Proteins are robustness against point mutations: most mutations do not abolish function. How can such robustness be reconciled with the effective evolution of protein function? We examine these issues using photoactive yellow protein (YPY), a prototype of the PAS domain superfamily. High-throughput biophysical measurements of active site properties, functional kinetics, stability, and production level on libraries of PYP mutants reveal that almost all mutants retain photocycle activity, but that the majority of substitutions significantly alter functional properties. Thus, PYP combines robustness with evolvability. The data also reveal the mysterious role of the conserved residues that define protein superfamilies: most PAS-conserved residues are required for maintaining protein production. Asn43, the most conserved residue in PAS domains, regulates PYP signaling kinetics. This residue is often substituted by Ser, Asp, and Thr in PAS domains while retaining two side chain hydrogen bonds. Thus, not residue identity at position 43 but the pattern of side chain hydrogen bonds is conserved.

1WDEH was supported by NIH GM063805 and OCAST HR07-135S.

10:48AM V38.00007 Deciphering evolutionary instructions for specifying protein fold and function, WALRAJ GOSAL, RAMA RANGANATHAN, UT Southwestern Medical Center — Classical studies show that proteins have evolved to fold into functional native states that are, at best, only marginally stable through weak non-covalent interactions encoded by their primary sequences. How such fold and functional information is stored in a single amino acid sequence remains elusive. Using the statistical analysis of covariation between pairs of amino acids at all positions in a protein, here we identify groups of a few key physically-interconnected residues, which we term sectors. What information about the fold and function is captured by sectors? Using simulated-annealing Monte Carlo, we introduce variation in the sequence of a single member of the PDZ family in a manner that either preserves or disrupts sector correlations, and strikingly, even in the absence of a native state. Thus, we suggest that native-state stability is not a fundamental requirement for function, and is encoded in the sequence in an idiosyncratic manner in the PDZ family.
The structure of water/hydroxyl phases at metal interfaces, Andrew Hodgson.

The University of Liverpool — On all but the least reactive metals, the first contact layer with water is a mixture of water and hydroxyl, often formed by spontaneous dissociation [1]. Understanding the composition and stability of these layers is a key step in describing both the wetting and the redox behavior of the surface. Here we discuss the wetting of Cu(110) and the formation of mixed water-hydroxyl layers by reaction with adsorbed O. This surface does not conform to the traditional hexagonal symmetry associated with an ice Ih, and the hydrogen bonding structure must accommodate to the surface symmetry. A number of unusual structures are seen, including 1D chains of interlocking pentagons [2], an intact 2D network with a (7×8) unit cell at higher coverage [3] and several partially dissociated structures, including both 1D and 2D phases [4]. The composition of these structures and hydrogen bonding arrangements will be discussed, highlighting the way changing the composition and relative metal-adsorbate and adsorbate-adsorbate interactions drives the structural rearrangement of these phases.

References:
9:48AM V41.00006 How Water Meets Graphene , HUA ZHOU, PAUL FENTER, Argonne National Laboratory, JAKE MCDONOUGH, VOLKER PRESSER, YURI GOGOTSI, Department of Materials Science and Engineering, Drexel University, MATTHEW WANDER, KEVIN SHUFORD, Department of Chemistry, Drexel University — The interactions of water and many interfaces are not understood at a mechanistic level. The accuracy of simulations of the system are limited by the accuracy of the water model used. Classical models such as SPC/E use empirically derived parameters to match their behavior to desired bulk water properties, but cannot participate in reactions that require the making or breaking of bonds. Ab initio quantum mechanical methods such as Car-Parrinello (CP) do allow water to dissociate, but are computationally intractable for large systems. A potential middle ground is the self-consistent charge density-functional tight-binding method (SCC-DFTB), which has a smaller associated computational cost, and therefore can access larger systems than CP, while still allowing for the making and breaking of bonds. The DFTB+ implementation of SCC-DFTB allows for 2nd and 3rd order expansions of the density fluctuations in the energy and, in the 3rd order expansion, an optional damping correction factor. For each of these models we compare the structural, dynamic, and spectroscopic properties of bulk SCC-DFTB water to classical SPC/E and experimental results.

10:00AM V41.00007 The Dynamics of Supercooled Water , FRANCESCO MALLAMACE, Dept of Physics, University of Messina, Italy — We present an overview of recent experiments performed on transport properties of water in the deeply supercooled region, a temperature region of fundamental importance in the science of water. We report data of nuclear magnetic resonance, quasi-elastic neutron scattering, Fourier-transform infrared spectroscopy, and Raman spectroscopy, studying water confined in nano-meter-scale environments (nano-tubes and the protein hydration water) and in bulk solutions. When contained within small pores, water does not crystallise, and can be supercooled well below its homogeneous nucleation temperature Th. On this basis it is possible to carry out a careful analysis of the well known thermodynamical anomalies of water. Studying the temperature and pressure dependencies of water dynamics, we show that the liquid-liquid phase transition (LLPT) hypothesis represents a reliable model for describing liquid water. In this model, water in the liquid state is a mixture of two different local structures, characterised by different densities, namely the low density liquid (LDL) and the high-density liquid (HDL). The LLPT line should terminate at a special transition point: a low-T liquid-liquid critical point. In particular We discuss the following experimental findings on liquid water: (i) a crossover from non-Arrhenius behaviour at high T to Arrhenius behaviour at low T in transport parameters; (ii) a breakdown of the Stokes-Einstein relation; (iii) the existence of a Widom line, which is the locus of points corresponding to maximum correlation length in the p-T phase diagram and which ends in the liquid-liquid critical point; (iv) the direct observation of the LDL phase; (v) a minimum in the density at approximately 70K below the temperature of the density maximum. In our opinion these results represent the experimental proofs of the validity of the LLPT hypothesis.

10:36AM V41.00008 Structural, Dynamic, and Spectroscopic Properties of the SCC-DFTB Water Model , LAURA KINNAMAN, KATHIE NEWMAN, STEVEN CORCELLI, University of Notre Dame — The interactions of water and many interfaces are not understood at a mechanistic level. The accuracy of simulations of the system are limited by the accuracy of the water model used. Classical models such as SPC/E use empirically derived parameters to match their behavior to desired bulk water properties, but cannot participate in reactions that require the making or breaking of bonds. Ab initio quantum mechanical methods such as Car-Parrinello (CP) do allow water to dissociate, but are computationally intractable for large systems. A potential middle ground is the self-consistent charge density-functional tight-binding method (SCC-DFTB), which has a smaller associated computational cost, and therefore can access larger systems than CP, while still allowing for the making and breaking of bonds. The DFTB+ implementation of SCC-DFTB allows for 2nd and 3rd order expansions of the density fluctuations in the energy and, in the 3rd order expansion, an optional damping correction factor. For each of these models we compare the structural, dynamic, and spectroscopic properties of bulk SCC-DFTB water to classical SPC/E and experimental results.

10:48AM V41.00009 Interfacial water on TiO2 anatase (101) and (001) surfaces: First-principles study with TiO2 slabs dipped in bulk water, YOSHITAKA TATEYAMA, MASATO SUMITA, International Centre for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), CHUNPING HU, Tokyo University of Science — Density functional molecular dynamics simulations using supercells with “bulk” water between the TiO2 anatase (101) and (001) surfaces were carried out to elucidate the behaviour of water molecules and hydrogen bond networks on the interfaces of representative photocatalysts. It is demonstrated that the adsorption manners (molecular or dissociative) of water molecules on the vacuum surfaces still hold in the presence of “bulk” water on the interfaces. We also showed explicit atomistic structures of strong and weak hydrogen bonds on the TiO2/water interfaces, which had been proposed experimentally so far. We then suggested a two-layer model for the interfacial water on both surfaces investigated. Our results also give insights into the H2O2, OH adsorption coverage on the interfaces and their hydrophobicity- hydrophilicity, which is important to understand the photocatalytic reaction mechanisms microscopically.

3This work was supported by JST-PRESTO, JST-CREST and KAKENHI.

Thursday, March 24, 2011 11:15AM - 2:03PM —
Session W41 DCP: Focus Session: Electronic Structure and Applications to Energy Conversion

11:15AM W41.00001 Tuning the electronic structure of II-VI semiconductors and nanostructures for energy applications, SHENYUAN YANG, Molecular Foundry, Lawrence Berkeley National Laboratory — Using first-principles calculations within density functional theory (DFT), we study the impacts of quantum confinement, strain, and surface ligand passivation on the electronic structure of typical II-VI wurtzite semiconductors and nanostructures. In CdSe/CdTe core/shell nanowires, large anisotropic strains develop due to the large lattice mismatch. These strains result in significant reductions in band gap in the CdSe core with increasing CdTe shell thickness, by amounts comparable to structural models from the fully analyzed data reveal the intrinsic interfacial structures. It is noted that the interfacial water structure above the first graphene layer exhibits remarkable differences with those of subsequent graphene layers. The latter one, resembling water on freestanding graphene, is well predicted by parallel computational simulations. Moreover, the pH of aqueous solutions was found to have a subtle influence on the interfacial water structure above the first graphene layer. This may well be an indication of the interfacial structural distortions that might exist in this layer, and which may play an important role in controlling the chemical activity of monolayer epitaxial graphene.

11:51AM W41.00002 TR-2PPE Studies of Ultrafast Charge Separation at Organic Photovoltaic Interfaces, S.W. ROBEY, G.J. DUTTON, NIST, W. JIN, J.E. REUTT-ROBEY, University of MD — Dissociation of excitons in organic photovoltaic (OPV) devices occurs exclusively at interfaces between donor and acceptor molecular materials. To help understand critical charge separation processes, we have performed time-resolved two-photon photoemission (TR-2PPE) studies of sub-picosecond exciton dynamics at well-characterized organic donor-acceptor interfaces. Interfaces between phthalocyanines and C60 were engineered using organic MBE and characterized using STM, STS, and UPS. Ultrafast TR-2PPE measurements were performed on CuPc/C60 structures by pumping the lowest optical π → π* transitions (Q-band) to generate CuPc singlet (S1) excitons and probing this population with a time-delayed UV pulse. For thick films, CuPc S1 decay is dominated by vibrational relaxation (several 100’s femtoseconds) and singlet-to-triplet conversion (∼1 picosecond). Directly at the interface, however, charge transfer to C60 dominates decay of S1 exciton (∼100 femtoseconds). We also find evidence for important recombination routes from the charge separated state back to lower-lying CuPc T1 triplet excitons.

To test the impact of intersystem crossing to triplet levels, we have performed analogous investigations for H2Pc/C60 interfaces. Results for this interface will be compared and contrasted with the CuPc/C60 case.

12:03PM W41.00003 Near- and Far-Field Effects on Excited States at Organic Semiconductor and Metal Interfaces, OLIVER MONTI, MARY STEELE, NAHDIL ILAYS, LEAH KELLY, University of Arizona — We present an investigation of the evolution of excited states at the interface of the dipolar organic semiconductor vanadyl phthalocyanine on highly oriented pyrolytic graphite. Using two-photon photoemission we observe several excited states at sub-monolayer to few-monolayer coverages. Excited states of this organic semiconductor are progressively stabilized with coverage, an effect that is somewhat mirrored in the image state manifold as well. These findings can be understood in the context of a simple electrostatic model that considers how molecular levels and vacuum level are influenced differentially by the strong electrostatic fields present at the interface with dipolar molecules. While the vacuum level rises continuously with coverage, the molecular states are significantly depolarized as a function of electric fields in the near-field regime. This indicates that the interfacial excited state electronic structure is strongly sensitive to long-range intermolecular interactions mediated by the surface, with direct implications for energy level alignment and charge transfer dynamics at the interface. Interfacial electrostatic fields may therefore be used to manipulate in a concrete fashion interfacial charge transfer processes such as photoinduced interfacial electron transfer.

12:15PM W41.00004 Time-domain ab initio studies of excitation dynamics in semiconductor quantum dots, OLEG PREZHDO, University of Rochester — Solar energy applications require understanding of dynamical response of novel materials on nanometer scale. Our state-of-the-art non-adiabatic molecular dynamics techniques, implemented within time-dependent density functional theory, allow us to model such response at the atomic level and in real time. The talk will focus on single and multiple exciton generation, relaxation, and annihilation and dephasing in semiconductor quantum dots.

References:

12:51PM W41.00005 Hole Localization in Molecular Crystals From Hybrid Density Functional Theory, MA SAI, PAUL F. BARBARA, University of Texas at Austin, KEVIN LEUNG, Sandia National Laboratory — Charge trapping in organic solids and interfaces plays an important role in organic photovoltaic efficiencies. Experimental confirmation of intrinsic charge trapping at the atomic scale and the tools to directly probe the trap energy landscape, however, remain lacking. We use first principles computational methods to examine hole trapping in organic molecular crystals. We present a computational scheme based on the tuning of the fraction of exact exchange in hybrid density functional theory to eliminate the many-electron self-interaction error [1]. With small organic molecules, we show that this scheme gives accurate descriptions of ionization and dimer dissociation. We demonstrate that the excess hole in perfect molecular crystals can form self-trapped hole polymers. The predicted absolute ionization potentials of both localized and delocalized holes are consistent with experimental values.

[1] The work is supported by Energy Frontier Research Center funded by the U.S. DOE Office of Basic Energy Sciences under Award number DE-SC0001091. KL is also supported by the DOE under Contract DE-AC04-94AL85000.

1:03PM W41.00006 Linear Dichroism and Photoluminescence Microscopy Imaging of Grain Boundaries in Crystalline Metal-Free Phthalocyanine Thin Films, ZHENWEN PAN, CODY LAMARCHE, ISHIVIE COUR, NAJEEV RAWAT, LANE MANNING, RANDALL HEADRICK, MADALINA FURIS, PHYSICS DEPT. AND MATERIAL SCIENCE PROGRAM, UNIVERSITY OF VERMONT, BURLINGTON, VT 05405 TEAM — We employed a combination of linear dichroism and photoluminescence microscopy with spatial resolution of 5μm to study the excitonic properties of solution-processed metal-free phthalocyanine (H2Pc) crystaline thin films with millimeter-sized grains. We observe a highly-localized, sharp, monomer-like emission at the high angle grain boundaries, in contrast to samples with more uniform grain orientation where no such feature has been observed. The energy difference between the grain boundary luminescence and the HOMO-LUMO singlet exciton recombination of the crystalline H2Pc is measured to be 160meV. Our systematic survey of grain boundaries indicates this localized state is never present at low angle boundaries where the π-orbital overlap between adjacent grains is significant. It supports recent results which associated a decrease in carrier mobility with the presence of large angle boundaries in similar crystalline pentacene films.

[1] This project is supported by DMR-0722451; DMR-0348354; DMR-0821268.

1:15PM W41.00007 Theories and applications for characterizing electronic coupling factors, CHAO-PING HSU, Academia Sinica — The transport of charges and excitation energy are two processes of fundamental importance in many biological and material systems. One of the fundamental parameters in the transport rates is the electronic coupling, which is essentially an off-diagonal Hamiltonian matrix element between the initial and final diabatic states. We have developed ways to define the diabatic states and calculate the coupling factors, including those for electron transfer (ET) and excitation energy transfer (EET). The fundamental method development and applications will be discussed. For characterizing TEET, the Fragment Spin Difference (FSD) was developed and it can be to calculate the TEET coupling over a general class of systems. TEET in bacterial light-harvesting complex LH2 and the peridinin chlorophyll-a protein (PCP) of dinoflagellates were calculated and analyzed. Our results are in good agreement with experimental results and it offers limits to the photoprotection models. Therefore, with the FSD scheme, it is possible to quantify and analyze the electronic couplings in TEET processes in large systems, and to derive insights and limits of theoretical models.
1:51PM W41.00008 Ab initio calculation of optical spectra of solvated molecules: GW+BSE method for liquid environments. JEEHYE LEE, TOMAS ARIAS, Cornell University — Electronic excitations for solvated systems have drawn a great interest in the energy community because they provide a possibility to engineer photoexcitation processes. Time-dependent DFT (TDDFT) and the hybrid QM/MM approach successfully calculate the solvent shift in excitation energies (solvatochromic shift) for confined systems, but are well known to work best for small systems and Frenkel excitons. Here we present a new modification of the GW and Bethe-Salpeter equation (GW+BSE) methods which allows treatment of solvated systems beyond the TDDFT level by including the frequency-dependent polarizability of the solvent at the diagrammatic level. In this initial work, we present the solvatochromic and ionization potential shifts for a series of molecules in aqueous solution.

Thursday, March 24, 2011 2:30PM - 5:18PM – Session X38 DCP DBP: Focus Session: Non-Equilibrium Insights into Single Molecules and Cell Function | A130/131

2:30PM X38.00001 The Statistical Mechanics of Trajectories and Weights: Applications to Gene Expression. ROB PHILLIPS, California Institute of Technology — Many fascinating questions concerning the behavior of systems ranging from chemical reaction patterns to the patterns of gene expression in living systems do not concern their terminal states, but rather the various microscopic trajectories connecting those states. Some of the most intriguing examples of these kinds of phenomena center on the time evolution of the many molecular machines that populate living cells. Motivated by studies of the time evolution of gene expression, this talk will review both classic approaches to time evolution using rate equations (but couched in the language of trajectories and weights) and more controversial ideas based upon the principle of maximum entropy.

3:06PM X38.00002 Challenges in Characterizing and Controlling Complex Cellular Systems. JOHN WIKSWO, Vanderbilt University — Multicellular dynamic biological processes such as developmental differentiation, wound repair, disease, aging, and even homeostasis can be represented by trajectories through a phase space whose extent reflects the genetic, post-translational, and metabolic complexity of the process - easily extending to tens of thousands of dimensions. Intra- and inter-cellular sensing and regulatory systems and their nested, redundant, and non-linear feed-forward and feed-back controls create high-dimensional attractors in this phase space. Metabolism provides free energy to drive non-equilibrium processes and dynamically reconfigure attractors. Studies of single molecules and cells provide only minimalist projections onto a small number of axes. It may be difficult to infer larger-scale emergent behavior from linearized experiments that perform only small amplitude perturbations on a limited number of the dimensions. Complete characterization may succeed for bounded component problems, such as an individual cell cycle or signaling cascade, but larger systems problems will require a coarse-grained approach. Hence a new experimental and analytical framework is needed. Possibly one could utilize high-amplitude, multi-variable driving of the system to infer coarse-grained, effective models, which in turn can be tested by their ability to control systems behavior. Navigation at will between attractors in a high-dimensioned dynamical system will provide not only detailed knowledge of the shape of attractor basins, but also measures of underlying stochastic events such as noise in gene expression or receptor binding and how both affect system stability and robustness. Needed for this are wide-bandwidth methods to sense and actuate large numbers of intracellular and extracellular variables and automatically and rapidly infer dynamic control models. The success of this approach may be determined by how broadly the sensors and actuators can span the full dimensionality of the phase space.

3:42PM X38.00003 Maximizing efficiency of molecular machines. GAVIN CROOKS, Lawrence Berkeley Natl. Lab. — I will discuss how to locate protocols that minimize dissipation in non-equilibrium, molecular scale processes, adapting ideas from finite-time thermodynamics.

4:18PM X38.00004 Autonomous Boolean models for logic, timing, and stability in regulatory networks. JOSHUA E.S. SOCOLAR, Physics Department and Center for Systems Biology, Duke University — The dynamics of gene expression in a cell is controlled by a dizzying array of biochemical processes. Natural selection, however, has created regulatory systems with a level of logical organization that can be modeled without detailed knowledge of the biochemistry. In cases where graded responses are not relevant, autonomous Boolean network (ABN) models can effectively represent the logic of gene regulation. These are models in which Boolean logic governs the output value of each node and the timing of updates is determined according to delay parameters associated with each link. An advantage of ABNs over synchronous or random asynchronous Boolean models can effectively represent the logic of gene regulation. These are models in which Boolean logic governs the output value of each node and the timing of updates is determined according to delay parameters associated with each link. An advantage of ABNs over synchronous or random asynchronous Boolean models is that noise associated with molecular concentrations or transport times can be represented through fluctuations in the timing of updates. We have used ABN models to investigate the stability of oscillations in a model of transcriptional oscillations in yeast and the parameter constraints in a model of segment polarity maintenance in the fly embryo, and also to characterize chaotic dynamics observed in a free-running digital electronic circuit. The yeast study highlights architectural and dynamical features of oscillators that rely on pulse transmission rather than a frustrated feedback loop, the fly study reveals timing constraints that are hidden in ODE models, and the electronics study shows that Boolean chaos can occur if and only if time delays are history dependent.

1 Supported by the Defense Threat Reduction Agency HDTRA-09-1-0013, NIH National Institute on Drug Abuse RC2DA028981, the National Academies Keck Futures Initiative, and the Vanderbilt Institute for Integrative Biosystems Research and Education

4:54PM X38.00005 Maximum Caliber Analysis of Ion-Channel Gating. ROY CAMPBELL, Walla Walla University — The principle of maximum caliber, MaxCal, is a generalization to nonequilibrium statistical mechanics of the principle of maximum entropy, MaxEnt. E. T. Jaynes introduced the MaxEnt approach to equilibrium statistical mechanics in 1957 and its MaxCal generalization in 1980. MaxCal has recently been used to derive dynamical laws of transport, analyze single particle two-state dynamics, and study few state models of non-equilibrium processes. We use MaxCal to analyze ion-channel gating data and make logical inferences concerning the underlying dynamics. The inferred trajectory probabilities are used to calculate the fluctuations responsible for channel noise.

5:06PM X38.00006 Designing denaturation: Nanoscale thermal transport as a probe of DNA melting. YONATAN DUBI, School of Physics and Astronomy, Tel-Aviv University, Tel-Aviv, Israel, KIRILL VELIZHANIN, CHIH-CHUN CHIEN, MICHAEL ZWOLAK, Los Alamos National Laboratory — The microscopic dynamics of DNA denaturation have long been a subject of intense study but many aspects of this phenomenon remain poorly understood. Experiments typically measure the degree of denaturation versus temperature which, unfortunately, introduces only a relatively weak constraint: Although many existing models reproduce this denaturation transition well, they give, e.g., incorrect time scales for fluctuations in base pair unbinding. Here, we propose a critical test of DNA models based on driving DNA out of thermal equilibrium via two heat reservoirs. Contrary to what might be expected, we find that the green part of model predictions is not directly connected to the thermal conductance to ice substantially as DNA melts. Furthermore, we show that different models can possess qualitatively different thermal transport properties. Measuring the thermal conductance of DNA will thus shed new light on the nonlinear physics of this important molecule and may lead to novel thermal technologies, such as a DNA thermal switch.
2:30PM X41.0001 Fundamental understanding and computational design of thin-film photovoltaic materials, JEFFREY C. GROSSMAN, Massachusetts Institute of Technology — The search for abundant and clean energy sources has placed photovoltaics at the focus of research over a variety of disciplines spanning physics, chemistry and materials science. However, the quest for more cost-efficient photovoltaics is challenged by limitations in efficiency of charge excitation and collection in the materials and their interfaces. We will present our recent ab initio calculations aimed at understanding important microscopic mechanisms in solar photovoltaic materials. Our goal is to predict accurately key properties that govern the efficiency in these materials, including structural and electronic effects, interfacial charge separation, electron and hole traps, excited state phenomena, band level alignment, and binding energies. Examples of our work in the areas of organic and thin-film photovoltaics will be presented. We use these examples to illustrate how accurate electronic structure approaches can improve our understanding and lead to more efficient materials.

3:06PM X41.0002 Effect of environment and long range behaviour of exciton exchange on polaron formation in \( \pi \)-conjugated polymers, IFFAT NAYYAR, Theoretical Div, Los Alamos National Lab, NM and NanoScience Technology Center, Dep. of Physics, University of Central Florida, Orlando, FL, ENRIQUE BATISTA, SERGEI TRETIAK, AVADH SAXENA, DARRYL SMITH, RICHARD MA, Theoretical Division, Los Alamos National Lab, NM — Organic conjugated polymers find a variety of applications in devices such as solar cells, light emitting diodes and lasers. An accurate understanding of the role of nonlinear excitations as polarons in charge carrier transport is critical to improve the efficiency of these devices. PPV and MEH-PPV are the candidates of choice for the extensive experimental data and relative simplicity compared to other polymers. This motivated us to perform a density functional theory study to describe the charge defects in these systems. We emphasize on the role of surrounding dielectric medium and the amount of long range orbital exchange in the density functional to predict the polaron localization in agreement with experiment. The particle-hole symmetry observed in trans-geometries is broken by introducing certain cis defects.

3:18PM X41.0003 Photo-induced modulation in the dipole moment of a donor-acceptor pair of organic molecules, YOSHIYUKI MIYAMOTO, National Institute of Advanced Industrial Science and Technology, Japan, MINA YOON, ORNL, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der Max-Planck-Gesellschaft — We have investigated the photo-induced electron dynamics in donor-acceptor pairs of organic molecules. Specifically we will discuss TTF and TCNQ molecules and study their electron dynamics under illumination by means of time-dependent density functional theory within the local-density approximation. In their stable molecular structure, we find that these molecules align in parallel and show maximum optical oscillator strength with an optical polarization parallel to their molecular axis. Without illumination, a dipole moment from TTF to TCNQ directs perpendicular to the molecular axis. This dipole-moment is further increased upon illumination with an optical polarization parallel to the molecular axis. Experiments have shown that energetic disorder alone reduces the exciton diffusion length more than one order of magnitude, from values typically encountered in molecules (>50nm) to values actually measured in CPs (<10nm). 2) A number of organic crystals show anisotropic excitedon couplings, with weak interlayer interactions between molecules that are more strongly coupled within the layers. The resulting energy carriers are intra-layer 2D excitons that diffuse along the molecular axis. Here we demonstrate that energetic disorder alone reduces the exciton diffusion length more than one order of magnitude, from values typically encountered in molecules (>50nm) to values actually measured in CPs (<10nm). 2) A number of organic crystals show anisotropic excitedon couplings, with weak interlayer interactions between molecules that are more strongly coupled within the layers. The resulting energy carriers are intra-layer 2D excitons that diffuse along the molecular axis. Here we demonstrate that energetic disorder alone reduces the exciton diffusion length more than one order of magnitude, from values typically encountered in molecules (>50nm) to values actually measured in CPs (<10nm).

3:30PM X41.0004 Exciton transport and dissociation at organic interfaces, DAVID BELJONNE, University of Mons — This paper focuses on modeling studies of exciton transport and dissociation at organic interfaces and includes three parts: 1) Experiments have shown that the values of exciton diffusion length \( L_D \) in conjugated polymers (CPs) are rather low, in the range of 5-10 nm, apparently regardless of their chemical structure and solid-state packing. In contrast, large \( L_D \) values have been reported in molecular materials that are chemically more well-defined than CPs. Here we demonstrate that energetic disorder alone reduces the exciton diffusion length more than one order of magnitude, from values typically encountered in molecules (>50nm) to values actually measured in CPs (<10nm). 2) A number of organic crystals show anisotropic excitedon couplings, with weak interlayer interactions between molecules that are more strongly coupled within the layers. The resulting energy carriers are intra-layer 2D excitons that diffuse along the interlayer direction. We model this analytically for infinite layers and using quantum-chemical calculations of the electronic couplings for anthracene clusters. We show that the exciton hopping rates and diffusion lengths depend in a subtle manner on the size and shape of the interacting aggregates, temperature and the presence of energetic disorder. 3) The electronic structure at organic/organic interfaces plays a key role, among others, in defining the quantum efficiency of organic-based photovoltaic cells. Here we perform quantum-chemical and microelectrostatic calculations on molecular aggregates of various sizes and shapes to characterize the interfacial dipole moment at pentacene/C60 heterojunctions. The results show that the interfacial dipole mostly originates in polarization effects due to the asymmetry in the multiplar expansion of the electronic density distribution between the interacting molecules. We will discuss how the quadrupoles on the pentacene molecules produce direct electrostatic interactions with charge carriers and how these interactions in turn affect the energy landscape around the interface and therefore also the energy barrier for exciton dissociation into free carriers.

4:06PM X41.0005 Correlating First-Principles Electronic Structure with Device Performance of Organic Photovoltaic Cells, ERIC B. ISAACS, SAHAR SHARIFZADEH, BIWU MA, JEFFREY B. NEATON, Molecular Foundry, Lawrence Berkeley National Laboratory — Organic photovoltaic cells (OPVs) are promising candidates for low-cost solar energy conversion. Here, we employ static and dynamic calculations aimed at understanding important microscopic mechanisms in solar photovoltaic materials. Our goal is to predict accurately key properties that govern the efficiency in these materials, including structural and electronic effects, interfacial charge separation, electron and hole traps, excited state phenomena, band level alignment, and binding energies. Examples of our work in the areas of organic and thin-film photovoltaics will be presented. We use these examples to illustrate how accurate electronic structure approaches can improve our understanding and lead to more efficient materials.

4:18PM X41.0006 Photo-induced Charge Separation in Nanoscale Donor-Bridge-Acceptor Systems: Theory and Experiment, PETER DOAK, Molecular Foundry, LBNL; Department of Chemistry, UC-Berkeley, PIERRE DARANCET, Molecular Foundry, LBNL, KASPER MOTH-POULSEN, Department of Chemical and Biological Engineering, Chalmers U. of Technology, JESSE JENKINS, Department of Chemistry, UC-Berkeley, RACHEL SEGALMAN, Department of Chemical Engineering, UC-Berkeley, DON TILLEY, Department of Chemistry, UC-Berkeley, JEFF NEATON, Molecular Foundry, LBNL — Understanding and control of light-harvesting processes at the molecular-scale remains a fundamental challenge in solar energy conversion. Donor-bridge-acceptor molecules (DBAMs), with atomically-defined interfaces made by a covalently bound bridge between donor and acceptor moieties, allow probing of excited states relevant to optical absorption and charge separation. In close collaboration with experiment, we use first-principles many-body perturbation theory, within the GW approximation and the Bethe-Salpeter equation approach, to compute excited states for six DBAMs. We compare with experiments, and quantitative agreement is obtained. Implications of our results for nanoscale light-harvesting are thoroughly discussed. Support: DOE via the Molecular Foundry and Helios SERC, and NSF via NCN. Computational support provided by NERSC.
4:30PM X41.00007 Exciton Scattering in Branched Conjugated Molecules: Towards Photoinduced Dynamics and Energy Transfer, VLADIMIR CHERNYAK, Wayne State University — The exciton scattering (ES) approach attributes excited electronic states in quasi-one-dimensional (branched) conjugated molecules with perfect geometry to standing waves on the linear segments of a molecule formed by scattering of quantum quasi-particles (excitons). We extract their dispersion and frequency-dependent scattering matrices at termini, including donor/acceptor substitutions, joints, and branching centers from time-dependent density functional theory (TD-DFT) calculations, with applications to for conjugated phenylacetylene-based molecules. This allows electronic spectra for any structure of arbitrary size within the considered molecular family to be obtained with insignificant numerical effort. To extend the capability of the ES approach to treating photoinduced dynamics, including absorption and fluorescence line shapes and energy transfer, the methodology should be modified to account for non-ideal molecular geometry. Geometry distortions break down translational symmetry of the linear segments, and excitations are not represented by perfect standing waves anymore. To overcome this difficulty we associate electronic excitations with the eigenstate of a quantum particle on an irregular lattice (graph), referred to as a tight-binding model. The morphology of the underlying lattice, together with the tight-binding parameters, can be identified by studying the topological and analytical properties of excitons at molecular termini, joints, and branching centers. The dependence of the tight-binding parameters on geometry distortions that controls effects of disorder and coupling to vibrational modes can be extracted from quantum chemical calculations by studying exciton scattering on localized geometry distortions, the latter considered as scattering centers.

5:06PM X41.00008 NA-ESMD modeling of photoinduced dynamics in conjugated molecules, TAMMIE NELSON, Los Alamos National Laboratory, SEBASTIAN FERNANDEZ-ALBERTI, Universidad Nacional de Quilmes, VLADIMIR CHERNYAK, Wayne State University, ADRIAN ROITBERG, University of Florida, SERGEI TRETIAK, Los Alamos National Laboratory — The evolution of electronic excitations in optically active molecules can generally be defined by non-adiabatic (NA) dynamics. A number of fundamental and complex processes are associated with NA dynamics. To treat ultrafast excited state dynamics we have developed a non-adiabatic excited state molecular dynamics (NA-ESMD) framework incorporating quantum transitions. Our calculations combine the Collective Electronic Oscillator (CEO) package with the Tully’s fewest switches algorithm for surface hopping, and the actual potential energy surfaces of the excited states are used. This method is applied to model the photoinduced dynamics of distyrylbenezene. Our analysis shows intricate details of vibronic relaxation and identifies specific slow and fast nuclear motions that are strongly coupled to the electronic degrees of freedom. Non-adiabatic relaxation of the highly excited mAg state is predicted to occur on a femtosecond timescale at room temperature and on a picosecond timescale at low temperature.

Friday, March 25, 2011 8:00AM - 11:00AM – Session Y5 DCMP DCP: Opening the Gap: Chemical Functionalization and Substitution in Graphene Ballroom C1

8:00AM Y5.00001 Magnetic Moment and Electronic Correlations in Chemically Functionalized Graphene, JORGE SOFO, Penn State — Magnetic moments in extended systems are the result of local electronic correlations. In the case of graphene functionalized with chemisorbed atoms such as hydrogen, fluorine, or oxygen, the Anderson Model picture, where correlations in a localized state are responsible for the formation of a magnetic moment, has to be modified to properly describe the magnetic moment formation and their interactions. We use a tight-binding model with local correlations to analyze the results obtained with Density Functional Theory calculations for these systems. The model allows the treatment of local correlations beyond the mean field level and the investigations of a possible Kondo effect. We find that the Coulomb repulsion at the carbon atoms near the impurity play a crucial role in the magnetic moment formation. External doping with a gate voltage can control the nature of the binding and the formation of the magnetic moment. This effect could be observed in transport experiments as the scattering of the graphene electrons at the Fermi energy strongly depends on the structure of the defect.

8:36AM Y5.00002 A theoretical study of chemical functionalisation of graphene: graphane and graphXene, OLLE ERIKSSON, Uppsala University — Chemical functionalisation of graphene is reported from a first principles, theoretical study [1]. The electronic structure, including band gap, of H adsorbed on graphene (i.e. graphane) is discussed in this presentation [2]. In addition, adsorption of Group VII elements on graphene (named graphXene) is also reported [3]. Similarities and differences in the chemical binding and electronic structure of graphane and graphXene are analyzed. The adsorption on graphene is found to, depending on adatoms, result in sp2 or sp3 binding, where in general the sp3 bonded systems show a bandgap. The theoretical calculations make use of both GGA functionals as well as the GW approximation. In addition to large graphene layers, theoretical analysis of functionalised graphene nano-ribbons will also be presented [4]. References:


9:12AM Y5.00003 Gap control via graphene solid-state reactions, BORIS I. YAKOBSON, Rice University — While a gapless dispersion law of Dirac fermions in graphene does warrant admiration, to serve as useful semiconductor graphene needs a gap. Relatively inert, it can nevertheless be induced to react. A generic outcome of a reaction, C + A -> C1..A2, is a transition of some C-atoms from their sp2- to sp3-state, corresponding to a situation of the insulating, ultimate (mono- or few-layer) diamond slab [1]. Computations support a concept that the product of such reactions (A = H, F, O, Cl, etc.) forms a well-defined phase [2], permitting a patterning of 2D-geometries with useful properties: interconnects-nanoroads [3], quantum isles-dots [4], etc. Comparison of hydrogenation (A = H) into graphXene with fluorination (A = F) into 2D-teflon, shows the former as hindered by nucleation barrier and reversible (H-storage), in contrast to barrier-less reaction into a stable CF in the latter. *** In collaboration with F. Ding, E. Penev, M.A. Ribas, and A.K. Singh.***

References:

9:48AM Y5.00004 Spin-polarized semiconductor induced by magnetic impurities in graphene

M. DAGHOFER, IFW Dresden — Magnetic impurities adsorbed on graphene sheets are coupled antiferromagnetically via the itinerant electrons in the graphene. We study this interaction and its impact on the electrons' spectral density by use of unbiased Monte-Carlo simulations. The antiferromagnetic order breaks the symmetry between the sublattices, and a gap for the itinerant electrons opens. Our simulations show that the itinerant states below and above the gap are not dispersionless states trapped by the impurities, but are instead mobile states with a large dispersion. We compare various scenarios for the impurity distribution and find that random doping produces a standard semiconductor. If, on the other hand, all or most of the impurities are localized in the same sublattice, the spin degeneracy is lifted and the conduction band becomes spin-polarized. We also discuss the properties of edge states at edges or magnetic domain boundaries.


1Supported by the DFG under the Emmy-Noether Program, and the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. DOE.

10:24AM Y5.00008 Graphene monofluoride: a wide bandgap material derived from graphene

JUN ZHU, Penn State University — Fluorination provides an effective way of controlling the properties of carbon materials. In this talk, I will describe our experimental and theoretical work on the synthesis, structural, electrical and optical properties of fully fluorinated graphene and graphite, i.e., graphene monofluoride CF and graphite monofluoride (CF)\textsubscript{n}. (CF)\textsubscript{n} is synthesized by reacting HOPG graphite with F\textsubscript{2} gas at high temperature. Transmission electron microscopy and electron diffraction measurements show that the lattice constant is 4% larger than that of graphene, in agreement with first principle calculations. We observe the E\textsubscript{g} and A\textsubscript{1g} Raman modes of graphene monofluoride using UV Raman spectroscopy. Photoluminescence measurements of (CF)\textsubscript{n} using variable excitation wavelength (244-514 nm) and temperature (5-295 K) show several emission modes in the visible spectrum, which likely originate from mid-gap defect states. The absence of the band edge emission suggests a large band gap of greater than 5 eV. Partially fluorinated graphene monofluoride exhibits non-linear, strongly insulating transport with variable-range hopping temperature dependence, consistent with the presence of localized states due to missing fluorine atoms. Highly conductive graphene can be recovered by annealing CF in Ar/H\textsubscript{2} at high temperature, resulting in a conductance improvement of five orders of magnitude. As a transparent and atomically thin insulator, graphene monofluoride may find its use in graphene electronics and photonics. In collaboration with: Wei Wang, Shih-Ho Cheng, Justin Sparks, Humberto Gutierrez, Ke Zou, Ning Shen, Youjian Tang, Qingzhen Hao, Awnish Gupta, Peter Eklund, Vincent Crespi, Jorge Sofo and Fujio Okino (Shinshu University, Japan). References: Cheng et al., "Reversible fluorination of graphene: towards a two-dimensional wide band gap semiconductor." Phys. Rev. B 81, 205435 (2010) Wang et al., "Photoluminescence from nanocrystalline graphite monofluoride." Appl. Phys. Lett. 97, 141915 (2010)

Friday, March 25, 2011 8:00AM - 10:48AM –
Session Y38 DCP DBP: Focus Session: Non-Equilibrium Insights into Single Molecules and Cell Function II A130/131

8:00AM Y38.00001 Can Simple Biophysical Principles Yield Complicated Biological Functions? . JAN LIPHARDT, Physics Dept., UC Berkeley — About once a year, a new regulatory paradigm is discovered in cell biology. As of last count, euarkyotic cells have more than 40 distinct ways of regulating protein concentration and function. Regulatory possibilities include site-specific phosphorylation, epigenetics, alternative splicing, mRNA (re)localization, and modulation of nucleo-cytoplasmic transport. This raises a simple question. Do all the remarkable things cells do, require an intricately choreographed supporting cast of hundreds of molecular machines and associated signaling networks? Alternatively, are there a few simple biophysical principles that can generate apparently very complicated cellular behaviors and functions? I will discuss two problems, spatial organization of the bacterial chemotaxis system and nucleo-cytoplasmic transport, where the latter might be true. In both cases, the ability to precisely quantify biological organization and function, at the single-molecule level, helped to find signatures of basic biological organizing principles.

8:36AM Y38.00002 Single-Molecule Analysis of Protein Large-Amplitude Conformational Transitions . HAW YANG, Princeton University — Proteins have evolved to harness thermal fluctuations, rather than frustrated by them, to carry out chemical transformations and mechanical work. What are, then, the operation and design principles of protein machines? To frame the problem in a tractable way, several basic questions have been formulated to guide the experimental design: (a) How many conformational states can a protein sample on the functionally important timescale? (b) What are the inter-conversion rates between states? (c) How do ligand binding or interactions with other proteins modulate the motions? (d) What are the structural basis of flexibility and its underlying molecular mechanisms? Guided by this framework, we have studied protein tyrosine phosphatase B, PtpB, from M. tuberculosis (a virulence factor of tuberculosis and a potential drug target) and adenylate kinase, AK, from E. coli (a ubiquitous energy-balancing enzyme in cells). These domain movements have been followed in real time on their respective catalytic timescales using high-resolution single-molecule Förster resonance energy transfer (FRET) spectroscopy. It is shown quantitatively that both PtpB and AK are capable of dynamically sampling two distinct states that correlate well with those observed by x-ray crystallography. Integrating these microscopic dynamics into macroscopic kinetics allows us to place the experimentally measured free-energy landscape in the context of enzymatic turnovers.

9:12AM Y38.00003 Unfolding proteins with mechanical forces: From toy models to atomistic simulations1 . DMITRI MAKAROV, University of Texas at Austin — The remarkable combination of strength and toughness, displayed by certain biological materials (e.g. spider silk) and often unmatched by artificial materials, is believed to originate from the mechanical response of individual load-bearing protein domains. Single-molecule pulling experiments carried out during the last decade showed that those proteins, when loaded, respond in a non-equilibrium fashion and can dissipate large amounts of energy through the breaking of sacrificial bonds. In my talk, I will discuss what structural properties correlate with mechanical strength and toughness at the single-molecule scale, how thermodynamic stability is related to the mechanical stability, and why both atomistic simulations and simple models seem to fail to reconcile the mechanical responses of the same proteins measured under varied loading regimes. I will further discuss whether it is easier to unfold a protein mechanically by pulling at its ends or by threading it through a narrow pore. The latter process is believed to commonly occur in living organisms as an intermediate step in protein degradation.

1Supported by the NSF and the Robert A. Welch Foundation

9:48AM Y38.00004 Non-equilibrium microeomeology of living cells . MING-TZO WEI, Bioengineering, Lehigh University, Bethlehem, PA, USA 18015, H. DANIEL OU-YANG, Physics and Bioengineering, Lehigh University, Bethlehem, PA, USA 18015 — Intracellular stresses generated by molecular motors can actively modify cytoskeletal network and change intracellular mechanical properties. We study the out-of-equilibrium microeomeology in living cells using endogenous organelle particles as probes. This paper reports measurements of the intracellular mechanical properties using passive, particle-tracking and active, optical tweezers-based microeomeology approaches. Using arguments based on the fluctuation-dissipation theorem, we compared the results from both approaches to distinguish thermal and non-thermal mechanical fluctuations in living cells.
10:00AM Y38.00005 Dissecting the heterogeneity of gene expressions in mouse embryonic stem cells¹, LING-NAN ZOU, MATT THOMSON, S. JOHN LIU, FAS Center for Systems Biology, Harvard University, SHARAD RAMANATHAN, Department of Molecular and Cellular Biology, FAS Center for Systems Biology, Harvard University — A population of genetically identical cells, of the same nominal cell type, and cultured in the same petri dish, will nevertheless often exhibit varying patterns of gene expression. Taking mouse embryonic stem (ES) cells as a model system, we use immunofluorescence and flow cytometry to examine in detail the distribution of expression levels for various transcription factors key to the maintenance of the ES cell identity. We find the population-level distribution of many proteins, once rescaled by the average expression level, have very similar shapes. This suggests the largest component of observed heterogeneity comes from a single source. More subtly, we find the expression many of genes appears to correlate with the cell cycle. This may suggest that the program for maintaining ES cell identity is tightly coupled to the cell cycle machinery.

¹ This work is supported by the Harvard Stem Cell Institute and the Jane Coffin Childs Memorial Fund for Medical Research.

10:12AM Y38.00006 Synchronization of Cell Cycle Oscillator by Multi-pulse Chemical Perturbations, YIHAN LIN, YING LI, AARON DINNER, NORBERT SCHERER, University of Chicago — Oscillators underlie biological rhythms in various organisms and provide a timekeeping mechanism. Cell cycle oscillator, for example, controls the progression of cell cycle stage and drives cell cycle progression by the level of a histidine kinase. Here, we present our recent effort to synchronize the division of a population of bacterium cells by external pulsatile chemical perturbations. We were able to synchronize the cell population by phase-locking approach: the external oscillator (i.e. periodic perturbation) entrains the internal cell cycle oscillator which is in analogous to the phase-locking of circadian clock to external light/dark oscillator. We explored the ranges of frequencies for two external oscillators of different amplitudes where phase-locking occurred. To our surprise, non-periodic chemical perturbations could also cause synchronization of a cell population, suggesting a Markovian cell cycle oscillation dynamics.

10:24AM Y38.00007 Analysis of Cell Cycle Phase Response Captures the Synchronization Phenomena and Reveals a Novel Cell Cycle Network Topology, YING LI, YIHAN LIN, NORBERT SCHERER, AARON DINNER, University of Chicago — Cell cycle progression requires a succession of temporally-regulated sub-processes, including chromosome replication and cell division, which are each controlled by their own regulatory modules. The modular design of cell cycle regulatory network allows robust environmental responses and evolutionary adaptations. It is emerging that some of the cell cycle modules involve their own autonomous periodic dynamics. As a consequence, the realization of robust coordination among these modules becomes challenging since each module could potentially run out of sync. We believe that an insight into this puzzle resides in the coupling between the contributing regulatory modules. Here, we measured the phase response curve (PRC) of the cell cycle oscillator by driving the expression of a master regulator of the cell cycle in a pulsatile manner and measuring the single cell phase response. We constructed a return map that quantitatively explains the synchronization phenomena that were caused by periodic chemical perturbation. To capture the measured phase response, we derived a minimalist coupled oscillator model that generalizes the basic topology of the cell cycle network. This diode-like coupling suggests that the cell is engineered to ensure complete coordination of constituent events with the cell cycle.

10:36AM Y38.00008 Swimming Response of Individual Paramaecia to Variable Forces¹, ILYONG JUNG, MICHAEL WAGMAN, JAMES M. VALLES, JR., Brown University — Experiments demonstrate that swimming paramaecia exhibit a negative force-kinetic response. In particular, upward swimming paramaecia exert a stronger propulsive force as they fight their tendency to sediment. This response is remarkable because it suggests that paramaecia can sense forces as small as their apparent weight, which is less than 100 pN. We are investigating the origins of this response by applying variable magnetic forces to individual swimming paramaecia and measuring how their swimming trajectories change. We conduct the experiments at the National High Magnetic Field Laboratory where it is possible to achieve forces sufficient to stall the swimmers. We will present our latest data on how paramaecia adjust the geometry of their helical trajectories under varying forces.

¹ This work is supported by the NSF through PHY0750360 and the NHMFL.

Friday, March 25, 2011 8:00AM - 10:48AM –
Session Y39 DCP: Focus Session: Imaging and Interfaces in Energy Science A124/127

8:00AM Y39.00001 Imaging Interfacial Structure and Reactivity with X-ray Reflectivity and Microscopy¹, PAUL FENTER, Argonne National laboratory — A fundamental understanding of interfacial reactions is best achieved with ability to observe the systems of interest directly, ideally with molecular-scale resolution and/or sensitivities. X-ray-based approaches offer broad opportunities for probing complex interfaces in environments (e.g., liquids) that are normally inaccessible. I will describe two complimentary approaches for imaging interfaces. The first, X-ray reflection interface microscopy (XRM), uses the weak interface-reflected X-ray beam to image laterally heterogeneous interface structures and processes using a full-field imaging approach. This approach incorporates all of the sensitivities of X-ray reflectivity (XR, including sensitivity to interfacial topography, structure and composition) as potential contrast mechanisms. Recent applications of XRM will be described, including the ability to observe: elementary surface topography (i.e., ~5 Å-high steps) with ~100 nm spatial resolution; interfacial reactivity; and liquid-solid interfaces, in-situ. A second, complementary, approach images the vertical distributions of element-specific sub-structures at an interface through the use of resonant dispersion at X-ray energies close to element’s absorption edge (resonant anomalous X-ray reflectivity, RAXR). Recent applications of RAXR will be described including the ability to image element-specific distributions (i.e., ions near a charged liquid-solid interface) and its sensitivity for probing oxidation state specific structures at interfaces. The use of these techniques to observe charge transport at interfaces with respect to energy-related processes will be discussed.

¹ This work supported by the Geoscience Research Program of the US Department of Energy, Office of Basic Energy Sciences. This work is done in collaboration with M. J. Bedzyk, J. Catalano, S. S. Lee, C. Park, N. C. Sturchio, Z. Zhang, and P. Zschack.

8:36AM Y39.00002 Small-Pore Molecular Sieves SAPO-34 with Chabazite Structure: Theoretical Study of Silicon Incorporation and Interrelated Catalytic Activity, HONG WANG, JAMES LEWIS, West Virginia University, ZHONGMIN LIU, Dalian Institute of Chemical Physics — The catalytic conversion of methanol to olefin (MTO) has attracted attention both in industrial and academic fields. Strong evidence shows that small-pore molecular sieves with certain amount silicon incorporated (SAPO) present promising high catalytic activity in MTO conversion. Using DFT, we study the structural and electronic properties of chabazite SAPO-34. Although there are extensive experimental results show that silicon incorporation does not change the overall structure as the original AIPO structure, local structural changes are still created by silicon substitution, which probably accounted for the high catalytic activity. It is noted that the catalytic activity of SAPO-34 presents increasing trend along with the silicon incorporation amount increasing and maintain a flat peak even with more silicon incorporated. Hence, there is an optimal silicon incorporation amount which possibly yields the highest catalytic MTO conversion.
8:48AM Y39.00003 Nanosecond Scanning Tunneling Microscopy: resolving spin dynamics at the atomic scale, SEBASTIAN LÖTH, IBM Research - Almaden — With the advent of nanoelectronics, functional electronic elements advance towards atomic dimensions and analysis techniques need to keep pace. Scanning tunneling microscopes (STM) have evolved into standard tools to measure the static electronic properties of nanostructures, molecules and atoms. Here we show how the STM can be used to access the equally important dynamical properties on time scales ranging from pico- to nanoseconds. We combine inelastic electron tunneling spectroscopy (IETS) with an all-electronic pump-probe measurement scheme and record the dynamical evolution of magnetic atoms on surfaces in the time domain [1]. We focus on the dynamics of electron spin relaxation in transition metal atoms placed onto a copper nitride decoupling layer on Cu(100). On this surface Fe atoms experience large magneto-crystalline anisotropy [2] that enables long spin lifetimes. At the same time the quantum mechanical nature of the discrete spin states allows for an additional path of spin relaxation: quantum tunneling of magnetization. We probe the dynamic behavior associated with this process and find that placing a Cu atom close to a Fe atom boosts the uniaxial anisotropy energy and creates a long-lived spin state with relaxation times in excess of 200 ns. The ability to probe individual nanostructures with atomic spatial and nanosecond temporal resolution opens a new avenue to explore spin dynamics and other dynamical phenomena on the intrinsic length scale of the underlying interactions.


9:24AM Y39.00004 Tracking Oxygen Vacancies in Thin Film SOFC Cathodes1, DONOVAN LEONARD, AMIT KUMAR, STEPHEN JESSE, SERGEI KALININ, Oak Ridge National Laboratory. YANG SHAO-HORN, ETHAN CRUMLIN, EVA MUTORO, Massachusetts Institute of Technology. MICHAEL BIEGALSKI, HANS CHRISTEN, STEPHEN PENNYCOOK, ALBINA BORISEVICH, Oak Ridge National Laboratory. Oxygen vacancies have been proposed to control the rate of the oxygen reduction reaction and ionic transport in complex oxides used as solid oxide fuel cell (SOFC) cathodes [1,2]. In this study oxygen vacancies were tracked, both dynamically and statically, with the combined use of scanned probe microscopy (SPM) and scanning transmission electron microscopy (STEM). Epitaxial films of La0.8Sr0.2CoO3 (LSC113) and LSC113/LaSrCoO4 (LSC214) on a GDC/YSZ substrate were studied, where the latter showed increased electrocatalytic activity at moderate temperature. At atomic resolution, high angle annular dark field STEM micrographs revealed vacancy ordering in LSC113 as evidenced by lattice parameter modulation and EELS studies. The evolution of oxygen vacancy concentration and ordering with applied bias and the effects of bias cycling on the SOFC cathode performance will be discussed.

1 Research is sponsored by the DoE Materials Sciences and Engineering Division, U.S. DOE.

9:36AM Y39.00005 First principles study of GaN(1010)/Water interface, JUE WANG, MARIA VICTORIA FERNANDEZ-SERRA, XIAO SHEN, Stony Brook University — GaN/ZnO alloy semiconductors have been shown to be promising materials to serve as photo-anode in photocatalytic fuel cells. In recent studies by Shen et al. [1], the non polar GaN(1010) surface has been studied with atomistic modeling and a sequence of intermediate steps for the water oxidation process at the interface are proposed. Here we present a first principles molecular dynamics study of the GaN(1010)/Water interface. We found dissociation events happen within 1ps and we show a detailed analysis of the changes in structure and dynamics of water molecules interacting with a dissociating wet surface. The complex hydrogen bond network near the surface is also analyzed in detail, including a thorough study of the proton diffusion processes. We perform a detailed analysis of the dynamics of the hole localization. The link between water surface dissociation and quantum efficiency will be discussed.


9:48AM Y39.00006 Ions at interfaces and their spectroscopic consequences, PHILLIP GEISSLER, U.C. Berkeley — The affinity of relatively small ions for air-water interfaces challenges our basic understanding of the basic driving forces for solvation. Here I will discuss the structural and vibrational properties of hydrogen and methyl-terminated Si(111) surfaces both in air and in contact with water, by combining density functional theory and many-body perturbation theory within the GW approximation. The computed surface dipole moments for both H-Si(111) and CH3-Si(111) surfaces were found to be consistent with measured electron affinities (EAs), and can be explained by simple electronrenergizee trends. While GW self-energy corrections greatly improve the absolute values of EAs, the EA difference of the two surfaces remains overestimated by about 0.3 eV. The variations in CH3 frequencies, e.g. the umbrella mode and CH stretching mode, for the surface in air and water are also well reproduced by our calculations. The influence exerted by the adsorption of water molecules on the hydrophobic H-Si(111) and CH3-Si(111) surfaces, in particular, on the EAs and the surface vibrational frequencies will be discussed and compared with recent experiments.


1 This work was funded by NSF under Grant No. CHE-0802907.

10:24AM Y39.00007 First-Principles Studies of Functionalized Si(111) in Air and in Water1, YAN LI, Brookhaven National Laboratory, GIULIA GALLI, University of California, Davis — We have investigated structural, electronic and vibrational properties of hydrogen and methyl-terminated Si(111) surfaces both in air and in contact with water, by combining density functional theory and many-body perturbation theory within the GW approximation. The computed surface dipole moments for both H-Si(111) and CH3-Si(111) surfaces were found to be consistent with measured electron affinities (EAs), and can be explain by simple electronrenergizee trends. While GW self-energy corrections greatly improve the absolute values of EAs, the EA difference of the two surfaces remains overestimated by about 0.3 eV. The variations in CH3 frequencies, e.g. the umbrella mode and CH stretching mode, for the surface in air and water are also well reproduced by our calculations. The influence exerted by the adsorption of water molecules on the hydrophobic H-Si(111) and CH3-Si(111) surfaces, in particular, on the EAs and the surface vibrational frequencies will be discussed and compared with recent experiments.


1 This work was funded by NSF under Grant No. CHE-0802907.

10:36AM Y39.00008 Interaction between surfaces with ionizable sites, STEPHEN BARR, ATHANASSIOS PANAGIOTOPoulos, Chemical and Biological Engineering, Princeton University — A key factor controlling the interaction between surfaces in aqueous solutions is the surface charge density. Surfaces typically become charged through a titration process where surface groups can become ionized based on their dissociation constant and the pH of the solution. In this work we use a Monte Carlo method to treat this process explicitly in a system with two planar surfaces in a salt solution. We find that the surface charge density changes as the surfaces come close to contact due to interactions between the ionizable groups on each surface. In addition, we observe an attraction between the surfaces above a threshold surface charge, in good agreement with previous theoretical predictions based on uniformly charged surfaces. However, close to contact we find the force is significantly different than the uniformly charged case. We also explore the role of salt concentration and the density of the ionizable sites.

INSTITUTE OF PHYSICS, ACADEMIA SINICA

11:15AM Z39.00001 Two-dimensional soft solids: a rheological study1. GABRIEL ESPINOSA, Department of Physics, Simon Fraser University, Burnaby, BC, DUYANG ZANG, Laboratory of Materials Science in Space, Northwestern Polytechnical University, Xi’an, China, DOMINIQUE Langevin, Laboratoire de Physique des Solides, Université Paris Sud, Orsay, France, BERNARD BINKS, Department of Chemistry, University of Hull, Hull, UK — Many soft solids, such as concentrated suspensions, emulsions, foams, behave in a similar way under an applied shear: they exhibit a Maxwell-type relaxation with a characteristic relaxation time that varies inversely with the applied shear rate. When the storage and loss moduli are measured at different frequencies and constant shear rate, the curves obtained can be rescaled [1]. We will show here that the behavior in two dimensions can be strikingly similar. We will present data on monolayers of nanoparticles and on mixed layers made with DNA and surfactant. The physical origin of the relaxation time will be discussed. The nonlinear behavior will also be discussed. Depending on the compaction degree, the layers can behave as brittle or plastic solids. This has been confirmed by images of the layers after a shear deformation made using Brestaver angle microscopy.


1G.E. Acknowledge to Conacy for a doctoral fellowship.

11:27AM Z39.00002 ABSTRACT WITHDRAWN —

11:39AM Z39.00003 Direct measurement of short range colloidal interactions using digital holographic microscopy1, REBECCA W. PERRY, Harvard University, Sch. of Engineering and Applied Sciences, JEROME FUNG, DAVID M. KAZ, GUANGNAN MENG, Harvard University, Dept. of Physics, VINOTHAN N. MANOHARAN, Harvard University, Dept. of Physics and Sch. of Engineering and Applied Sciences — Using digital holographic microscopy, we record the 3D positions of micron-sized polystyrene particles as they approach and retreat from each other. Analysis of the holograms using an exact solution for the scattering from pairs of spheres allows us to separate vibrational, translational, and rotational motion. The vibrational mode supplies the information needed to characterize the inter-particle interactions down to separation distances on the order of 10 nm. In particular, we study an aqueous system of one micron diameter sulfate-coated polystyrene beads suspended in a solution of 95 nm hydrogel particles. The attractive depletion interaction we measure deviates from the Asakura-Oosawa model, likely because of electrostatic interactions at these short distances.

1We acknowledge support from NSF through grant no. CBET-0747625 and the NSF graduate research fellowship program.

11:51AM Z39.00004 Fabrication of Monolayer of Polymer/Colloids Hybrid at a Water-Air Interface, CHI-CHIH HO, TING-HUI CHEN, PO-YUAN CHEN, KENG-HUI LIN, WEN-TAU JUAN, WEI-LI LEE, Institute of Physics, Academia Sinica, INSTITUTE OF PHYSICS, ACADEMIA SINICA TEAM — Polymer-assisted assembly of polystyrene (PS) colloids with diameter ranging from 100 nm to 1 μm at water-air interface is demonstrated. Initially, PS colloids were slowly spread onto water surface and crystallized into triangular lattice with finite separation between colloids due to the coulomb repulsive force. By adding merely 1-3 ppm water-soluble polyethylene oxide (PEO) in water, the colloids gradually moved closer. Eventually, the separation between colloids was equal to or less than 60 nm determined from the fluctuation-dissipation theorem by a laser beam. In addition, the Brownian motion of colloids was suppressed by the PEO adsorption effect which was demonstrated from the analysis of colloids trajectory recorded by ultra high speed camera. We showed that the resulting monolayer of colloids /PEO hybrid can be deposited on various substrates, including a plastics sheet, curved surface and even across 10 μm-diameter hole. Our method may further extend the scope of nanosphere lithography technique for large area nanostructure fabrication.

12:03PM Z39.00005 Heterogeneous crystallization of hard-sphere colloids near a wall1, KYRIL SANDOMIRSKI, Heinrich-Heine-Universitaet Duesseldorf, IPKm, Universitaetstrasse 1, D-40225 Duesseldorf, Germany, ELSHAD ALLAHYAROV2, Physics Department, CWRU, Cleveland OH, USA, HARTMUT LOEWEN, Heinrich-Heine Universitaet Duesseldorf, Institut fuer Theoretische Physik II, Universitaetstrasse 1, D-40225 Duesseldorf, Germany, STEFAN EGELHAFF, Heinrich-Heine-Universitaet Duesseldorf, IPKm, Universitaetstrasse 1, D-40225 Duesseldorf, Germany — Confocal microscopy experiments and equilibrium Brownian Dynamics computer simulations were combined to investigate heterogeneous crystallization near a hard wall in a suspension of hard-sphere colloids. Particles near the wall initially rearrange, before an extended regime of steady-state crystal growth is observed. Finally, a depletion zone develops which slows down the progressing crystal-fluid interface. In good agreement between experiment and simulation, the steady-state growth velocity shows a maximum in its dependence on the bulk volume fraction. Beyond this, these techniques allow us to obtain local microscopic information on the level of individual particles, namely the temporal evolution of the density profiles in the fluid and crystal phase as well as the width of the interface.

1This work was supported by the DFG (SPP 1296). E.A. gratefully acknowledges support from a US DoE Grant (DE-FG02-05ER46244).

12:15PM Z39.00006 19F NMR Study of Molecular Aggregation of Lithium Perfluorooctylsulfonate in Water at Temperatures from 30 to 250 °C, DOBRIN BOSSEV, Indiana University, MUTSUO MATSUMOTO, MASARU NAKAHARA, Kyoto University — 19F NMR chemical shifts have been measured to determine the critical micelle concentration (cmc) and aggregation number (n) of lithium perfluorooctylsulfonate (LiFOS) in water at temperatures ranging from 30 to 250 °C under the saturation pressure. The cmc slightly increases in the temperature range from 30 to 100 °C, whereas above 125 °C the increase is much steeper; cmc is 6.5, 13.2, and 161 mmol kg−1 at 30, 100, and 250 °C, respectively. The aggregation number, estimated on the basis of a mass action model exhibits a rapid decrease in the temperature range of 30-125 °C and becomes almost constant at higher temperatures; n is 36, 6.8, and 2.4 at 30, 100, and 250 °C, respectively. Thermodynamic parameters indicate similar values for the free energy at all temperatures, and constant values for the enthalpy and entropy of aggregation at high temperatures.

12:27PM Z39.00007 Dielectric dispersion of clustered living cells via the boundary integral equation method, SAII KIT YUNG, KIN LOK CHAN, KIN WAH YU, The Chinese University of Hong Kong — We have developed a boundary integral equation (BIE) method for computing the dielectric response of clusters of biological particles like living cells. In the BIE, we formulate a surface integral equation for the scalar potential for an arbitrary number of particles of various shapes [1]. BIE method avoids matching the complicated boundary conditions on the surfaces of the particles. Numerical solutions of the eigenvalue equation yield a dielectric dispersion spectrum through the spectral representation [2]. While BIE method is valid for arbitrary surfaces, we confirm it for two approaching cylinders and a concentric cylinder. In many typical cases, the numerical results are in excellent agreement with the exact analytic results. Moreover, BIE method offers a convenient way to compute the alternating current responses, and hence the dielectric dispersion of clustered cell suspensions.

12:39PM Z39.00008 Multi scale computer simulations of the self-assembly of block copolymeric beta-peptides

JAGANNATH MONDAL, ARUN YETHIRAJ, University of Wisconsin Madison — There is considerable interest in a class of molecules made from \( \beta \)-amino acids (which contain an additional backbone carbon atom when compared with natural amino acids). Block copolymers of \( \beta \)-peptides, where one block is hydrophobic and the other is hydrophilic, self-assemble into micelles. In this work we use computer simulations to provide insight into the self-assembly of these molecules. All-atom simulation results for the free energy of association of a pair of these block co polymeric \( \beta \)-peptides show that a homochiral hydrophobic block promotes self assembly compared to a heterochiral hydrophobic block, consistent with experiment. We have also developed a coarse-grained model for these block co-polymers and simulations using this model show that these molecules spontaneously forms micelles, and the morphology of these micelles is concentration dependent, with spherical micelles at low concentrations and worm-like micelles at high concentrations.

12:51PM Z39.00009 Ab initio Study of Structure and Hydrogen Bonding of Cellulose Crystals and Surfaces

JAMES DAVENPORT, YAN LI, Brookhaven National Laboratory — We have studied the equilibrium structure and hydrogen bonding of cellulose crystals and surfaces using semi-empirical dispersion corrections to density functional theory (DFT-D)[1], which has been shown to be an efficient alternative to more advanced methods for weakly bound aromatic assemblies[2]. The predicted crystal structures for both \( \alpha \) and \( \beta \) phases agree well with experiments. The cohesive energy was decomposed into interchain and intersheet interactions and analyzed in terms of hydrogen bonding and van der Waals dispersion forces. Both interactions were found to be responsible for holding cellulose sheets together. In particular, the dispersion corrections to DFT proved to be indispensable in reproducing the equilibrium intersheet distance and binding strength. Adsorption energy and configuration of water molecules on cellulose surfaces were found to depend sensitively on the surface orientation, adsorption site and contribution from vdW interactions.

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1:03PM Z39.00010 Interfacial free energy and stiffness of the solid-melt interface of NaCl

TATYANA ZYKOVA-TIMAN, Chemistry Department, Cambridge Uni — The importance of the interfacial free energy for the equilibrium morphology of crystals is well understood. In contrast, much less is known about the so-called “interfacial stiffness” that governs fluctuations of, e.g., solid-liquid interfaces. We carried out molecular dynamics simulations of capillary wave fluctuations on various faces of NaCl crystals in contact with its melt, that provides new information on the behaviour of this interface at the atomistic level. The capillary fluctuations connect directly with the interfacial stiffness, and indirectly also to the interface free energy. In our simulations we studied the (100)-liquid interface and adjacent vicinals. From the angular dependence of the surface stiffness, we deduce an estimate of NaCl(100)-melt interfacial free energy and discuss limitations of the fluctuation approach. Finally we compare this estimate of the surface free energy with values obtained through other methods [1,2,3] and discuss the differences [4].


1:15PM Z39.00011 Utilization of Metal Oxides and Chalcogenides Stabilized in Organic Solvents

LESTER LAMPERT, ROBBY FLAIG, JORGE CAMACHO, JAMES HAMILTON, University of Wisconsin-Platteville — Metal oxides and metal chalcogenides are important materials for a variety of applications including photocatalysis for decomposition of water, conductive and optical coatings, catalysts, photovoltaics, ptyo-electrics, self-cleaning surfaces, pigments, and high efficiency Li-insertion materials in batteries among many other applications. Fundamental discoveries of surprising solubility of insoluble materials such as single and multi-walled carbon nanotubes and graphene has lead us to discover that certain metal oxides and metal chalcogenides such as TiO2 are soluble in certain solvents. Due to the industrial importance of TiO2, discovering stable pure solvent systems demonstrates a possibility to avoid surface modification of TiO2 nanoparticles by use materials such as of (3-methacryloxypropyl)-trimethoxysilane and various other methods of artificial stabilization. We have created thin films of TiO2, transparent ultraviolet (UV) –absorptive polymers, and Li-ion battery anodes with graphene-TiO2 hybrid materials.

1:27PM Z39.00012 EPR, Endor and DFT Studies on X-Irradiated Single Crystals of L-Lysine HCl 2H2O and L-Arginine HCl H2O

YIYING ZHOU, WILLIAM H. NELSON — When proteins and DNA interact, arginine and lysine are the two amino acids most often in close contact with the DNA. In order to understand the radiation damage to DNA in vivo, which is always associated with protein, it is important to learn the radiation damage of arginine and lysine independently, and then complexed to DNA. This work studied X-irradiated HCl·Lysine and HCl·Arginine single crystals of L-lysine-HCl·2H2O and L-arginine-HCl·H2O with EPR, ENDOR techniques and DFT calculations. In both crystal types irradiated at 66k, the carbonyl anion radical and the decarboxylation radical were identified. Specifically, the calculations performed on the cluster models for the carbonyl anion radicals reproduced the proton transfers to the carboxyl group from the neighboring molecules through the hydrogen bonds. Moreover, computations supported the identification of one radical type within irradiated arginine as the guanidyl radical anion with an electron trapped by the guanidyl group. Based on the radicals detected in the crystal irradiated at 66k and at 298k, and the annealing experiments from the irradiation at 66k, the mechanisms of the irradiation damage on lysine and arginine were proposed, and the possible effects of irradiated arginine and lysine to the DNA within chromatin were analyzed.

1:39PM Z39.00013 Detection of Nitro aromatics via fluorescence quenching of pegylated and siloxanated 4, 8-dimethylcoumarins

ABHISHEK KUMAR, MUKESH PANDEY, JAYANT KUMAR, University of Massachusetts Lowell — There is considerable interest in developing chemical sensors for detection of trace explosives. Optical sensors, which rely on the change in optical properties of the material, proved to be very effective. Therefore, there is a need to develop materials for optical sensors which interact specifically with analytes and detect them sensitively. Here, we report the synthesis of co-polymers of 4, 8-dimethylcoumarins with poly (ethylene glycol) (PEG) and polydimethylsiloxane (PDMS) using Candida Antartica lipase as a catalyst under solvent-less condition. The low Tg of PEG and PDMS may facilitate porous structure in solid films which allows quencher molecules to easily diffuse in and out of these films. In addition, the co-polymers prevent aggregation and lend themselves easily for thin film fabrication which otherwise is difficult because of low molecular weight of coumarin. Fluorescence quenching of these co-polymer in presence of nitro aromatics, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene, in solution and in vapor phase will be reported.

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[1] National Science Foundation
Correlated electrolyte solutions and ion-induced attractions between nanoparticles, JOS ZWANIKKEN, MONICA OLVERA DE LA CRUZ — Information about the degree of association can be obtained from a nonlinear Debye-Hückel theory [1], in agreement with simulation and experimental results [2], in strong contrast with the widely applied (linear) Debye-Hückel limiting law. The radial distribution functions calculated within this nonlinear theory are indistinguishable from molecular dynamics simulations of the restricted primitive model for divalent salts up to 0.1 molar concentrations. We apply the method to study the cohesive effects of strong couplings between ions on the effective interactions between nanoparticles, and the screening cloud around functionalized nanoparticles.


ABSTRACT WITHDRAWN