2009 APS March Meeting
Pittsburgh, Pennsylvania
http://www.aps.org/meetings/march/index.cfm
8:00AM A37.00001 Insights and Progress in Density Functional Theory. WEITAO YANG\textsuperscript{1}, Duke University — Density functional theory of electronic structure is widely and successfully applied in simulations throughout engineering and sciences. However, there are spectacular failures for many predicted properties, which can be traced to the delocalization error and static correlation error of commonly used approximations. These errors include underestimation of the barriers of chemical reactions, the band gaps of materials, the energies of dissociating molecular ions and charge transfer excitation energies. Typical DFT calculations also fail to describe degenerate or near degenerate systems, as arise in the breaking of chemical bonds, and strongly correlated materials. These can all be characterized and understood through the perspective of fractional charges and fractional spins introduced recently. Understanding the errors of functionals in the simplest way possible — as violations of exact conditions for fractional charges and fractional spins — opens the path forward for reduction of the errors and for applications of density functional theory in new frontiers. [P. Mori-Sanchez, A. J. Cohen, and W. T. Yang, Phys. Rev. Lett. 100:146401(2008); Phys. Rev. B,77:115123(2008); J. Chem. Phys. 129:121104(2008); Science, 321:792(2008)]

\textsuperscript{1}in collaboration with A. J. Cohen, P. Mori-Sanchez, and E. R. Johnson

8:36AM A37.00002 Semiclassical origins of density functional theory\textsuperscript{1}, KIERON BURKE, University of California, Irvine — Until the seminal work of Hohenberg, Kohn, and Sham of the mid 60’s, most density functional theory (DFT) was derived from semiclassical approximations. This non-empirical approach shows an intrinsic difference between solids (for which DFT was originally developed) and molecules, and explains many of its more mysterious manifestations. For example, the success of DFT for molecules has nothing to do with the uniform gas. Results include\textsuperscript{[1]} a derivation of the empirical parameter in the B88 exchange functional, \textsuperscript{[2]} PBEsol, a new GGA that restores the exchange gradient expansion and improves lattice constants in solids.\textsuperscript{[3]} A novel approach to “orbital-free” DFT that, in preliminary tests, is 40 times more accurate than its DFT counterpart. The talk is aimed at a general theoretical audience. Detailed technical knowledge of DFT is neither needed, nor desirable.

\textsuperscript{1}Research Supported by NSF grant CHE-0809859.

9:12AM A37.00003 Semiclassics in Density Functional Theory\textsuperscript{1}, DONGHYUNG LEE, ATTILA CANGI, Department of chemistry, University of California, Irvine, PETER ELLIOTT, Department of physics, University of California, Irvine, KIERON BURKE, Department of chemistry and physics, University of California, Irvine — Recently, we published an article \cite{1} about the semiclassical origin of density functional theory. We showed that the density and the kinetic energy density of one dimensional finite systems with hard walls can be expressed in terms of the external potential using the semiclassical Green’s function method. Here, we show a uniformization scheme for the semiclassical density and the kinetic energy density for turning-point problems.

\textsuperscript{1}NSF CHE-0809859

9:24AM A37.00004 Correlated Thomas-Fermi: Semiclassical ground-state energies of many-electron systems, BRIAN LANDRY, Harvard University, ADAM WASSERMAN, Purdue University, ERIC HELLER, Harvard University — A new semiclassical method is proposed to obtain accurate ground-state energies for many-electron systems. The method borrows its semiclassical character from Thomas Fermi theory (TF), but improves upon it by including correlation effects, at least approximately. We illustrate our method (CTF) on simple models of 1D-interacting electrons, showing that it yields dramatic improvements over TF, particularly in the strongly-correlated regime.

9:36AM A37.00005 Dimensional crossover of the exchange-correlation energy at the semilocal level\textsuperscript{1}, LUCIAN CONSTANTIN — Commonly used semilocal density functional approximations for the exchange-correlation energy fail badly when the two dimensional limit is approached. We show, using a quasi-two-dimensional uniform electron gas in the infinite barrier model, that the semilocal level can correctly recover the exchange-correlation energy of the two-dimensional uniform electron gas. We derive new exact constraints at the semilocal level for the dimensional crossover of the exchange-correlation energy and we propose a method to incorporate them in any exchange-correlation density functional approximation.

\textsuperscript{1}L.A.C. acknowledges NSF support (Grant No. DMR05-01588).

9:48AM A37.00006 Towards a semiclassical theory of electronic structure\textsuperscript{1}, ATTILA CANGI, DONGHYUNG LEE, Department of Chemistry, University of California, Irvine, PETER ELLIOTT, Department of Physics, University of California, Irvine, KIERON BURKE, Department of Chemistry, University of California, Irvine — Modern density functional theory (DFT) - formulated in the context of the Kohn-Sham scheme-evolved from “old” Thomas-Fermi theory to an accurate theory for predicting various properties of molecules and solids. We discuss the interrelation of semiclassical physics\textsuperscript{[1]} with the fundamental gradient approximation, which is the basis of all functional construction. We speculate that applying semiclassical methods in the context of a DFT-like theory is a path towards more accurate and efficient approximations to electronic properties of condensed systems.\textsuperscript{[2]}

\textsuperscript{1}National Science Foundation, CHE-0809859
Correlation, and Constraint Satisfaction

To circumvent this problem, a number of long-range-corrected functionals (based on GGAs) have recently been developed, which possess the correct asymptotic scaling. The scheme will integrate smoothly into the current widely-used Car-Parrinello electronic- and atomic-structure and quantum-dynamics codes.

To describe a new order-N scheme based on a new conceptual structure, density-functional partition theory. In partition theory, the system is broken up into mono- or multinuclear parts and its electron density exactly decomposed into contributions from each part. A common partition potential and partition forces acting on each part carry the influence of the rest of the system to that part. A novel functional for the partition potential and a new iteration scheme achieve linear scaling. The scheme will integrate smoothly into the current widely-used Car-Parrinello electronic- and atomic-structure and quantum-dynamics codes.

Astronomy, Rutgers University, ROBERTO CAR, Department of Chemistry, Princeton University — Large Complex Systems pose a challenge to first-principles computations. We construct a nonlocal density functional with full exact exchange, balanced nonlocality of correlation, and constraint satisfaction. This work supported by NSF Grant No. DMR-0705460.

To study spin-orbit coupled systems, spin-transfer torque devices, or even systems with pseudospin coupling like graphene, non-Abelian vector potentials and their conjugate variables, the spin-current densities, should be incorporated in the density functional theory. The general formalism for doing this has been known for some time [K. Bencheikh, J. Phys. A: Math. Gen. 36 11929 (2003)], but explicit functionals of the spin currents are not known. Here we identify the most general form of an exchange-correlation (xc) functional of the spin-currents, which satisfies the SU(2) gauge invariance and construct the local density approximation (LDA) for it. As an illustration we present the LDA functional for a two-dimensional (2D) electronic system, using as reference system a homogeneous 2D electron gas subjected to isotropic SU(2) vector potentials (i.e., linear spin-orbit coupling). The numerical results for the xc energy of this reference system will be presented.

Supported by Robert A. Welch Foundation.

This work supported by NSF.

Monday, March 16, 2009 8:00AM - 11:00AM —
Session A38 DCP: Focus Session: The Chemical Physics of Biological and Biologically-inspired Solar Energy Harvesting I

8:00AM A38.00001 Investigation of Excitonic Coherence in LHCII by 2D Electronic Spectroscopy, TESSA CALHOUN, University of California, Berkeley — Photosynthesis has evolved with the ability to transfer energy through a matrix of light-harvesting pigment-protein complexes with almost no loss. The accomplishment of this near unity quantum efficiency is a feat that man has yet to understand or replicate. One proposed mechanism integral to this process requires long-lived coherent superpositions of the excitons, delocalized electronic excitations, in these systems. Two-dimensional Fourier transform electronic spectroscopy, already proven to be an ideal technique for investigating these coherences, has been employed to study Light Harvesting Complex II (LHCII), the most abundant light harvesting complex in higher plants. As in other photosynthetic systems previously studied, we observe long-lived coherence lasting beyond many of the excitons’ lifetimes. Furthermore, unique coherence signatures allow the energies of the individual excitons to be located in an otherwise highly congested spectrum. This technique, by which 2D FT electronic spectroscopy can pinpoint excitonic spectral positions, and the resulting implications for LHCII will be discussed.
8:36AM A38.00002 Luminescent Solar Concentrators Employing Phycobilisomes1, MARC BALDO, MIT — At current manufacturing growth rates, it is expected to take at least 20 years to produce enough Si-based solar cells to make a significant impact on the world energy supply. Solar concentrators could alleviate manufacturing constraints by focusing light on small solar cells. Luminous solar concentrators (LSCs) are especially promising because they do not need to track the sun to obtain high optical concentration factors. Light incident on an LSC is absorbed by dyes, re-emitted into a guided mode in the slab, and finally collected by a PV cell mounted at the edge of the slab. The maximum optical concentration of an LSC is theoretically limited by the wavelength shift between absorption and emission in the dye. In this presentation, we describe LSCs that mimic a four energy level laser design, maximizing the wavelength shift and minimizing re-absorption losses. We employ phycobilisomes – photosynthetic antenna complexes that concentrate excited states in red algae and cyanobacteria. The phycobilisomes are cast in a solid-state matrix that preserves their internal F"orster energy-transfer pathways and large wavelength shift between absorption and emission. Casting is a simple fabrication technique that also eliminates any need for expensive high-index glass or plastic. By comparing the performance of intact and decoupled complexes, we establish that energy transfer within intact phycobilisomes reduces LSC self-absorption losses by approximately (48±5)%. These results suggest that phycobilisomes are the model for a new generation of cast LSCs with improved efficiency at high optical concentrations.

1Supported by the Department of Energy and the National Science Foundation

9:12AM A38.00003 Coherent Multidimensional Spectroscopy of Photosynthetic Complexes: Manipulating Quantum Pathways by Optical Pulse Sequences, DARIUS ABRAMAVICIUS1, University of California, Irvine — The response of chromophore aggregates to sequences of femtosecond laser pulses is simulated using the nonlinear equations. The nonlinear response can be interpreted in terms of the scattering of elementary excitations, quasiparticles, rather than as transitions among eigenstates. Applications are made to the Fenna-Matthews-Olson (FMO) and the PSI light harvesting complexes. Some fundamental symmetries of multidimensional optical signals are used to design techniques that can selectively resolve coherent quantum dynamics and incoherent energy dissipation. Simulations show damped oscillations of cross peaks corresponding to evolution of coherences, without interference from incoherent population relaxation. Energy transfer pathways are seen through the redistribution of crosspeak amplitudes. Resolution is enhanced by employing specific pulse polarization configurations to generate chirality-induced signals. New pulse sequences are designed to generate signals that are induced by correlations among elementary excitations. Specific phase-matching directions can target the correlated dynamics of double excitations. Cross peaks in 2D correlation plots are interpreted in terms of quasiparticle scattering and shown to reveal the double-exciton wavefunction, projected into products of single-excitons. Uncorrelated double-exciton states do not show up in the spectra due to quantum interference among pathways. The proposed techniques amplify cooperative dynamical features and reveal information on the robustness of quantum states to fluctuating environments. In collaboration with Darius Abramavicius and Dmitri Voronine, University of California, Irvine, CA 92697.

9:48AM A38.00004 Exploring Nanophotovoltaic Molecules using STM, CHENGGANG TAO, University of California at Berkeley, JIBIN SUN, XIAOWEI ZHANG, R. YAMACHIKA, D. WEGNER, Y. BAHRI, G. SAMSONIDZE, S. LOUIE, T. TILLY, R. SEGALMAN, M. CROMMIE — Composite molecular solar cells are a promising and exciting alternative to traditional silicon or gallium arsenide solar cells, but the power conversion efficiency remains low. In order to further increase this efficiency, a deeper understanding of the microscopic mechanisms at work in organic solar cells is needed. Using scanning tunneling microscopy and spectroscopy we have investigated nanophotovoltaic molecules that combine both donor and acceptor elements. Submolecular spectral resolution reveals the energy level alignment within these composite molecular structures. This information should be useful for understanding the energy conversion pathways within molecular solar cells, and for developing higher efficiency solar cell materials.

10:00AM A38.00005 New highly polar semiconductor ferroelectrics for solar energy conversion devices , ANDREW M. RAPPE, ILYA GRINBERG, JOSEPH W. BENNETT, University of Pennsylvania — Solar energy is a promising long-term solution for future energy requirements; however, current solar energy conversion devices are plagued by low efficiency. The use of ferroelectric ABO3 perovskite oxides is one approach for boosting conversion efficiency. Ferroelectric oxides possess spontaneous polarization and have been shown to produce a bulk photovoltaic effect, in which charged carriers, specifically electrons and holes, separate to prevent recombination. Once separated, the high-energy electrons are available for electrical work or for the catalytic splitting of water into hydrogen and oxygen. Currently, most solid oxide ferroelectrics have a band gap of at least 3 eV, absorbing primarily in the ultra-violet (UV) region. Since UV light comprises only 8% of the solar spectrum, new materials with a decreased band gap and large polarization would be highly desirable. We use first-principles density functional theory (DFT) calculations to investigate the ground state structures of PbTiO3 solid solutions containing Ni, Pd and Pt. We predict that these proposed materials will display a decreased band gap when compared to PbTiO3, while maintaining or enhancing polarization. They are promising candidates for use as semi-conducting ferroelectric substrates for solar conversion devices.

10:12AM A38.00006 Femtosecond electronic relaxation in cylindrical molecular aggregates, ANDREW MORAN, JORDAN WOOMIC, STEPHEN MILLER, University of North Carolina — Natural light harvesting systems have evolved with correlated pigment fluctuations whose fine-tuning promotes efficient energy transfer and photosynthesis. We investigate similar correlations in a double-walled cylindrical molecular aggregate with a diameter of 10 nm. A variety of nonlinear laser spectroscopies are utilized in this work. Excitons localized on different regions of the cylindrical structure are found to undergo correlated energy level fluctuations by analysis of photon echo line shapes. Particular electronic relaxation channels are resolved with a specialized coherent Raman spectroscopy. The importance of correlated pigment fluctuations for excitonic energy transfer is discussed.

10:24AM A38.00007 Förster coupling in realistic nanoparticle circuits, PATRICK REBENTROST, MIKE STOPA, ALAN ASPURU-GUZIK, Harvard University — Semiconductor nanoparticles could potentially be used to build artificial light-harvesting systems and electrically controlled excitonic circuits. We derive a new method for computing the Förster coupling between nanoparticles in an arbitrary electrostatic environment. We calculate the self-consistent electronic structure of an exciton, including the electron-hole attraction, in a nanoparticle within the two band effective mass approximation. Self-interaction of the electron and the hole are removed and the eigenstate is approximated as a product state of the electron and the hole wavefunctions. The environment is incorporated via boundary conditions on Poisson’s equation and arbitrary dielectric background. The transfer rate of the exciton via F"orster coupling to a neighboring nanoparticle is computed, without making a dipole approximation, from the results of the self-consistent calculation. Departure from the usual 1/R6 dependence are calculated, as well as specific cases where gates or additional nanoparticles are present.

10:36AM A38.00008 Non-Markovian Environmental Contributions to the Efficiency of Energy Transfer, CESAR RODRIGUEZ-ROSARIO, PATRICK REBENTROST, ALAN ASPURU-GUZIK, Harvard University — Non-Markovian environmental effects have been experimentally observed in the Fenna-Matthews-Olson photosynthetic complex, but their role is not understood. We study the dynamical contribution of the environment to the energy transfer by considering a non-Markovian environment and its interaction with the system Hamiltonian. We focus on the role of memory effects of different orders in time, and their competition that affect the energy transfer by defining the efficiency of the non-Markovian process. This efficiency measure has applications to the study of the quantum transport efficiency and engineering of light-harvesting devices.
are systematically shifted and broadened with respect to conventional density functional theory calculations due to photoelectron self-energy effects. We have undertaken the task of exploring this possibility from a theoretical point of view, by making use of time-dependent density-functional theory to describe the electrons, a real-space numerical representation, and various optimization techniques.

We use the phase-space density variable instead of the usual co-ordinate space density, to deal with these challenges. In this talk we will discuss some of these, and introduce a new extension of the theory where the basic variable is the phase-space density $W(r,p,t)$ (that contains information on both the co-ordinate- and momentum distributions of the electrons), instead of the usual co-ordinate space density $n(r,t)$, to deal with these challenges.

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Monday, March 16, 2009 11:15AM - 2:15PM –

Session B37 DCP: Focus Session: Fundamental Developments in Density Functional Theory II

10:48AM A38.00009 Spatially correlated fluctuations and coherence dynamics in photosynthesis1, Z. G. YU, M. A. BERDING, SRI International, HAOBIN WANG, New Mexico State University — Recent multicolor photon-echo experiments revealed a long-lasting quantum coherence between excitations on donor and acceptor in photosynthetic systems. Identifying the origin of the quantum coherence is essential to fully understand photosynthesis. Here we present a generic model in which a strong intermolecular steric restoring force in densely packed pigment-protein complexes results in a spatial correlation in conformational (static) variations of chromophores, which in turn induces an effective coupling between high-frequency (dynamic) fluctuations in donor and acceptor. The spatially correlated static and dynamic fluctuations provide a favorable environment to maintain quantum coherence, which can consistently explain the photon-echo measurements [1]. [1] Z. G. Yu, M. A. Berding, and Haobin Wang, Phys. Rev. E 78, 050902 (Rapid Communications) (2008).

1This work was supported by the U.S. Army Research Office under Contract W911NF05C0070. HW also acknowledges the support from the National Science Foundation CAREER award CHE-0348956.

11:15AM B37.00001 Phase-Space Explorations in Time-Dependent Density Functional Theory1, NEEPA MAITRA, Hunter College and the Graduate Center of the City University of New York — Time-Dependent Density Functional Theory is increasingly popular for calculating excitation and response properties of atoms, molecules, clusters and solids. It has achieved an unprecedented balance between accuracy and efficiency for a wide range of systems, but not all. Although not limited to the linear response regime, there are particular challenges for applications to strongfield processes; for example obtaining momentum distributions, certain electronic quantum control problems, and including memory-dependence necessary in the fundamental dependence. In this talk we will discuss some of these, and introduce a new extension of the theory where the basic variable is the phase-space density $W(r,p,t)$ (that contains information on both the co-ordinate- and momentum distributions of the electrons), instead of the usual co-ordinate space density $n(r,t)$, to deal with these challenges.

1Supported by NSF and Research Corporation

11:51AM B37.00002 Time-dependent density-functional theory for electronic excitations in materials1, CARSTEN A. ULLRICH, University of Missouri — There is currently an intense effort underway to study the optical properties of bulk and nanostructured materials using time-dependent density-functional theory (TDDFT). This talk will discuss challenges and recent advances of TDDFT in this area, and present some new applications to excitonic effects in bulk insulators and to collective charge- and spin-density excitations in doped quantum wells. A TDDFT version of the semiconductor Bloch equations is presented, which describes ultrafast electron dynamics, including excitonic effects, in insulators and semiconductors. From this, an excitonic Wannier equation is derived featuring a nonlocal effective electron-hole interaction determined by long-range exchange-correlation effects. Excitonic binding energies are calculated for several direct-gap insulators. The spin Coulomb drag (SCD), which constitutes an intrinsic source of dissipation for spin currents in metals and semiconductors, originates as a dynamical exchange-correlation effect in time-dependent current-DFT. We develop a linear-response description of collective spin-density excitations in quantum wells including SCD as well as Rashba and Dresselhaus spin-orbit coupling, and show that spin plasmon line widths in quantum wells allow a purely optical, quantitative measurement of the SCD effect.

1In collaboration with V. Turkowski and I. D’Amico. This work was supported by NSF DMR-0553485 and by Research Corporation.

12:27PM B37.00003 Many-Pole Self-Energy Model Corrections to Kohn-Sham Calculations of Excited State Spectra1, J. J. KAS, M. PRANGE, J. J. REHR, H. M. LAWLER, University of Washington — Experimental x-ray spectra are systematically shifted and broadened with respect to conventional density functional theory calculations due to photoelectron self-energy effects. We have recently developed an efficient many-pole model of the GW self-energy based calculations of dielectric response using a real-space Green’s function approach. The model is applied a posteriori to Kohn-Sham calculations of excited state spectra using a convolution of the spectrum with an energy dependent Lorentzian. The method is found to be widely applicable over a broad range of energies, with little computational cost. Several illustrative examples are presented which show improved agreement between theoretical calculations and experiment for both optical and x-ray spectra.

1Supported by NIH NCRR BTP grant RR-01209 (JK) and DOE Grant DE-FG02-97ER45623 (JJR and MP).

12:39PM B37.00004 First principle calculations of long range correlation effects within the random phase approximation1, DEYU LU, YAN LI, HUGH WILSON, GIULIA GALLI — The local and semi-local approximations to Density Functional Theory fail to describe correctly certain types of weak interactions (e.g. van der Waals forces) due to incorrect account of long range correlation effects. Such effects may be described by computing correlation energies within the random phase approximation (RPA), using the fluctuation-dissipation theorem and the adiabatic connection. We present an approach to compute RPA correlation energies based on an eigenmode expansion of the dielectric matrix [1,2]. By solving the frequency dependent Sternheimer equation within linear response theory [3], we eliminate the need to compute single particle unoccupied states, which makes our approach more efficient than methods using the direct-summation technique. Furthermore, the use of a dielectric eigenmode representation allows for a physical interpretation of several, different contributions to correlation energies. Results for graphite and the benzene crystal will be discussed. [1] H. Wilson, F. Gyggi and G. Galli, Phys. Rev. B, 78:113303, (2008). [2] D. Lu, F. Gyggi and G. Galli, Phys. Rev. Lett., 100:147601(2008). [3] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. 73:515, (2001).

1Work supported by DOE SciDAC grant DE-FC02-06ER25794.

12:51PM B37.00005 Tailoring High-Order Harmonics: A Computational Approach Based on Time-Dependent Density-Functional Theory, ALBERTO CASTRO, Department of Physics, Free University of Berlin, ALI AKBARI, ANGEL RUBIO, Universidad del País Vasco, EBERHARD GROSS, Department of Physik, Free University of Berlin — Atoms and molecules react in complex manners when they are irradiated with high-intensity electromagnetic pulses: multi-photon, tunnelling and over-the-barrier ionisation, laser driven photo-induced isomerisations or fragmentations, and high harmonic generation are some of the non-linear effects that are observed. The so-called pulse shaping techniques can be used to design pulses that produce a desired effect. A technologically appealing possibility is to tailor the harmonic emission spectrum: enhancement of some given orders, supressions of others, etc. We have undertaken the task of exploring this possibility from a theoretical point of view, by making use of time-dependent density-functional theory to describe the electrons, a real-space numerical representation, and various optimization techniques.


1:03PM B37.00006 Ab initio calculations of optical spectra by solving the Bethe-Salpeter equation without empty states.Work[1]. DARIO ROCCA, DEYU LU, GIULIA GALLI, University of California, Davis — We present a novel first principle approach to solve the Bethe-Salpeter equation (BSE) that builds on recent progress in time-dependent density functional perturbation theory [1], and uses an eigenvalue decomposition representation of the dielectric matrix [2]. This approach does not require the explicit calculation of excited single particle electronic states, making it suitable for calculations involving large basis sets and/or a large number of transitions. The numerical solution of the BSE is obtained through a generalized, non-Hermitian Lanczos iterative algorithm and does not require the use of the Tamm-Dancoff approximation. Furthermore, since Lanczos coefficients are frequency independent, optical spectra may be obtained in a very broad energy range. The efficiency and accuracy of the new approach are demonstrated by calculating the optical properties of silicon nanoclusters with up to 1 nm diameter. [1] D. Rocca, R. Gebauer, Y Saad, and S. Baroni, J. Chem. Phys. 128, 154105 (2008). [2] H.Wilson, F.Gygi and G.Galli, Phys. Rev. B 78, 113303 (2008).

1:15PM B37.00007 Time-dependent transition densities[1], YONGHUI LI, CARSTEN A. ULLRICH, University of Missouri — To visualize and interpret the induced charges and electron-hole coherences of electronic excitations in molecules, a real-space density matrix analysis is a useful computational tool. We extend this technique into the nonlinear, real-time domain and define the time-dependent transition densities in the context of time-dependent density-functional theory. This opens up the possibility of a real-time monitoring of the optical excitation dynamics in molecules, providing a visualization tool for processes such as exciton migration or charge-transfer excitations. The method will be illustrated for simple one-dimensional model systems.

1:27PM B37.00008 Is the Kohn-Sham Oscillator Strength Exact at the Ionization Threshold?[2] ZHENHUI YANG, University of California, Irvine, CA 92697, USA, META VAN FAASSEN, Afdeling Theoretische Chemie, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, Kingdom of the Netherlands, KIERON BURKE, University of California, Irvine, CA 92697, USA — It is well-established that the highest occupied orbital of the exact Kohn-Sham potential of any system is at $\lambda$=1, where $\lambda$ is the ionization energy. Therefore, in optical response, the non-interacting Kohn-Sham electrons in the ground-state potential have a first ionization threshold that exactly matches that of the real system[1]. We show that corresponding the Kohn-Sham oscillator strength is not exact at the first ionization threshold by explicit demonstration for the helium atom. We use a simple fit of the entire photoabsorption spectrum of both the Kohn-Sham potential for helium and that of real helium. We use oscillator strength sum rules[2] to determine the fit parameters, so this fit should be generally useful. [1] M. A. L. Marques, C. A. Ullrich, F. Nogueira, et al. Time-Dependent Density Functional Theory. Springer-Verlag, Berlin, 2006 [2] U. Fano and J. W. Cooper. Rev. Mod. Phys., 40(3), 441-507, 1968

1:39PM B37.00009 An Exact Condition for the Integrand of Adiabatic Connection[1], ZHENFEI LIU, KIERON BURKE, University of California, Irvine, CA 92697, USA, MARIANA M. ODASHIMA, KLAUS CAPELLE, Universidade de Sao Paulo — A simple and completely general representation of the exact condition of the integrand of the adiabatic connection integral[1,2]. The integrand should satisfy several exact conditions [3]. We show that for the low-density limit (as $\lambda \to \infty$), the $\lambda^{-1}$ term in the expansion of the integrand $W(\lambda)$ should vanish. We propose a simple parametric form for $W(\lambda)$, satisfying the new exact condition. We apply this interpolation form to Hooke's atom and helium atom and show that it is accurate for weakly-correlated two-electron systems.


3:03PM B37.00011 Non-empirical hyper-generalized-gradient functionals constructed from the Lieb-Oxford bound[1], MARIANA M. ODASHIMA, KLAUS CAPELLE, Universidade de Sao Paulo — A simple and completely general representation of the exact exchange-correlation functional of density-functional theory is derived from the universal Lieb-Oxford bound for Coulomb-interacting systems. This representation leads to an alternative point of view on popular hybrid functionals. A similar representation of the exact correlation functional allows to construct a family of non-empirical hyper-generalized-gradient approximations (HGGAs), departing from established paradigms of functional construction. Numerical tests and applications of these HGGAs to atoms and molecules demonstrate that even simple Lieb-Oxford based HGGAs are competitive with correlation functionals currently used in solid-state physics and quantum chemistry.

3:15PM B37.00012 A simple and completely general representation of the exact condition of the integrand of the adiabatic connection integral[1,2]. The integrand should satisfy several exact conditions [3]. We show that for the low-density limit (as $\lambda \to \infty$), the $\lambda^{-1}$ term in the expansion of the integrand $W(\lambda)$ should vanish. We propose a simple parametric form for $W(\lambda)$, satisfying the new exact condition. We apply this interpolation form to Hooke's atom and helium atom and show that it is accurate for weakly-correlated two-electron systems.

4:15PM B37.00013 Coherence and Decoherence in the Excited States of Light Harvesting Complexes, ROBERT J. SILBEY, Massachusetts Institute of Technology — No abstract available.
Electronic coherence in electronic energy transfer despite fast dephasing

GREGORY SCHOLES, University of Toronto — Förster resonance energy transfer (FRET) is a common and fundamental photophysical process in life and materials sciences. FRET is an interchromophore relaxation process that transmits the electronic excitation from an initially excited donor to a ground state acceptor chromophore (light-absorbing molecule). FRET is used, for example, to harvest light in photosynthesis, measure distances in proteins, and it accelerates the photodgradation of polymers. In recent years attention has turned to the study of FRET in complex assemblies of molecules. While Förster theory has enabled the efficiency of FRET to be predicted and analyzed in numerous and diverse areas of study, recent work has aimed to discover ways beyond the Förster mechanism by which the electronic excitation can be transferred. The talk will compare and contrast theoretical and experimental studies of excitation relaxation in photosynthetic antenna systems with the conjugated polymer poly[2-methoxy,5-(2'-ethyl-hexoxy)-1,4-phenylenevinylene] (MEH-PPV). I will report new work where we have used a new anisotropy experiment to examine coherent energy transfer and a complementary technique using two-dimensional electronic spectroscopy expose the role of coherence transfer in the fastest time dynamics. We find that coherent energy transfer occurs for many tens of femtoseconds, even at room temperature. That leads us to examine the nature and implications of the so-called intermediate coupling regime for EET.

12:27PM B38.00003 Photosynthetic nanoparticle complexes
ALEXANDER GOVOROV, Ohio University — We investigate structures composed of a photosynthetic molecule and a semiconductor (metal) nanoparticle [1]. The rate of optical generation of electron–hole pairs inside a photosynthetic system can be greatly increased through conjugation with nanoparticles. In the case of a semiconductor nanoparticle, the enhancement effect comes from the essentially larger optical absorption cross-section of a semiconductor nanoparticle compared to a photosynthetic system. In this hybrid complex, excitons are transferred via the Förster mechanism to the photosynthetic system, where charge separation takes place. For metal nanoparticles conjugated with a photosynthetic system, we predicted a strong enhancement effect due to the plasmon resonance. Such an enhancement effect was recently observed at Munich U. [2] In summary, we have shown that one can use crystalline nanoparticles to create a 10-fold enhancement of the initial stage of photosynthesis, i.e. the absorption process. Potential applications of nanocrystal complexes are in light-harvesting. [1] A. O. Govorov and I. Carmeli, Nano Lett. 7, 620 (2007); A. O. Govorov, Adv. Mater. online, DOI: 10.1002/adma.200702999. [2] S.Mackowski, S. Wörnke, A.J. Maier, T.H.P. Brotosudarmo, H. Harutyunyan, A. Hartschuh, A.O. Govorov, H. Scheer, C. Bräuchle, Nano Lett. 8, 558 (2008).

12:39PM B38.00004 Quantum coherence, decoherence and entanglement in light harvesting complexes
MARTIN PLENIO, FILIPPO CARUSO, Imperial College London, ALEX CHIN, University of Hertfordshire, ANIMESH DATTA, Imperial College London, SUSANA HUELGA, University of Hertfordshire — Transport phenomena in networks allow for information and energy to be exchanged between individual constituents of communication systems, networks or light-harvesting complexes. Environmental noise is generally expected to hinder transport. Here we show that transport of excitations across dissipative quantum networks can be enhanced by dephasing noise. We identify two key processes that underly this phenomenon and provide instructive examples of quantum networks for each. We argue that Nature may be routinely exploiting this effect by showing that exciton transport in light harvesting complexes and other networks benefits from noise and is remarkably robust against static disorder. These results point towards the possibility for designing optimized structures for transport, for example in artificial nano-structures, assisted by noise. Furthermore, we demonstrate that quantum entanglement may be present for short times in light-harvesting complexes. We describe how the presence of such entanglement may be verified without well defined full state tomography and with minimal model assumptions. This work is based on M.B. Plenio & S.F. Huelga, New J. Phys. 10, 113019 (2008) and F. Caruso, A. Chin, A. Datta, S.F. Huelga & M.B. Plenio, in preparation.

12:51PM B38.00005 Non-radiative decay processes in InAs nanocrystals
MARCO CALIFANO, University of Leeds — The mechanisms governing excited state relaxation in semiconductor nanocrystals (NCs) are still not well understood. The validity of the Auger electron cooling and multiexciton recombination hypotheses, which would explain much of the experimental data available to date, has recently been questioned. Moreover the recent observation of sub-picosecond electron relaxation times and bieciton recombination rates of the order of 0.1-1 ps−1 in InAs, although qualitatively ascribed to Auger processes, still awaits a quantitative theoretical interpretation. Multie exciton recombination is particularly important as its signatures are used to detect and quantify carrier multiplicity efficiency in NCs. Furthermore efficient non-radiative (multi-) exciton decay represents a major obstacle for application of NCs in lasing and photovoltaics. A quantitative theoretical understanding of these processes is therefore critical for any technological implementation of quantum-dot-based devices. The results of a detailed investigation using the pseudopotential method provide an explanation of the observed lifetimes in terms of Auger-like decay mechanisms, supporting the Auger interpretation of excited state relaxation in NCs.

1:03PM B38.00006 Exciton Transport Simulations in Phenyl Cored Thiophene Dendrimers
KWISOE KIM, MUHAMMET EKREN KOSE, PETER GRÅF, NIKOS KOPIDAKIS, GARRY RUMBLES, National Renewable Energy Laboratory, SEAN E. SHAHEEN, University of Denver — Phenyl cored 3-arm and 4-arm thiophene dendrimers are promising materials for use in photovoltaic devices. It is important to understand the energy transport mechanism for these molecules to guide the synthesis of novel dendrimers with improved efficiency. A method is developed to estimate the exciton diffusion lengths for the dendrimers and similar chromophores in amorphous films. The approach exploits Fermi’s Golden Rule to calculate the diffusion lengths of the excitons. The method is verified using the conjugated polymer poly[2-methoxy,5-(2’-ethyl-hexoxy)-1,4-phenylenevinylene] (MEH-PPV). Simulated diffusion lengths correlate well with experiments. The chemical structure of the chromophore, the shape of the transition densities and the exciton lifetime are found to be the most important factors that determine the exciton diffusion length in amorphous films.

1:15PM B38.00007 Efficient and Long-lived Charge Separation in a Heteroleptic Ruthenium(II) Polypyridyl Complex
JOSEPH HENRIC, HAOYU ZHANG, JEREMY WHITE, PRABIR DUTTA, BERN KOHLER, The Ohio State University — The excited-state dynamics of a tris-bidentate mononuclear ruthenium(II) complex, [bpy]2RuL3DQ, where L3DQ = 1-[4-(4-methyl)-2,2’-bipyridinium]) was investigated by femtosecond transient absorption spectroscopy in bulk solution and tethered nanocrystal. [(bpy)2RuL3DQ]4+ is a promising photosensitizer molecule for artificial photosynthesis. Broadband transient absorption experiments in bulk acetonitrile solution reveal that excitation of the MLCT absorption bands transfers an electron within one picosecond from the metal center to the bipyridinium (DQ) ligand. Back electron transfer then takes place with a time constant of 1.45 ns. Highly efficient charge separation is attributed to the conjugated nature of the bipyridinium-terminated ligand. When [(bpy)2RuL3DQ]4+ is tethered to a zeolite Y particle, charge can be transferred to a methyl viologen molecule encapsulated in the zeolite. Zeolites are promising materials for solar energy conversion because of their ability to slow rates of charge recombination. The effects of the zeolite on the photoprocesses of the ruthenium poly(pyridyl) complex will be presented.

Supported by NSF and Air Force Research Labs

Supported by NSF and Air Force Research Labs

Supported by NREL’s LDRD program

Supported by NREL’s LDRD program

Supported by NREL’s LDRD program
There are many collaborators in the application review that will follow, not only those who worked in the physics department at Rutgers University — The van der Waals density functional which we introduced half a decade ago. Our recent review article, through Kr with only two adjustable parameters in the dispersion cutoff, agreement with exact Hartree-Fock repulsion curves. The result is a simple GGA+dispersion theory giving excellent noble-gas pair interaction energies for He binding to severe over-repulsion depending on the choice of functional. We rectify these problems by — adding a dispersion term with nonempirical \( C_6, C_8, \) and \( C_{10} \) coefficients depend strongly on the bonding type and geometry of molecules/solids. Finally, we analyze the vdW radii and the damping function in the two-dimensional systems [collaborators: C´ esar Proetto, Esa R¨ as¨ anen and Stefano Pittalis], and (iv) a connection between the Lieb-Oxford bound and common binding and van der Waals (vdW) interactions, are crucial for the formation, stability and function of molecules and materials. At present, vdW interactions can be satisfactorily accounted for by high-level quantum-chemical wave function or by the Quantum Monte Carlo (QMC) method. In contrast, (semi)-local DFT and Hartree-Fock approximation fail for the description of vdW forces. We present a parameter-free method for describing the long-range vdW interaction in (semi)-local DFT. The leading \( C_6 \) coefficients are derived from the electron density of a molecule/solid and accurate reference values for the free atoms. The mean absolute error in the \( C_6 \) coefficients is 5.5% when compared to accurate experimental values for 1225 intermolecular pairs. We show that the \( C_6 \) coefficients depend strongly on the bonding type and geometry of molecules/solids. Finally, we analyze the vdW radii and the damping function in the \( C_6 R^{-6} \) correction method for DFT calculations.
Efficient van der Waals density functional interactions

Jose M. Soler, Guillermo Roman-Perrez, Univers Autonoma de Madrid — The LDA and GGA functionals are the non empirical methods of choice for large system calculations, but they cannot describe nonlocal dispersion forces. This limits severely their application to many systems of large interest, like molecular solids and liquids, physisorbed molecules, and interactions between biological molecules. Several schemes have been proposed to add ad-hoc atom-atom or atom-electron potentials. But dispersion is an electron-electron correlation effect, that must be described by an appropriate electron density functional, such as that proposed by Dion et al (PRB 92, 245401, 2001). It is a true universal and general-purpose DFT functional that describes semiquantitatively the week dispersion interactions, without compromising the accuracy of the best GGA functionals for stronger bonds. Its direct evaluation for large molecular systems is very expensive, however, because it requires a double integral in real space. We present a new implementation that avoids this $N^2$ scaling by applying Fourier convolution techniques to an accurately interpolated kernel. The resulting method scales as $N \log N$ and it allows to perform vdW-DFT simulations of essentially any system that can be simulated with GGA.

This work has been founded by grant FIS2006-12117 from the Spanish Ministry of Science.

The discontinuous nature of the exchange-correlation functional — critical for strongly correlated systems

Paula Mori-Sanchez, Aron Cohen, Weitao Yang, Duke University — Standard approximations for the exchange-correlation functional have been found to give big errors for the linearity condition of fractional charges, leading to delocalization error, and the constancy condition of fractional spins, leading to static correlation error. These two conditions are now unified for states with both fractional charge and fractional spin: the exact energy functional is a plane, along the fractional charge coordinate and constant along the fractional spin coordinate with a line of discontinuity at the integer. This sheds light on the nature of the derivative discontinuity and calls for explicitly discontinuous functionals of the density or orbitals that go beyond currently used smooth approximations. This is key to understand the physics of strongly correlated systems within DFT, for example the band-gap of Mott insulators. [arXiv:0809.5106]

Advances in Local Hybrid Functionals

Alexey Arbuszakov, Martin Kaupp, Hilke Bahnmann, University of Wuerzburg — Local hybrids provide a promising new generation of exchange-correlation functionals for the simultaneous accurate description of various properties (atomization energies, reaction barrier heights, NMR chemical shifts, energetics of transition-metal systems, etc.) Compared to traditional hybrids (e.g., B3LYP, 2003), it is a true universal and general-purpose DFT functional that describes semiquantitatively the week dispersion interactions, without compromising the accuracy of the best GGA functionals for stronger bonds. Its direct evaluation for large molecular systems is very expensive, however, because it requires a double integral in real space. We present a new implementation that avoids this $N^2$ scaling by applying Fourier convolution techniques to an accurately interpolated kernel. The resulting method scales as $N \log N$ and it allows to perform vdW-DFT simulations of essentially any system that can be simulated with GGA.

Calculation of functional derivatives with respect to the external potential

Nick Sablon, Tim Fievez, Frank De Proft, Paul W. Ayers, Paul Geerlings, Vrije Universiteit Brussel — Apart from its many computational advantages, density functional theory (DFT) presents a conceptual framework for the reactivity and stability interpretation of chemical systems. The central idea is to identify chemical concepts with first and higher order (functional) derivatives of the electronic energy with respect to the number of electrons $N$ and the external potential $v(r)$. The local interpretation of chemical reactivity is generally done with the Fukui function and the dual descriptor. These reactivity indices are usually calculated by a finite difference approach, which is entirely justified in an exact theory. Practical DFT calculations make however use of approximate exchange-correlation functionals for which the DFT concepts can only correctly be obtained by an effective evaluation of the electronic energy derivatives. A recent methodology for the calculation of functional derivatives with respect to $v(r)$ is presented. Results are shown for a wide range of molecules among which substituted benzenes. A reactivity description of the alkaline earth oxides’ (100) surface is expounded on as well.

Calculation of functional derivatives with respect to the external potential


Simple Illustration of Partition Theory

Adam Wasserman, Department of Chemistry - Purdue University, Morrel Cohen, Department of Physics - Rutgers University, and Department of Chemistry - Princeton University, Kieron Burke, Department of Chemistry - UC-Irvine, Roberto Car, Department of Chemistry - Princeton University — In Partition Theory (PT) [M.H. Cohen and A. Wasserman, J. Phys. Chem. A 2007, 111, 2229], the density of a system is decomposed exactly into a superposition of the densities of its parts through the introduction of a common partition potential acting on each of the parts as if they were isolated. In this talk we illustrate PT on a simple one-dimensional model of a heteronuclear diatomic molecule. We show that a sharp definition for the charge of the fragments emerges from PT, and that the ensuing population partition potential. The former hopes that PT will prove useful in chemical applications.

Session D38 DCP: Focus Session: The Chemical Physics of Biological and Biologically-inspired Solar Energy Harvesting III

2:30PM D38.00001 Exciton migration and fluorescence quenching in photosystem II

Leonas Valkunas, Institute of Physics, Savanoriu 231, 02300 Vilnius and Theoretical Physics Chair, Vilnius University, Sauluteikio 9, build. 3, 10222 Vilnius, Lithuania — When exposed to excess light illumination photosynthetic organisms switch into a photoprotective quenched state where the excess energy is safely dissipated as heat. It was recently discovered that the main light-harvesting complex of plants, LHCII, plays a key role in the dissipation of excess energy. Here we — When exposed to excess light illumination photosynthetic organisms switch into a photoprotective quenched state where the excess energy is safely dissipated as heat. It was recently discovered that the main light-harvesting complex of plants, LHCII, plays a key role in the dissipation of excess energy. Here we — When exposed to excess light illumination photosynthetic organisms switch into a photoprotective quenched state where the excess energy is safely dissipated as heat. It was recently discovered that the main light-harvesting complex of plants, LHCII, plays a key role in the dissipation of excess energy. Here we
Environment-assisted quantum transport in photosynthetic complexes. ALAN ASPURU-GUZIK, Harvard University — Transport phenomena at the nanoscale are of interest due to the presence of both quantum and classical behavior. In this work, we demonstrate that quantum transport efficiency can be enhanced by a dynamical interplay of the system Hamiltonian with the pure dephasing dynamics induced by a fluctuating environment. This is in contrast to fully coherent hopping that leads to localization in disordered systems, and to highly incoherent transfer that is eventually suppressed by the quantum Zeno effect. We study these phenomena in the Fenna-Matthews-Olson protein complex as a prototype for larger photosynthetic energy transfer systems. We also show that disordered binary tree structures exhibit enhanced transport in the presence of dephasing. We address the question of the role of coherence in the energy transfer in the FMO complex and discuss details about the theoretical modeling of photosynthetic complexes and organic photovoltaic materials.

Engineering Efficient Exciton Energy Transfer in Artificial Arrays, LESLIE VOGT, ALEJANDRO PERDOMO, SEMION SAIKIN, ALAN ASPURU-GUZIK, Harvard University — A critical component of light harvesting devices is efficient transfer of excitonic energy. Biological systems have optimized this process over time for the particular molecular components involved. Understanding this energy transfer in model arrays will allow us to engineer new materials for solar cell technology. In particular, we explore a perturbative approach to optimize both coherent and incoherent transport in small arrays. By following the evolving coherences and populations over time using a density matrix formalism, we gain an intuition about the importance of coherent processes in exciton transfer in natural and designed light harvesting systems.

Coherent Excitonic Transfer in the Fenna Matthews Olson Complex, GREGORY ENGEL, The University of Chicago — Evidence for a purely quantum mechanical mechanism of energy transfer in photosynthetic complexes was discovered in the Fenna-Matthews-Olson complex of Chlorobium tepidum in 2007. The quantum beating phenomenon observed in this complex is now much better understood. Specifically, detailed, testable microscopic models for the mechanism of this energy transfer have emerged, and precise quantum dynamical models now predict that this mechanism accounts for approximately one quarter of the energy transferred at room temperature. Further, new data indicate that this mechanism is not specific to FMO, but manifests in reaction centers of purple bacteria and antenna complexes of higher plants. A new experimental effort to observe quantum coherence at room temperature will be discussed. Specifically, by comparing population transfer rates and coherence transfer quantum beating signals, we calculate the fraction of the energy moving through the wave-like mechanism. Further, by studying the temperature dependence of the energy transfer, we elucidate the microscopic mechanism for wavelike energy transfer and be able to comment on the robustness of the mechanism. Are light harvesting proteins delicately “tuned” by evolution to support coherence transfer or should any proteinaceous environment support this mechanism? Details of the experimental apparatus, results and future experiments will be presented.

Excitation transport in open quantum systems: the role of environmental correlations, MOHAN SAROVAR, YUAN-CHUNG CHENG, BIRGITTA WHALEY, University of California, Berkeley — The recent discovery of quantum coherent phenomena in photosynthetic complexes [Engel et al., Nature, 446, 782 (2007), Lee et al., Science, 316, 1462 (2007)] has prompted several studies into the efficiency of transport processes in open quantum systems. Several of these studies have revealed a subtle interplay between coherent and decoherent dynamics in the overall efficiency of transport in these open systems. Some have shown that decoherence can improve efficiency. However all studies have used simple uncorrelated models of decoherence that are not accurate for photosynthetic complex environments, which are known to be spatially and temporally correlated. In this work we investigate the role of environmental correlations in quantum transport in open systems and show that the exact nature of the correlations can have a large impact on the efficiency of energy harvesting. We illustrate our results using the Fenna-Matthews-Olsen photosynthetic complex.

Local Correlation Calculations Using Standard and Renormalized Coupled-Cluster Methods, PIOTR PIECUCH, WEI LI, JEFFREY GOUR, Department of Chemistry, Michigan State University — Local correlation variants of the coupled-cluster (CC) theory with singles and doubles (CCSD) and CC methods with singles, doubles, and non-iterative triples, including CCSD(T) and the completely renormalized CR-CC(2,3) approach, are developed. The main idea of the resulting CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) methods is the realization of the fact that the total correlation energy of a large system can be obtained as a sum of contributions from the occupied orthonormal localized molecular orbitals and their respective occupied and unoccupied orbital domains. The CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) algorithms are characterized by the linear scaling of the total CPU time with the system size and embarrassing parallelism. By comparing the results of the canonical and CIM-CC calculations for normal alkanes and water clusters, it is demonstrated that the CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) approaches recover the corresponding canonical CC correlation energies to within 0.1 % or so, while offering savings in the computer effort by orders of magnitude. By examining the dissociation of dodecane into C_{11}H_{23} and CH_{3} and several lowest-energy structures of the (H_{2}O)_{n} clusters, it is shown that the CIM-CC methods accurately reproduce the relative energetics of the corresponding canonical CC calculations.

Tuesday, March 17, 2009 8:00AM - 11:00AM — Session H37 DCP: Focus Session: Spectroscopic Probes of Biomolecular Structure and Function
8:00AM H37.00001 Structure and dynamics in B12 enzyme catalysis revealed by electron paramagnetic resonance spectroscopy\textsuperscript{1}. KURT WARNCKE, Emory University — Challenges to the understanding of how protein structure and dynamics contribute to catalysis in enzymes, and the use of time-resolved electron paramagnetic resonance (EPR) spectroscopic techniques to address the challenges, are examined in the context of the coenzyme B12-dependent enzyme, ethanolamine ammonia-lyase (EAL), from Salmonella typhimurium. EAL conducts the homolytic cleavage of the coenzyme cobalt-carbon bond, intraprotein radical migration (5-6 Å), and hydrogen atom transfers, which enable the core radical-mediated rearrangement reaction. Thermodynamic and activation parameters are measured in two experimental systems, which were developed to isolate sub-reactions from the multi-step catalytic cycle, as follows: (1) A dimethylsulfoxide (DMSO)/water cryosolvent system is used to prepare the kinetically-arrested enzyme/coenzyme/substrate ternary complex in fluid solution at 230 K.[1] Temperature-step initiated cobalt-carbon bond cleavage and radical pair separation to form the Co(II)-substrate radical pair are monitored by using time-resolved, full-spectrum EPR spectroscopy (234°C ≤ T ≤ 250 K).[1] (2) The Co(II)-substrate radical pair is cryotrapped in frozen aqueous solution at T ≤ 150 K, and then promoted to react by a temperature step. The reaction of the substrate radical along the native pathway to form the diamagnetic bound products is monitored by using time-resolved, full-spectrum EPR spectroscopy (187°C ≤ T ≤ 217 K).[2] High temporal resolution is achieved, because the reactions are dramatically slowed at the low temperatures, relative to the initiation and spectrum acquisition times. The results are combined with high resolution structures of the reactant centers, obtained by pulsed-EPR spectroscopies,[3] and the protein, obtained by structural proteomics[4] and EPR and electron spin echo envelope modulation (ESEEM) in combination with site directed mutagenesis,[5] to approach a molecular level description of protein contributions to catalysis in EAL.

\textsuperscript{1}Supported by NIH grant DK54514.

8:36AM H37.00002 Time-resolved X-ray scattering of proteins in solution: a new method for probing biomolecular structure and function\textsuperscript{1}. PHILLIP ANFINRUD, National Institutes of Health/NIDDK/LCP — X-ray scattering patterns from proteins in solution exhibit a radial intensity distribution that is sensitive to protein size, shape, and structure. When acquired in a time-resolved fashion, these ‘fingerprints’ unveil conformational changes that occur as a protein executes its designed function. We recently developed the infrastructure required to record X-ray scattering snapshots with ∼100-ps time resolution on the BioCARS beamline at the Advanced Photon Source in Argonne, IL. This methodology was used to probe structural changes in hemoglobin after photodissociating a bound ligand. Remarkably, the scattering fingerprint exhibited changes at the earliest times resolved, evidently corresponding to small amplitude tertiary structure changes. On longer time scales, the allotropic quaternary structure transition was resolved. These scattering fingerprints provide robust constraints for structural models of intermediates and their dynamics, which are crucial to develop a detailed understanding of biophysical processes.

\textsuperscript{1}This work was supported by grants from NSF and NIH.

9:12AM H37.00003 Ultrafast Photodynamics in Diverse DNA Structures from A-tracts to Z-DNA\textsuperscript{1}. BERN KOHLER, Department of Chemistry, The Ohio State University — The vulnerability of the genome to UV photodamage has sustained interest in excited electronic states in DNA for over 50 years. Progress in understanding the nature and dynamics of electronic excitations in DNA has accelerated rapidly thanks in part to ultrafast spectroscopy. Most excitations in single DNA bases decay nonradiatively in hundreds of femtoseconds. Surprisingly, much longer-lived excited states are observed in femtosecond pump-probe experiments on single- and double-stranded DNAs. Localized charge transfer states are prominent in runs of adenine bases (A-tracts). DNA is polymorphic and can adopt a range of structures beyond the iconic B-form double helix. The effect of helix conformation on excited-state dynamics has been studied in a double-stranded oligonucleotide that can be switched between B- and Z-forms. Experiments on G quadruplex structures and on + motif DNA reveal that these forms have significantly slower relaxation than B-DNA. By altering π−π stacking and hydrogen bonding, structure profoundly affects the complex photophysics observed in DNA.

\textsuperscript{1}This work was supported in part by the Intramural Research Program of the NIH, NIDDK.

9:48AM H37.00004 Charge Transfer States of Aqueous B-DNA at Energies Above the Bright \textsuperscript{1ππ}\textsuperscript{*} Exciton States. ADRIAN LANGE, Chemistry Dept. (Physical), JOHN HERBERT, Chemistry Dept. — Charge transfer states have been proposed to explain experimentally observed long-lived excited state dynamics in aqueous DNA oligomers.\textsuperscript{1} Due to the large number of atoms, tractably describing such excited states in DNA systems with \textit{ab initio} theory is limited to TD-DFT. However, standard TD-DFT exchange-correlation functionals significantly underestimate CT excitation energies owing to incorrect asymptotic behavior. To circumvent this error, we instead apply recently developed and optimized long-range corrected TD-DFT functionals to better assess the low lying CT and exciton states of DNA oligomers. We show that long-range corrected TD-DFT yields results comparable to correlated wave function models, placing CT states of aqueous B-DNA at energies above the optically bright \textit{1ππ}\textsuperscript{*} exciton states, contrary to TD-DFT results which find CT states below the exciton states.


10:00AM H37.00005 Low frequency dynamics of Cytochrome c. KARUNAKARAN VENUGOPAL, PAUL CHAMPION, Department of Physics and Center for Interdisciplinary Research on Complex System, Northeastern University, Boston — Femtosecond coherence spectroscopy is used to investigate the low frequency dynamics of cytochrome c (cyt c). There is good agreement between the higher frequency oscillatory components of the coherence spectra and the low frequency Raman spectra. A mode near ∼40 cm\textsuperscript{-1} is a universal feature of heme systems and has been assigned to doming motions that are strongly enhanced upon ligand photolysis [1]. A dominant heme ruffling mode near ∼60 cm\textsuperscript{-1} [2] appears in ferric cyt c for excitation in the region 425-432nm, to the red of the Soret maximum (408nm). This, along with a phase jump of ∼π in this region, suggests the ruffling mode is coupled to a charge transfer (CT) band underlying the Soret band [3] and that it is a potentially important electron transfer reaction coordinate. [1] F. Gruia, M. Kubo, X. Ye, P. M. Champion, Biophys. J. 2008, 94, 2252. [2] M. Kubo, F. Gruia, A. Benabas, A. Barabanschikov, W. R. Montfort, E. M. Maes, P. M. Champion, J. Am. Chem. Soc. 2008, 130, 9800. [3] K. T. Schomacker, P. M. Champion, J. Chem. Phys., 1986, 84, 5314.
10:12 AM H37.00006 Ultrafast Dynamics of Leu-Enkephalin in Water and Membranes 1. SOOHWAN SUL, YUAN FENG, UYEN LE, NIEN-HUI GE, Department of Chemistry, University of California, Irvine — Ultrafast two-dimensional infrared (2D IR) spectroscopy has been applied to investigate the peptide-membrane interaction and conformational distribution of Leu-enkephalin (Lenk) in bilayer membranes. We compare the results from linear and 2D IR experiments on p-cresol in water, Lenk in water, and Lenk in membranes, focusing on the ring stretching mode of the Tyr side chain. Frequency-frequency correlation functions obtained from a series of waiting-time-dependent 2D IR spectra reveal a fast decaying component with a ~1 ps time constant that is common for all three systems. This spectral diffusion component is attributed to hydrogen-bond making-breaking dynamics of the Tyr side chain. Unlike p-cresol in water, both Lenk systems exhibit substantial spectral inhomogeneity that does not decay within the 4 ps window. The observed hydrogen-bond dynamics suggests that the Tyr side chain of Lenk in membranes is located at the water-abundant region at the water-membrane interface. The experimental results are compared with those from MD simulations and DFT calculations.

1Partially supported by NSF

10:24 AM H37.00007 Flap Conformations in HIV-1 Protease are Altered by Mutations. GAIL FANUCCI, MANDY BLACKBURN, ANGELO VELORO, LUIS GALIANO, University of Florida, DING FANGU, CARLOS SIMMERLING, Stony Brook — HIV-1 protease (PR) is an enzyme that is a major drug target in the treatment of AIDS. Although the structure and function of HIV-1 PR have been studied for over 20 years, questions remain regarding the conformations and dynamics of the β-hairpin (flaps) that cover the active site cavity. Distance measurements with pulsed EPR spectroscopy of spin labeled constructs of HIV-1 PR have been used to characterize the flap conformations in the apo and inhibitor bound states. From the most probably distances and the breadth of the distance distribution profiles from analysis of the EPR data, insights regarding the flap conformations and flexibility are gained. The EPR results clearly show how drug pressure selected mutations alter the average conformation of the flaps and the degree of opening of the flaps. Molecular dynamics simulations successfully regenerate the experimentally determined distance distribution profiles, and more importantly, provide structural models for full interpretation of the EPR results. By combining experiment and theory to understand the role that altered flap flexibility/conformations play in the mechanism of drug resistance, key insights are gained toward the rational development of new inhibitors of this important enzyme.

10:36 AM H37.00008 An Investigation of Ionic Binding to Fatty Acid Monolayers by Broadband Sum Frequency Generation Vibrational Spectroscopy 1. CHENG TANG, HEATHER ALLEN, Ohio State University — Model study of ionic binding of fatty acid monolayer is a good proxy towards understanding the fundamental chemistry in biological processes. In this study, we used broad-bandwidth sum frequency generation (BBSFG) vibrational spectroscopy to investigate the ionic binding event that leads to deprotonation of the fatty acid head groups. Palmitic acid (C15C00H) exists as monolayer on aqueous surfaces, and on aqueous alkali and alkaline solutions surfaces. Surface vibrational stretching modes of palmitic acid from 1400 cm$^{-1}$ to 3700 cm$^{-1}$ were observed (COO$^-$, C=O, C-H, and O-H). Palmitic acid is mostly protonated at the aqueous surface at neutral pH (~6). However, various degrees of deprotonation are initiated by introduction of different cations in the salt solutions albeit at neutral pH.

1 NSF Chemistry Grant (analytical and surface science div.)

10:48 AM H37.00009 Using Rotationally Resolved Electronic Spectroscopy to Probe Chiral Molecules in the Gas Phase 1. JUSTIN YOUNG, LEONARDO ALVAREZ-VALTIERRA, DAVID PRATT, University of Pittsburgh — It is well established that biological processes involving chiral molecules can show a preference of one enantiomer relative to the other. Reported here are high resolution spectroscopy experiments that allow one to distinguish one diastereomer from another, and thereby establish if the structural requirements for diastereomer are present.

1Work supported by NSF (CHE-0615755)

Tuesday, March 17, 2009 8:00 AM - 10:48 AM — Session H38 DCP: Focus Session: Theory of Electron Transport Through Molecules I 1410

8:00 AM H38.00001 The Role of Symmetry in Molecular Electronic Conduction. JEFFREY REIMERS, University of Sydney, Australia — The Greens Function Density-Functional Tight-Binding (gDFTB) method is applied to study the role that molecular symmetry in single-molecule conductivity. Both coherent elastic electron transport andinelastic electron-tunnelling spectroscopy (IETS) are considered. Symmetry becomes manifest in various ways: through the molecular point-group symmetry of the conducting molecule (D$_{2h}$ for chemisorbed benzenedithiol between two gold electrodes), the conductance point-group symmetry displayed by the gDFTB equations (this embodies junction asymmetry and may be very low and nominally non-existent), and through an approximate molecular-conductance point group (C$_{2v}$ for chemisorbed benzenedithiol). Indeed, the conductivities for a range of relevant problems are well approximated using the restriction of molecular-conductance point-group. This allows the complex transmission curves calculated by many research groups to be dramatically simplified and partitioned into symmetry-depicted channels. Means are introduced that isolate a very small number of component channels describing different aspects of single-molecule conductivity: input junction channels, through-molecule channels, and output-junction channels. For elastic transport, all through-molecule channels are totally symmetric and hence a rigorous selection rule appears that transport is allowed involving only input-junction and output-junction channels of the same symmetry. However, for IETS, the through-molecule channels have the symmetry of the scattering molecular vibration and hence the input-junction and output-junction channel symmetries may vary. In general, just one channel is expected to dominate the junctions, leading to the IETS propensity rule that totally symmetric transitions are the most intense ones. Simple physical pictures are presented showing the input, vibrational scattering, and output channels for IETS, leading to predictions of how this effect can be controlled chemically.

8:36 AM H38.00002 Molecular and Nano Scale Device-conductance: steady state and dynamical analysis. BARRY D. DUNIETZ, University of Michigan — A computational approach is used and developed to study electron transport through molecular and nano scale devices. New models and methods are employed to describe the dynamics of electron transport under the influence of time dependent (TD) perturbations. Quantum interferences affecting the TD conductance are analyzed for transient aspects, effects of present bound states and transport under the effect of coherent excitations. I will also discuss our modeling of several recent high-profile experimental studies achieving molecular scale (steady state) conductance which provides intriguing insight at the molecular structural level on the functionality of the conducting devices. The studies involve metal recognition properties of short peptides or fabricated molecular sockets based on surface confined terpyridine ligands. If time permits I will describe the required structural features for a gating field to tune the conductance of a molecular conjugated system.
9:12AM H38.00003 The spectroscopic dynamics of electron transport through molecular junctions, ALEXANDER PROCIUK, BARRY DUNIETZ, University of Michigan — A non-equilibrium Green’s-Function (NEGF) model based on time dependent perturbation theory is developed to compute the spectroscopic dynamics of electron transport through molecular junctions under the influence of weak time dependent classical fields. In this model, we use the two time variable nature of the Kadanoff-Baym equations of motion to formulate a mixed time-frequency representation for the electronic density. The resulting highly informative time dependent Wigner distributions are used to shed light on the features of dynamical observables, such as electron current, dipole moment and population. We analyze laser induced coherence and population transfer effects for both Markovian and non-Markovian electrode models. If time permits, the analysis of transient conductance with respect to the system’s fundamental parameters will be discussed.

9:24AM H38.00004 Model ab initio studies of solvation and excess charge localization on conjugated carbon chains, AL-AMIN DHIRANI, AMIR ZABET-KHOSOUSI — Single-nanoparticle (NP) devices formed by self-assembling NPs onto alkanedithiol-functionalized break junctions exhibit Coulomb blockade (CB) conductance suppressions at low temperatures. We have studied transport below and above the CB region, and find multiple activation energies \( \Delta V \). A small \( \Delta V \) at low temperatures, and a larger \( \Delta V \) at high temperatures. The small \( \Delta V \) is independent of NP size and is attributed to an energy state located at the metal-molecule contact. The larger \( \Delta V \) scales with NP size and is attributed to single electron charging energy of the NPs. Importantly, we observe a significant (~5–100 fold) discrepancy between values of charging energies obtained from CB voltage thresholds and \( \Delta V \). To account for the discrepancy, we propose a model in which electrons are temporarily localized at the energy states near the metal–molecule interface and lose energy. The proposed model is supported by ultraviolet photoelectron spectroscopy of alkanedithiol monolayers on gold which indicates a presence of energy states close to the Fermi level of gold likely arising from gold–thiolate bonds. A suitably modified Orthodox theory successfully describes our measurements.

9:36AM H38.00005 Measuring single electron charging energy in self-assembled single nanoparticle devices: Coulomb blockade threshold vs. Arrhenius energy, AL-AMIN DHIRANI, AMIR ZABET-KHOSOUSI — Single-nanoparticle (NP) devices formed by self-assembling NPs onto alkanedithiol-functionalized break junctions exhibit Coulomb blockade (CB) conductance suppressions at low temperatures. We have studied transport below and above the CB region, and find multiple activation energies \( \Delta V \). A small \( \Delta V \) at low temperatures, and a larger \( \Delta V \) at high temperatures. The small \( \Delta V \) is independent of NP size and is attributed to an energy state located at the metal-molecule contact. The larger \( \Delta V \) scales with NP size and is attributed to single electron charging energy of the NPs. Importantly, we observe a significant (~5–100 fold) discrepancy between values of charging energies obtained from CB voltage thresholds and \( \Delta V \). To account for the discrepancy, we propose a model in which electrons are temporarily localized at the energy states near the metal–molecule interface and lose energy. The proposed model is supported by ultraviolet photoelectron spectroscopy of alkanedithiol monolayers on gold which indicates a presence of energy states close to the Fermi level of gold likely arising from gold–thiolate bonds. A suitably modified Orthodox theory successfully describes our measurements.

9:48AM H38.00006 Molecular transport in the language of many-body states, MICHAEL GALPERIN, UCSD — Recent advancements in experimental techniques at nanoscale caused a surge in research of transport through molecular junctions. Nonlinearity of current-voltage characteristics at resonance makes this regime particularly important for potential molecular based memory, switches and logic devices. One of important differences of molecular junctions (comparing e.g. to semiconductor QDs) is sensitivity of electronic and vibrational structure of the junction to oxidation/reduction of the molecule. This implies necessity of treating the transport at resonance in the language of molecular states rather than single particle orbitals. The latter are the choice of majority of available ab initio approaches. We consider two possible schemes capable of incorporating isolated molecule (many-body) states as a basis for transport calculations. The schemes utilize Hubbard operators for description of single electron transitions between many-body states and go beyond previously proposed scattering theory and standard quantum master equation approaches.

10:00AM H38.00007 WKB modeling of single molecular transport and Molecular Nanometrology, VLADIMIR BURTMAN, Physics and Geophysics Department, University of Utah, SLC, ANDREI V. PAKOULEV, Department of Chemistry, University of Wisconsin, Madison — Wentzel–Kramers–Brillouin (WKB) approach to model transport mechanism in molecular nanostructures is discussed in content of molecular nanometrology. Two WKB models, direct tunneling (Simmons model) and field emission tunneling (Fowler–Nordheim tunneling), could be used to model conductivity in single molecular structure at low and elevated biased. Potentially, Simmons model could extract two molecular barriers, one for electrons and one for holes from conductivity spectra. Following this assumption electrical and optical gap-probed molecular nanometrology (GMN) could be developed. The main GMN principle is the small difference between the values of HOMO-LUMO energy gap detected by electrical and optical measurements. We will compare experimentally derived electrical and optical gap and energy offsets between E_{HOMO} and E_{LUMO} acting, which indicates a presence of energy states close to the Fermi level of gold likely arising from gold–thiolate bonds. A suitably modified Orthodox theory successfully describes our measurements.


10:24AM H38.00009 Theoretical study of electron transport through \( \pi \)-stacked ethynylene lines bonded to a Si surface, MANUEL SMEU, Center for the Physics of Materials and Department of Physics, McGill University, Montreal, QC, Canada, ROBERT WOLKOW, National Institute for Nanotechnology and Department of Physics, University of Alberta, Edmonton, AB, Canada, HONG GUO, Center for the Physics of Materials and Department of Physics, McGill University, Montreal, QC, Canada — Recently, experimental techniques were developed for lines of \( \pi \)-stacked ethynylene molecules to self-assemble on an H-terminated Si (100) surface in the laboratory of one of the authors. In this work, we use density functional theory (DFT) combined with the nonequilibrium Green’s function formalism (NEGF) to model electron transport through these ethynylene lines to determine if they could be used as molecular wires. In our calculations, the molecules are bonded to an H-terminated Si (100) surface and are bridging two Al leads. The transmission spectrum and its associated scattering states are determined by the NEGF-DFT technique. The presence of the Si substrate is found to play an important role for conduction: there is a dominant transmission peak near the Fermi level which is contributed by the Si substrate and not the \( \pi \)-stacked molecular line. The low-bias resistance is found to increase exponentially with the length of the molecular line, indicating a tunneling behavior in conduction.
10:36AM H38.00010 Stark Spectroscopy of Conjugated Oligomers and Polymers Important for Organic Devices , ALBERTO MOSCATELLI, DAVID C. COPPOCK, LINDA A. PETEANU, Carnegie Mellon University — Fluorescent conjugated polymers have attracted a great deal of attention among scientists and engineers for their potential use in opto-electronic devices. One of the points that remain to be fully understood, however, is the undesirable sensitivity of their charge transport efficiency and emission characteristics on variations of the polymer structure and morphology. Using Stark spectroscopy it is possible to measure directly two important photophysical molecular parameters: (i) the change in the dipole moment, which is related to the degree of charge transfer associated with an optical transition; and (ii) the change in polarizability, which is related to the extent of the electronic delocalization. Poly(phenylenevinylene) (PPV), poly(diallylfluorene) (PDAF) and ladder-type polyphenylenes (LPPP), as well as related oligomers, have been tested using this approach. Comparison of the results from single chains and from aggregates reveal how intermolecular interactions impact charge transfer and electronic delocalization in these technologically-important systems.


11:15AM J37.00001 Structures of Amyloid Fibrils and Protein Folding Intermediates: New Insights from Solid State NMR , ROBERT TYCKO, National Institutes of Health — I will present recent results from two projects: (1) We are using a combination of solid state NMR techniques and electron microscopy techniques to develop full molecular models for amyloid fibrils formed by the beta-amloid peptide of Alzheimer’s disease and by other peptides and proteins. Amyloid fibrils are often polymorphic, so that the detailed molecular structure depends on growth conditions or other factors. I will describe two structural models for beta-amloid fibrils with two distinct morphologies. I will also describe efforts to determine which fibril structure develops in the brains of Alzheimer’s disease patients, and solid state NMR methods that contribute to our amyloid studies; (2) Structural properties of unfolded or partially folded states of proteins are not well understood. In principle, solid state NMR measurements on free-taped samples can reveal specific, quantitative aspects of protein structures in unfolded states. I will describe experiments on thermodynamically unfolded states (i.e., denatured states) and on transient states that are trapped by freezing on the microsecond time scale. Both types of experiments reveal structural properties that are unanticipated and could not be detected by more conventional protein folding measurements.

11:51AM J37.00002 Two-Dimensional Infrared Probes of Peptide Conformations: the 3$_{10}$-Helical Secondary Structure$^1$ , NIEN-HUI GE, Department of Chemistry, University of California, Irvine — The 3$_{10}$-helix is a secondary structure that has important biological functions and has been proposed as a picosecond intermediate in the folding of alpha-helices. Two-dimensional infrared (2D IR) spectroscopy with its high structural sensitivity and time resolution is a powerful approach for investigating the structure and dynamics of peptides and proteins. In this talk, we will describe how we are using 2D IR and isotope labeling to study 3$_{10}$-helical oligopeptides that are rich in C$^{13}$-methylated amino acids. These peptides are attractive models for developing and refining experimental and theoretical approaches to peptide conformational analysis. By manipulating networks of vibrational modes using judicious choices of laser polarizations and pulse ordering, we demonstrate that 2D IR can provide diagnostic cross-peak patterns for distinguishing different helical structures and probe the onset of 3$_{10}$-helical secondary structure. Using a series of peptides with $^{13}$C$^{15}$O and $^{15}$N isotope labels, we observe cross-peak signature that reveals vibrational couplings between amide-I and amide-II modes across a 3$_{10}$-helical hydrogen bond. The results provide a direct evidence for local helical structure formation. Experimental spectra are compared to simulations based on nonlinear response theory, vibrational eigenstates and couplings derived from DFT-optimized structures, and trajectories from molecular dynamics simulations.

$^1$Partially supported by ACS PRF and NSF

12:27PM J37.00003 Earle K. Plyler Prize Talk: Using High Resolution Electronic Spectroscopy to Probe Reactive Chemical Intermediates , TERRY MILLER, Ohio State University — Gas phase chemical reactions, such as occur in atmospheric chemistry, combustion, plasma processing, etc. are of great importance to our economy and society. These reactions are typically very complex involving up to 1000’s of elementary steps with a corresponding number of reactive chemical intermediates. Spectroscopic diagnostics, based upon well analyzed and well understood spectra of the intermediates, are crucial for monitoring such reactions and unraveling their mechanisms. These spectral analyses often benefit from the guidance provided by quantum chemical calculations and conversely the molecular parameters, experimentally determined from the spectra, serve as “gold standards” for benchmarking such calculations. Such standards are especially valuable for reactive intermediates whose electronic or geometric structure is particularly complex because of electron-spin interactions, Jahn-Teller effects or other vibronic interactions, hindered internal motions, large molecular size and weight, etc. The alkyl radicals, RO·, and peroxy, RO$_2$· (R=alkyl group) free radicals are excellent examples of such species. The talk will focus on our recent characterization of these radicals via their “high-resolution,” mostly rotationally resolved, electronic spectra utilizing the techniques of laser induced fluorescence, stimulated emission pumping, and cavity ringdown spectroscopy. Selected spectra, their analysis, and the molecular information resulting therefrom will be discussed.

1:03PM J37.00004 Solvent induced fluctuations and the collective librational dynamics of myoglobin, hemoglobin, and lysozyme studied with infrared spectroscopy , KRISTINA WOODS, Carnegie Mellon University — We will discuss the use of (THz and Mid-) infrared spectroscopy to investigate the dynamics of several globular proteins under varying hydration and temperature conditions. Analysis of the experimental spectra has revealed that the amount of solvent in the hydration shell has a strong influence on the amplitude and the rate of relaxation associated with the low frequency protein conformational fluctuations and also the arrangement of hydrogen bonds in the protein secondary structure. At a hydration level > 0.2 we identify modes in the secondary structure of all of the proteins investigated that suggest extra mobility in the protein structure that is not present at low hydration. We will discuss how greater insight into the origin and nature of these detected solvent induced fluctuations may be important for developing a better understanding about energy localization and its relationship with biological function.

1:15PM J37.00005 Label-Free Determination of Protein Binding in Aqueous Solution using Overlayer Enhanced Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (OE-ATR-FTIR) , TRAVIS RUTHERBUNG, TOLULOPE AWEDA, SIMON PARK, CLAUDE MEARES, DONALD LAND, Department of Chemistry, University of California, Davis — Protein binding/affinity studies are often performed using Surface Plasmon Resonance techniques that don’t produce much spectral information. Measurement of protein binding affinity using FTIR is traditionally performed using high protein concentration or deuterated solvent. By immobilizing a protein near the surface of a gold-coated germanium internal reflection element interactions can be measured between an immobilized protein and free proteins or small molecules in aqueous solution. By monitoring the on and off rates of these interactions, the dissociation constant for the system can be determined. The dissociation constant for the molecule Yttrium-DOTA binding to the antibody 2D12.5 system was determined to be 100nM. Results will also be presented from our measurements of Bovine Serum Albumin (BSA) binding to anti-BSA.
12:39PM J38.00004 Many-body theory of electron transport in single-molecule junctions, CHARLES STAFFORD, JUSTIN BERGFIELD. University of Arizona — Currently, there is no general theory to treat the many-body problem of a single molecule coupled to metallic electrodes. Mean-field approaches such as density-functional theory—the dominant paradigm in quantum chemistry—have serious shortcomings because they do not account for important interaction effects like Coulomb blockade. We develop a systematic theoretical framework for this nonequilibrium many-body problem, starting from an exact diagonalization of the few-body problem of an isolated molecule, and including lead-molecule coupling perturbatively in a novel application of nonequilibrium Green’s functions.

12:51PM J38.00005 Quantum theory of image potential and resonant tunneling in molecular junctions, LYUDMYLA ADAMSKA, IVAN OLEYNIK, University of South Florida, MORTIKO KOZHUSHNER, Institute of Chemical Physics, Russian Academy of Sciences, Russia — It has recently been realized that the image potential plays an important role in charge transport through single organic molecules. In most cases, the classical image potential -1/4z is used to calculate the modified energy spectrum of the charge carriers in the molecule. In this talk, we will present the theory of resonant tunneling transitions that include the quantum mechanical effects of dynamic image potential due to the polarization interaction of the tunneling charge carrier (electron or hole) with surface plasmons. The application of this theory to molecular junctions of experimental interest will be discussed.

1:03PM J38.00006 Charge and Spin Memory Effects in Molecular Junctions1, P. D’AMICO, D.A. RYNDYK, Regensburg Uni, G. CUNIBERTI, T.U. Dresden, K. RICHTER, Regensburg Uni — In the field of molecular electronics, effects like charge-memory, bistability and switching between charged and neutral states have been observed in STM [1] and single-molecule junctions [2] experiments. In this work we use model hamiltonians to describe molecular junctions, including electron-electron and electron-vibron interactions as well as tunneling coupling to the leads. For a molecular level coupled to a vibron and in the presence of leads, we show that upon applying gate or bias voltage, it is possible to observe charge-bistability and hysteretic behavior. Physical quantities like lifetimes, charge-voltage and current-voltage curves are calculated by the master equation method for weak coupling to the leads [3] and at stronger coupling by the equation-of-motion method for noneq. Green functions, performing a systematic analysis of the bistable behaviour of the system for different internal parameters such as the electron-vibron and the lead-molecule coupling [4]. In the case of a spin-degenerate molecular level in a single and double dot molecule with vibrational coupling and in presence of ferromagnetic leads, we consider the possibility to obtain a spin-memory effect. [1] J.Repp et al, Science 305, 493 (04); [2] E.Lortscher et al, Small 2, 973 (06); [3] D.A.Ryndyk et al, PRB 78, 085409 (08); [4] P.D’Amico et al, NJP 10, 085002(08).

1We acknowledge support from the DFG project “Quantum Transport at the Molecular Scale.”


1We gratefully acknowledge financial support provided by NSERC.

1:27PM J38.00008 Effects of dephasing on molecular conduction1, JESSE MAASSEN, FERDOWS ZAHID, HONG GUO, Centre for the Physics of Materials and Department of Physics, McGill University, Montreal, Canada — In this work, we theoretically investigate effects of dephasing on electron transport in molecular wires. The quantum transport analysis is carried out using the density functional theory (DFT) combined with the nonequilibrium Green’s function framework (NEGF). The dephasing effect is included at a phenomenological level by introducing fictitious voltage probes to the NEGF-DFT formalism that mimics the randomisation of quantum phase information of the charge carriers. For three systems: (i) a 1,4-benzenedithiol (BDT) molecule connected to Au(001) leads; (ii) an atomic gold chain in contact with Au(001) leads; and (iii) a very narrow Al(001) nanowire, our results indicate that there are two behaviours. When the wires are not conductive as (i,ii), the dephasing effects can increase conduction for a range of system parameters; while for molecule connected to Al(001) leads; (ii) an atomic gold chain in contact with Au(001) leads; and (iii) a very narrow Al(001) nanowire, our results indicate that the dephasing effect is included at a phenomenological level by introducing fictitious voltage probes to the NEGF-DFT formalism.

1The authors acknowledge support from the FQRNT, NSERC and CIFAR.

Tuesday, March 17, 2009 2:30PM - 5:06PM —
Session L37 DCP: Focus Session: Spectroscopic Probes of Biomolecular Structure and Function

2:30PM L37.00001 UV Resonance Raman Discovery of Gibbs Free Energy Landscape for Protein Alpha Helix Folding, SANFORD ASHER, University of Pittsburgh — We developed a powerful method to follow the evolution of secondary structure in the amide peptide bonds of peptides and proteins. UV Raman excitation into these ~200 nm electronic transitions results in the enhancement of the amide vibrations of the peptide backbone. In our most recent studies we reassigned the amide III region and found a particular band (the amide IIIa band) which reports selectively on the Ramachandran $\Psi$ angle and the state of peptide bond hydrogen bonding. We demonstrate that this band is Raman scattered independently by each peptide bond with insignificant coupling between peptide bonds. We also show that isotope editing of a peptide bond (by replacing the $^{12}$C-H with $^{13}$C-D) allows us to determine the frequency of an individual peptide bond within a peptide or protein which gives us its $\Psi$ angle. Consideration of the Boltzmann equilibria allows us to determine the frequency of an individual peptide bond within a peptide or protein which gives us its $\Psi$ angle. Consideration of the Boltzmann equilibria allows us to determine the frequency of an individual peptide bond within a peptide or protein which gives us its $\Psi$ angle.
3:06PM L37.00002 IR/UV laser spectroscopy of secondary structures in isolated peptide chains: an original insight onto the non-covalent interactions that shape proteins, ERIC GLOAGUEN, Laboratoire Francis Perrin, URA 2453 CNRS, Service des Photons, Atomes et Molecules - CEA Saclay — Protein shape and flexibility is governed by non-covalent interactions that need to be accurately described by molecular structure simulations. However, the computational methods adapted for large molecules like proteins have difficulties to reproduce precisely these non-covalent interactions and cannot reach the level of structural details required to address many biological relevant issues. Special efforts are currently done to document these interactions by carrying out experiments on simple model systems. The selectivity of the IR/UV double resonance spectroscopy of gas phase isolated peptides (less than 10 residues) laser desorbed and cooled in a molecular beam enables us to discriminate the spectral signature of the several H-bonds shaping the molecular conformation. This can be carried out for each conformation detected in the molecular beam, providing a precise IR fingerprint of the intramolecular hydrogen bond network of these molecules and references therein. These IR frequencies are directly compared to the calculated frequencies of selected conformations of the isolated molecule for assignment purpose. Once the experimentally observed conformations are known, the accuracy and the predictability of several computational methods can then be assessed through their ability to provide structures for each conformation that are both geometrically and energetically in accordance with the experimental results. In addition to H-bonds, other weaker non-covalent interactions such as NH$-$H$\cdots$O or π$\cdots$π or π$\cdots$CH$\cdots$H are also at play in these systems. They can indeed impact the H-bond network in a measurable way, which makes the investigation of these computationally challenging weak forces also accessible to this powerful experimental technique.

3:42PM L37.00033 Inhibition of urinary calculi — a spectroscopic study, FELICIA MANCIU, JAYESH GOVANI, WILLIAM DURRER, LAYRA REZA, LUIS PINALES, Physics Department, University of Texas at El Paso, El Paso, TX 79968 — We present multi-technique spectroscopic investigations by Raman, infrared absorption, X-ray photoelectron spectroscopy (XPS), and photoluminescence on the effects of the herb Rotula Aquatica Lour (RAL) on the growth of synthetically prepared Mg-based calcii of similar composition to common urinary calculi. Three samples were prepared; one MgPO$_4$-based standard and two others, separately incorporating 1 wt.% and 2 wt.% RAL herbal extract. Raman and infrared data show a newbyerite structure for the crystals without and with inhibitor. XPS revealed the unexpected presence of Zn and a significant increase in Mg in the samples with RAL inhibitor. The presence of metallic Zn may contribute to the inhibition process by initiating rapid stone formation. XPS and Raman results also suggest another mechanism of inhibition by revealing evidence for Mg-O bonding between the plant extract and the phosphate units of urinary calculus. Similarity between our photoluminescence measurements and those of in vivo chlorophyll provides additional evidence of Mg-related inhibition.

3:54PM L37.00004 Application of a Newly Built Chirped-Pulse Fourier Transform Microwave (CP-FTMW) Spectrometer to Study Biomolecules in the Gas Phase, RYAN BIRD, DAVID PRATT, University of Pittsburgh, JUSTIN NEILL, BROOKS PATE, University of Virginia — Chirped-pulse Fourier Transform Microwave (CP-FTMW) spectroscopy is an exciting new technique that makes possible the recording of the complete microwave spectrum of a gas phase sample using a single 1 $\mu$s pulse. In this report, we will describe the recent introduction of a laser ablation nozzle for the study of small biomolecules using this technique. Potential applications to samples such as nucleic acid base pairs and small polypeptides will also be described.

4:06PM L37.00005 Optical Conformational Transition Pathways of DsRed, Elucidated by Polarization-Modulated Fourier Imaging Correlation Spectroscopy, ANDREW MARCUS, ERIC SENNING, GEOFFREY LOTT, University of Oregon, MICHAEL FINK, Omega Optical, Inc — This work presents a novel ‘phase-selective’ approach to fluorescence fluctuation spectroscopy that simultaneously determines the joint probability distributions and two-dimensional spectral densities of protein conformational transitions, and nanometer center-of-mass displacements. Fourier imaging correlation spectroscopy (FICS) combines polarization- and intensity-modulated photo-excitation with phase-sensitive signal detection to monitor the collective coordinate fluctuations from a large population of fluorescent molecules ($N \sim 10^6$). FICS is based on the principle that fluctuations of partially averaged molecular coordinates can be monitored through variations of an optical signal phase. Experiments are performed on DsRed, a tetrmeric complex of fluorescent protein subunits, derived from a reef-building coral. Thermally induced conformational transitions of the DsRed complex lead to fluctuations in the optical dipolar coupling between adjacent chromophore sites. An analysis of polarization-resolved FICS fluctuation data, in terms of two-dimensional spectra and joint probability distributions, provides detailed information about cooperative ‘transition pathways’ between distinct dipole-coupled DsRed conformations.

4:18PM L37.00006 Insights on the Structural Details of Endonuclease EcoRI-DNA Complexes by Electron Spin Resonance, JESSICA SARVER, University of Pittsburgh — Pulsed electron spin resonance (ESR) was used to probe the binding specificity of EcoRI, a restriction endonuclease. Using site-directed spin labeling, a nitroxide side chain was incorporated into the protein, enabling the use of ESR to study the structural details of EcoRI. Distance measurements were performed on EcoRI mutants when bound to varying sequences of DNA using the Double Electron-Electron Resonance experiment. These distances demonstrated that the average structure in the arm regions of EcoRI, thought to play a major role in binding specificity, is the same when the protein binds to different sequences of DNA. Also, it was determined that the arms exhibit higher flexibility when bound to sequences other than the specific sequence due to the larger distance distributions acquired from these spin labeled complexes. Molecular dynamics (MD) simulations were performed on the spin-label-modified specific EcoRI-DNA crystal structure to model the average nitroxide orientation. The distance distributions from MD were found to be narrower than experiment, indicating the need for a more rigorous sampling of the nitroxide conformers in silico.
4:30PM L37.00007 1D and 2D-IR spectroscopy of blended polymer-porphyrin thin films, AARON MASSARI, AUDREY EIGNER, PATRICK KONOLD, University of Minnesota, Twin Cities — One and two-dimensional IR spectroscopies are used to study the static and dynamic environments that form when ruthenium(II)tetraphenylporphyrin carbonyl is blended with regioregular poly(3-hexylthiophene). The 1D-IR spectra of the Ru-bound CO symmetric stretch indicate the development of several inhomogeneously broadened microenvironments as the concentration of porphyrin is increased. Transmission electron microscopy is used to characterize the blended films, which show evidence of phase-segregation. By correlating the degree of separation with the relative proportions of each component of the 1D-IR spectrum, we identify the IR spectra corresponding to the free and aggregated porphyrin-CO stretches. 2D-IR vibrational echo spectroscopy is then used to measure the ultrafast dynamics that are present in the polymer and porphyrin phases.

4:42PM L37.00008 Microtubule-associated-protein (MAP) Tau Regulates the Number of Protofilaments in Microtubules: A Synchrotron X-ray Scattering Study, MYUNG CHUL CHOI, UCSD, URI RAVIV, Univ. Jerusalem Israel, HERBERT MILLER, MICHELLE GAYLORD, ERKAN KIRIS, DONOVAN VENTIMIGLIA, UCSD, DANIEL NEEDLEMAN, Harvard Univ., MAHN WON KIM, KAIST, LESLIE WILSON, STUART FEINSTEIN, CYRUS SAFINYA, UCSD — Microtubules (MTs), 25 nm protein nanotubes, are a major filamentous element of the cytoskeleton involved in intracellular trafficking and cell division. MAP tau regulates tubulin assembly and MT stability. Dysfunction of tau has been correlated with numerous neurodegenerative diseases. We describe our recent findings about the effects of six naturally occurring central nervous system (CNS) tau isoforms on the assembly structure of taxol-stabilized MTs, using synchrotron small angle x-ray scattering (SAXS). Most significantly, we found that tau, at low binding density, regulates the distribution of protofilament numbers in MTs. DOE DE-FG02-06ER46314, NSF DMR-0803103, NIH RO1-NS35010 and NS13560.

Tuesday, March 17, 2009 2:30PM - 5:30PM — Session L38 DCP: Focus Session: Theory of Electron Transport Through Molecules III

2:30PM L38.00001 Statistical mechanics of non-equilibrium steady state systems, DANIEL KOSOV, University of Maryland — One of the important classes of non-equilibrium systems is the systems, which are maintained in non-equilibrium steady state by the contact with several external macroscopic reservoirs. These systems are ubiquitous and their theoretical description has been a challenging fundamental scientific problem for many years. They are also of significant practical interest for various nanotechnological and biological applications, such as quantum contacts, molecular motors, nanowires, and molecular junctions. There is no unique theoretical approach to wide variety of non-equilibrium steady states. General theoretical description of non-equilibrium steady states has not been developed yet and many fundamental theoretical questions are yet to be answered. For example, how to include many-particle correlation effects into theoretical treatment, is there exist a general variational principle for non-equilibrium steady state, do we enforce by the choice of a particular theoretical treatment a specific non-equilibrium steady state which is not the same as the real system would establish under the same boundary conditions, we have a unique steady state in a system of non-equilibrium interacting particles for given boundary conditions? In my talk, I will review these questions and their relevance to electron transport through molecules. I will also give account of our recent computational and theoretical work on non-equilibrium quantum transport through molecular nanostructures.

3:06PM L38.00002 Vibronic effects in single molecule conductance, MICHAEL THOSS, Department of Chemistry, Technical University of Munich — Recent experimental advances have allowed to study the conductance properties of single-molecule junctions and revealed a wealth of intriguing transport phenomena. An important aspect that distinguishes nanoscale molecular conductors from mesoscopic devices is the influence of the nuclear degrees of freedom of the molecular bridge. Due to the small size of molecules, the charging of the molecular bridge is often accompanied by significant changes of the nuclear geometry that indicate strong coupling between electronic and nuclear (in particular vibrational) degrees of freedom. In this contribution, the effect of electron-vibrational (vibronic) coupling on the transport properties of single molecule junctions is studied. The study is based on a combination of first-principles electronic structure calculations to characterize the system and different transport methods including inelastic scattering theory, master equations and nonequilibrium Green’s function theory. The basic mechanisms of vibrationally coupled electron transport are analyzed for a generic model of a molecular junction as well as benzenekanalnethiolates between gold electrodes. The results show that vibronic coupling can have a significant effect on the conductance of molecular junctions. It manifests itself in pronounced structures in the current-voltage characteristics. Moreover, the current-induced excitation of vibrational modes may result in a significant deviation of the vibrational degrees of freedom from their equilibrium distribution.

1Supported by CIFAR, NSERC, iCORE, Westgrid, NRC and INMS

3:42PM L38.00003 Controlling Current Flow Through Molecules With Electric Fields Emanating From Nearby Molecules: Theory and Experiment, G. KIRCZENOW, Simon Fraser U., P. G. PIVA, R. A. WOLKOW, NINT and U. of Alberta — We show that electrical conduction through molecules can be strongly modulated by electric fields of nearby polar molecules. We study 1D organic heterostructures consisting of contiguous lines of CF$_2$- and OCH$_3$-styrene molecules on H-terminated Si(100). For suitable alignment of the OCH$_3$ groups in the molecular chain, their combined electric fields are shown by density functional calculations to give rise to potential profiles along the OCH$_3$-styrene chain that result in strongly enhanced conduction through molecules near the CF$_2$-styrene/OCH$_3$-styrene heterojunction for moderately low negative substrate bias, as is observed by STM. Under similar bias, dipoles associated with CF$_2$ groups are found in both theory and experiment to depress transport in the underlying Si. Under positive substrate bias, simulations suggest that the structural and electrostatic properties of CF$_2$-styrene molecules may lead to more sharply localized conduction enhancement near the heterojunction. Thus choice of substituents, their attachment site on the host styrene molecules on Si and the orientations of the molecular dipoles and multipoles provide a means of differentially tuning transport on the molecular scale.

2Supported by CIFAR, NSERC, iCORE, Westgrid, NRC and INMS
3:54PM L38.00004 Effects of Dephasing on DNA Sequencing via Transverse Electronic Transport

3:06PM L38.00005 Single-Electron Transistors made by chemical patterning of silicon dioxide substrates and selective deposition of gold nanoparticles

5:06PM L38.00006 Contact Transparency of Nanotube-Molecule-Nanotube Junctions

4:30PM L38.00007 Quantum many-body effects on the electric and thermoelectric response of molecular heterojunctions

5:45PM L38.00009 Fabrication and characterization of vertically aligned and interconnected nickel oxide Nanowalls

5:06PM L38.00010 Conductance switching in organic monolayers

5:18PM L38.00011 ABSTRACT WITHDRAWN —
Wednesday, March 18, 2009 8:00AM - 10:36AM
Session P37 DCP: Focus Session: Structure and Dynamics of Interfacial Water I

8:00AM P37.00001 Electron Solvation Dynamics at D₂O Ice and Na/D₂O/Metal Interfaces, MARTIN WOLF, Free University Berlin and Fritz-Haber-Institut, Berlin, Germany — Electron transfer (ET) across interfaces is of vital importance in different areas of physics, chemistry and biology. Using time-resolved two-photon-photoemission spectroscopy we have studied the ultrafast dynamics of interfacial ET and solvation processes in amorphous and crystalline D₂O layers on single metal substrates and the influence of coadsorbed Na ions. In these experiments, photoionization of electrons from the metal into the adsorbate conduction band is followed by ultrafast localization and solvation of the excess electrons. The subsequent energetic stabilization of these solvated electrons due to nuclear rearrangements of the polar molecular environment is accompanied by an increasing degree of localization. The observed ET rates strongly depend on the local structure of the ice. In crystalline D₂O layers we monitor the stabilization of trapped electrons at the ice vacuum interface continuously from femtoseconds up to minutes. This behavior observed for crystalline ice is fundamentally different from amorphous D₂O layers where the excess electrons have a much lower survival probability, which lifetimes of the order of 100 fs, which extend to several 10 ps if Na ions are coadsorbed at the ice surface.

8:36AM P37.00002 Electron dynamics and intermolecular energy transfer in aqueous solutions studied by X-ray electron spectroscopy, BERND WINTER, BESSY, Albert-Einstein-Strasse 15, D-12489 Berlin, Germany — X-ray photoelectron spectroscopy measurements from a vacuum liquid microjet are performed to investigate the electronic structure of aqueous solutions. Here, focus is on the excited-state dynamics of chlorine and hydroxide anions in water, following core-level excitation. A series of Cl⁻ (aq) charge-transfer-to-solvent (CTTS) states, and their ultrafast relaxation, on the time scale of the core hole, is identified from the occurrence of spectator Auger decay. Resonant oxygen 1s excitation of aqueous hydroxide, in contrast, leads to non-local decay, involving energy transfer into a neighboring water molecule. This channel is argued to arise from the weak hydrogen bond of OH⁻ (aq), and thus identifies a special transient hydration configuration, which can explain hydroxide's unusual and fast transport in water. Analogue measurements from pure water point to a similar relaxation channel, which is concluded from a strong isotope effect. The characteristic resonance spectral features are considerably stronger for H₂O(aq) than for D₂O(aq). As for OH⁻ (aq) the results can be understood in terms of energy transfer from the excited water molecule to a neighbor water molecule.

1Support by the Deutsche Forschungsgemeinschaft (Project WI 132773-1) is gratefully acknowledged.

9:12AM P37.00003 Electrons tunneling through fluctuating water and proteins, DAVID BERATAN, Duke University — We have analyzed the characteristics of electron tunneling through thermally-fluctuating water and protein media [1]. A metric is defined that indicates when the tunneling propagation is well described by the average donor-acceptor tunneling interaction, as opposed to being dominated by medium fluctuations. Indeed, there is a transition distance that establishes a change in mechanism, and this distance is different for water-mediated compared to protein-mediated tunneling. Even in the fluctuation-dominated regime, we find that the three-dimensional protein fold controls the tunneling interactions. We also find that pairs of proteins in near contact may establish particularly strong water-mediated tunneling routes [2].


9:48AM P37.00004 Ultraviolet Induced Disordering of the Rutile TiO₂ (110) Surface, DANIEL HENNESSY, MICHAEL PIERCE, KEE-CHUL CHANG, Argonne National Laboratory, SATORU TAKAKUSAGI, KOHEI UOSAKI, Hokkaido University, HOY-DOO YOU, Argonne National Laboratory — We present x-ray crystal truncation rod (CTR) data collected on the water/rutile TiO₂ (110) surface before and after ultraviolet illumination. It is known that UV illumination transforms the surface superhydrophilic, with contact angle 0 degrees. [1] The wet, slightly hydrophilic surface of the clean, prepared samples exhibits a laterally ordered water adlayer that disorders under UV illumination. Contact angle measurements (CAM) show the surface exposed to ambient air is slightly hydrophobic, with contact angle 61(5) degrees. The well-protected dry surface is slightly hydrophilic, with contact angle 32(5) degrees. We propose a model based on domain growth of hydrophilic phases with laterally disordered water adatoms, consistent with some previous studies. [2] [1] R. Wang et al, Nature, 388, 431 (1997). [2] K. Hashimoto, H. Irie, and A. Fujishima, Jap J Appl Phys, 44, 8269 (2005).

10:00AM P37.00005 X-ray studies of the Density Depletion at Hydrophobic Water-Solid Interfaces, MARKUS MEZGER, Lawrence Berkeley National Lab, Berkeley, HARALD REICHERT, HEIKO SCHRODER, JOHN OKASINSKI, ROLAND ROTH, HELMUT DOSCH, Max Planck Institute for Metals Research, Stuttgart, Germany, SEBASTIAN SCHODER, VEJO HONKIKAMI, European Synchrotron Radiation Facility, Grenoble, France, JOHN RALSTON, Ian Wark Research Institute, Mawson Lakes, Australia — Deeply buried hydrophobic solid-water interfaces were probed with high-energy x-ray reflectivity. The experimental data provide clear evidence for a thin density depletion with an integrated deficit corresponding to approximately 40% of a water monolayer extending over a maximum of two molecular layers. In addition, measurements on the influence of gases (Ar, Xe, Kr, N₂, O₂, CO, CO₂) dissolved in the water have been performed. No effect on the hydrophobic water gap was found. The presence of nanobubbles at the interface could also be excluded. By comparing the experimental results with an generic DFT model we can give a quantitative estimation for different contributions to the observed gap size.


10:12AM P37.00006 First-principles study of water on Cu (110) surface, JUN REN, SHENG MENG — The persistent demand for cheaper and high efficient catalysts in industrial chemical synthesis, such as ammonia, and in novel energy applications, hydrogen generation and purification in fuel cells motivated us to study the fundamental interaction involved in water-Cu system, with an intention to examine Cu as a possible competitive candidate for cheaper catalysts. Water structure and dissociation kinetics on a model open metal surface: Cu (110), have been investigated in detail based on first-principles electronic structure calculations. We revealed that in both monomer and overlayer forms, water adsorbs molecularly, with a high tendency for dissociation rather than dissociation on clean surfaces at low temperature. With the increase of the water coverage on the Cu (110) surface, the H-bond pattern lowers the dissociation barrier efficiently. More importantly, if the water molecule is dissociated, the hydrogen atoms can diffuse freely along the [110] direction, which is very useful in the hydrogen collection. In addition, we extended to study water on other noble metal (110) surfaces. The result confirms that Cu (110) is the borderline between intact and dissociative adsorption, differing in energy by only 0.08 eV. This may lead to promising applications in hydrogen generation and fuel cells.
A self-consistent polarizable electron water potential: applications to clusters and bulk, LEIF JACOBSON, the Ohio State University — We have recently re-parameterized the electron–water potential due to Turi and Borgis (J. Chem. Phys. 117, 6186 (2002)) to be used with the polarizable water potential AMOBEA for use in hydrated electron simulations. In our model the single electronic wave function polarizes the water molecules and vice versa in a fully self-consistent manner. Comparison to binding energies and relative energetics of (H2O)n isomers (with n < 33) to ab initio results show a significant increase in accuracy over the previous parameterization which used a fixed charge water model. The relative importance of polarization in various binding motifs as well as cluster and bulk molecular dynamics simulations will be presented. The simulated optical absorption spectra will also be discussed.

Wednesday, March 18, 2009 8:00AM - 11:00AM — Session P38 DCP: Focus Session: Nanomaterials for Energy Applications I

8:00AM P38.00001 Nanoscale Architectures for Energy Applications1, STANISLAUS WONG, Department of Chemistry at the State University of New York at Stony Brook — In my group, we have developed a number of different potential architecture systems for gaining insights into energy storage and photovoltaics. In one manifestation of our efforts, generating a heterojunction comprising nanotubes and nanocrystals, externally bound and connected, has been significant. The unique, innovative, and important aspect of this particular nanoscale architecture is that it takes advantage of the tunability, in terms of size, shape, and chemistry, of nanotubes and nanocrystals, to create a sharp junction interface, whose properties are inherently manipulable, tailorable, and hence, predictable. For example, the electrical resistance of nanotube-nanoparticle networks is dependent on the nanoscale junctions that exist between these constituent nanomaterials as well as on microscale and macroscale connectivity. Thus, rational design of these nanomaterials is critical to a fundamental understanding of charge transport in single molecules and the determination of their conductance. Results on these systems can therefore be used to increase understanding of intrinsic factors affecting carrier mobility, such as electronic structure, carrier trapping, and delocalization. In a second manifestation, three-dimensional, dendritic micron-scale spheres of alkali metal hydrogen titanate 1D nanostructures (i.e.: nanowires and nanotubes) have been generated using a modified hydrothermal technique in the presence of hydrogen peroxide and an alkali metal hydroxide solution. Sea-urchin-like assemblies of these 1D nanostructures have been transformed into their hydrogen titanate analogues by neutralization as well as into their corresponding semiconducting, anatase titania nanostructured counterparts through a moderate high-temperature annealing dehydration process without destroying the 3D hierarchical structural motif. The as-prepared hollow spheres of titanate and titania 1D nanostructures have overall diameters, ranging from 0.8 µm to 1.2 µm, while the interior of these aggregates are vacuous with a diameter range of 100 to 200 nm. We have demonstrated that these assemblies are useful for example as active photocatalysts for the degradation of synthetic Procion Red dye under UV light illumination. In a third set of experiments, a size- and shape-dependent morphological transformation was demonstrated during the hydrothermal redox chemical transformation, in neutral solution, of titanate nanostructures into their anatase titania counterparts. Our results indicate that as-synthesized titania nanostructures possessed higher photocatalytic activity than the commercial titania precursors from whence they were derived.1

8:36AM P38.00002 High Capacity Hydrogen Sorption in Nanoscale Transition Metal Based Organometallic Complexes1, BELLAWE SHIVARAM, University of Virginia — Using a highly sensitive nanobalance we have discovered high capacity hydrogen absorption in a range of transition-metals(TM) based organometallic complexes prepared using physical vapor deposition techniques. Hydrogen absorption upto 14 wt% has been measured in titanium ethylene complexes and confirmed by mass doubling when deuterium is employed instead of hydrogen. I will present results of comprehensive measurements on other TM-complexes of alkenes, alkanes and ring compounds. I will also discuss these measurements in the context of theoretical calculations based on first principles quantum mechanics that have appeared in the recent literature. Finally, I will discuss the prospects for practical applications of these materials and the problems that might be encountered.1

9:12AM P38.00003 Electron Dynamics in Nanocrystalline TiO2 and ZnO Measured by Terahertz Spectroscopy, CHARLES SCHMUTTENMAER, Yale University, Department of Chemistry, JASON BAXTER, Dept. of Chemical and Biological Engineering — Understanding the microscopic details of carrier transport in nanocrystalline colloidal thin films is required for complete understanding of a variety of photochemical and photoelectrochemical cells utilizing interpenetrating networks. Measuring the photocconductivity in these materials, however, is a challenging problem because of the inherent difficulty of attaching wires to nanometer-sized objects. Furthermore, picosecond carrier dynamics play an important role in efficient charge separation and transport, but the low temporal resolution of traditional methods used to determine their photocconductivity precludes their use in studying sub-ps to ps dynamics. This talk will present recent advances utilizing THz spectroscopy to investigate and elucidate the microscopic behavior of carrier dynamics within the context of materials for energy applications such as dye-sensitized solar cells and solar-driven cells for catalytic chemistry.

9:24AM P38.00004 Theoretical investigation of the high energy excitations in silicon nanocrystals, ADAM GALI, MARTON VOROS, Budapest University of Technology and Economics, DARIO ROCCA, GERELY ZIMANYI, GIULIA GALLI, UC Davis — Recently, efficient multi-exciton generation (MEG) has been reported for several nanoclusters including silicon nanocrystals (SiNC), too. However, the existence of MEG has been disputed in the literature. The reported bi-exciton states in SiNC involve high energy empty states of SiNC. These states are expected to be very delocalized, and thus easily modified by the environment surrounding the SiNCs. In addition, the SiNCs are fabricated in a solution that usually contains CuII complexes, e.g. Cuacn, that may bind to the surface of SiNCs, and modify their absorption spectrum. We have studied the absorption spectra of hydrogenated SiNCs by first principles calculations. The geometry was optimized within density functional theory (DFT), while absorption spectra were determined by time-dependent DFT. The effect of the environment on the SiNC was modeled by i) varying the distance between the nanoparticles ii) allowing for surface reconstruction and iii) monitoring the effect of absorption of CnHm groups on absorption spectra. We found that the high energy spectrum of SiNCs strongly depends on the environment. Our findings indicate that taking into account effects of surface states and SiNCs concentration in solution is crucial, in order to understanding multi exciton generation.

9:36AM P38.00005 Fast exciton relaxation and multiple exciton generation (MEG) in semiconductor nanocrystals: the role of defects, CHRISTOPHE DELERUE, GUY ALLAN, IEMN-ISEN — Recent works have concluded that a single high-energy photon could generate multiple excitons in semiconductor nanocrystals but these results are debated and are not well understood theoretically. More generally, the physics of the relaxation of excitations in semiconductor nanocrystals receives growing interest. We show that surface defects must play an important role in these processes. We calculate the rate for the relaxation of hot carriers by impact ionization and we show that the presence of surface defects leads to an increase of the relaxation rate at lower excitation energy. We present simulations of the carrier multiplication in Si nanocrystals and we discuss the results of recent experiments in light of these results.
9:48AM P38.00006 First-principles study of LaSn₃ as an anode for lithium-ion batteries.
DONGWON SHIN, CHRISTOPHER WOLVERTON, Northwestern University, JOHN VAUGHY, MICHAEL THACKERAY, Argonne National Laboratory — Using both density functional theory (DFT) calculations and experiment, we investigate the tin-rich intermetallic compound LaSn₃ as a possible anode for lithium-ion batteries. We use DFT calculations to compare the relative energies of hypothetical insertion- and displacement-type reactions in an effort to elucidate the energetically-preferred reaction mechanism of Li with LaSn₃. From our DFT calculations, we find: (i) lithium insertion reactions with LaSn₃ are predicted to be energetically unfavorable and highly unlikely to occur; (ii) in contrast, the energetically preferred reaction is a displacement reaction in which La is partially displaced from LaSn₃ to yield LaSn₂ and Li reacts with the residual Sn to form Li₂Sn₃, corresponding to an electrochemical capacity of 307 mAh/g; (iii) this partial displacement reaction is preferred relative to the complete displacement and lithiation of Sn; and (iv) the lithiated-tin compound, Li₁₂Sn₄, is energetically more favorable than the commonly reported Li₁₂Sn₃ composition. Electrochemical and structural data largely confirm the DFT predictions; they demonstrate that lithium reacts with LaSn₃ via a displacement reaction to provide a reversible specific capacity of 200-250 mAh/g.

10:00AM P38.00007 Ab Initio Prediction of the Size-Dependence of Nano-scale Platinum Dissolution in Water.
KRISTIN PERSSON, LBNL, BYUNGCHAN HAN, GERBRAND CEDER, MIT — In low-temperature fuel cells, the mechanism behind the observed performance loss of the platinum catalyst is not well understood. Using ab initio methods, we calculate 0.5 - 2 nm diameter Pt nanoparticles with varying degrees of O and OH surface absorbates, optimized by site and particle surface structure. In fuel cells, the oxidation of the particle surface origins from the breakup of water molecules. To mimic these conditions we employ a grand canonical ensemble treatment of water as a source of O and H. Additionally, pH effects and dissolved species (from experiments) are incorporated, the latter by changing the experimental element reference state to that of calculated solids. This formalism allows us to determine the stability regions of nanoparticle Pt in equilibrium with water, as a function of particle size, potential and pH. As a result we find enhanced dissolution for the smaller Pt nano-particles, compared to the larger. Furthermore, surface passivation effects from O and OH adsorption do not significantly increase the stability of the nano-particle phases in the potential-pH region relevant for fuel cell operating conditions. Thus, we can identify size-dependent dissolution as a mechanism which will promote the growth of larger particles at the expense of smaller ones and ultimately cause a degradation in the nanoparticle Pt catalyst performance.

10:12AM P38.00008 First-principles theory of capacitive and electrochemical energy storage.
JOONGGOO KANG, YONG-HYUN KIM, National Renewable Energy Laboratory, Golden, CO 80401 — Recently there has been much interest in development of new electrochemical capacitors to meet high-power and high-energy applications. Pseudo-capacitors using fast surface redox reactions can store electrical energy of 10 to 100 times larger than supercapacitors and still exhibit fast and reversible charge-discharge responses in contrast to batteries. Yet, energy storage mechanisms in super- and pseudo-capacitors have not been fully understood at the level of electrons. Here we have performed first-principles calculations for electrical double layers of a TiO₂ (101) electrode and solvated lithium ions on the surface, with the ethylene carbonates (EC) as solvent molecules. As Li ions are desolvated from Li-EC₂ to Li-EC₃ and bare Li ions, the capacitance gets larger due to the reduced distance between the Li ions and the electrode. When Li ions are intercalated into the subsurface of the TiO₂ electrode as supposed in pseudocapacitors, the electrostatic energy due to charge separation is reduced for a given stored charge, but the electrochemical reaction starts to occur causing a large increase in the capacitance.

10:24AM P38.00009 Steps in hydrogen production from methanol on sub-nanometer palladium clusters.
FAISAL MEHMOOD¹, JEFFREY P. GREELEY², PETER ZAPOL¹, LARRY A. CURTISS¹,²,²¹ Material Science Division and Center of Nanoscale Materials, Argonne National Laboratory — Extensive experimental and theoretical work has been done to understand the decomposition of methanol on various metal and metal oxide nanoparticles for hydrogen production. The activity of sub-nanometer sized particles < 1nm however is not very well known, primarily because of technical challenges involved in preparation and stabilization of the clusters. To explore the properties of the Pd clusters computationally, we have carried out density functional calculations for the methanol decomposition reaction on Pd₃ and Pd₆ clusters. The thermodynamics and kinetics of three decomposition routes involving C–O, C–H and O–H scission were investigated; activation energy barriers were determined with the nudged elastic band method. A detailed analysis of the PES for methanol decomposition shows C–O activation to be the least favorable step. In addition, all possible reaction paths for the Pd₃ cluster are much lower in comparison to single crystal surface and large nanoparticles. To understand how particle size affects the elementary reaction steps, we also present a comparison of methanol decomposition on Pd₆ with Pd₆ clusters. Finally, we will discuss the implication of a linear correlation between the transition state and final state energies that is followed for all elementary reaction steps on Pd₃ and Pd₆ clusters.

10:36AM P38.00010 Two-Dimensional Boron-Nitride Layers as Flexoelectric Nanogenerators.
I. NAUMOV, A. BRATKOVSKY, Hewlett-Packard Labs, Palo Alto, V. RANJAN, North Carolina State U, Raleigh — The direct conversion of ambient motion into electrical energy, especially at nanoscale, is fundamental and technological challenge. Boron-Nitride non-centrosymmetric monolayers are piezoelectrics that can convert mechanical forces into electrical energy. Using both density functional theory (DFT) calculations and experiment, we investigate the tin-rich intermetallic compound LaSn₃ as a possible anode for lithium-ion batteries. The maximum values of specific capacitance of the carbon nanotube materials used in these devices were in the range of 14.6-21.57 F/g. The maximum value of power density and energy density of the whole supercapacitor devices were 1.48 W/kg and 2.7 KW/kg, respectively. These results show that the multiwall carbon nanotubes grown directly on conductive substrates are promising candidates as electrodes for electrochemical energy storage devices.
volumes. We will present results for simple geometries and discuss the implications of combining exclusion and charge.

We extend this technique to more realistic solutes, Ornstein-Zernike integral equations from liquid state theory are used to study hydration around small excluded instantaneous pulse. We have shown that this propagator can be used to reconstruct the dynamical hydration around prototypical charge distributions. To clarify the role that the chemical interaction between the water molecules and the walls of the confining host plays in determining the characteristics of the pores, the relaxational dynamics show a broad distribution of relaxation times. However, the Fickian diffusive behaviour is retained. The obtained results help the Relaxing Cage Model (RCM) for the dynamics of supercooled water. Because of the heterogenous environment experienced by the water molecules in the pores, the relaxation dynamics show a broad distribution of relaxation times. However, the Fickian diffusive behaviour is retained. The obtained results help clarify the role that the chemical interaction between the water molecules and the walls of the confining host plays in determining the characteristics of the water dynamics, as compared to purely geometric constraints such as the size and shape of the pores.

We report a series of surface specific studies of various water interfaces using surface-specific vibrational spectroscopies, both in equilibrium and on ultrafast (femtosecond) time scales. Our approach allows us to selectively investigate the one monolayer of water molecules at the different water interfaces. Water is characterized through its O-H stretch vibration. We find that interfacial hydrogen bonding depends strongly in the type of interface. Remarkably, for the water-air interface, interfacial hydrogen bonding is very similar to that occurring in bulk.

We combine inelastic x-ray scattering and x-ray absorption spectroscopy to study the nature of surface water in nanosized pores. The MCM-41-S sample. This latter is a silica matrix containing cylindrical sieves with diameter < 20 Å arranged in a hexagonal geometry. In the hydrophobically modified sample some of the sylanol groups in the pores' wall have been substituted with methanol groups resulting in a partially hydrophobic confining surface, and these mixtures modulate hydrophobicity two-dimensionally. Probe pulses with circular polarization impinge at the Brewster’s angle and are analyzed by a polarizer. The transient ellipticity shows a refractive index change of water by thermal conductance and novel insight into the peculiar qualities of interfacial water.

We present recent results of a new experimental approach where we use ir-ir pump-probe methods to measure the transition states and relative energies of isomers associated with the negatively charged water clusters. This is done by using a series of surface specific studies of various water interfaces using surface-specific vibrational spectroscopies, both in equilibrium and on ultrafast (femtosecond) time scales. Our approach allows us to selectively investigate the one monolayer of water molecules at the different water interfaces. Water is characterized through its O-H stretch vibration. We find that interfacial hydrogen bonding depends strongly in the type of interface. Remarkably, for the water-air interface, interfacial hydrogen bonding is very similar to that occurring in bulk.

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11:15AM Q38.00001 Nanostructured Multimetallic Catalysts in Fuel Cells1, CHUAN-JIAN ZHONG, Department of Chemistry, State University of New York, Binghamton, NY 13902 — There are two major driving forces for the global interests in research and development of fuel cells: the reality that fossil fuels are running out and the increasing environmental concern over pollution from using fossil fuels. Fuel cells utilizing hydrogen as fuels represent an important form of energy because hydrogen is a highly-efficient fuel and it is environmentally clean. Fuel cells such as proton exchange membrane fuel cell and direct methanol fuel cell are attractive because of their high conversion efficiency, low pollution, lightweight, and high power density. However, one of the important challenges for fuel cell commercialization is the preparation of active, robust and low-cost catalysts, which is key component in fuel cells counting for ~30% of the cost in manufacturing fuel cells. The durability of the catalysts can also be compromised by sintering and dissolution, especially at high electrode potentials or under load-cycling. We have been developing nanotechnological approaches and investigating nanostructured materials to address some of the fundamental issues in terms of catalyst activity, stability and cost. This presentation discusses recent findings of our investigations of the synthesis and processing for nanostructured catalysts with controlled size, composition, and surface properties by highlighting a few examples of bimetallic/trimetallic nanoparticles and supported catalysts. The results from the characterization of the nanoparticles and catalysts using an array of techniques and computational modeling will be discussed. The synergistic properties of the nanostructured materials in fuel cell reactions, including electrocatalytic methanol oxidation reaction and oxygen reduction reaction, will also be discussed, along with current challenges and opportunities.

Acknowledgement: NSF-NIRT

11:51AM Q38.00002 Reticular chemistry for clean energy, OMAR YAGHI, University of California, Los Angeles — Linking molecular building blocks by strong bonds to make networks (Reticular Chemistry) has yielded a number of new classes of materials such as metal-organic frameworks, zeolitic imidazolate frameworks and covalent organic frameworks. These are new classes of porous materials in which inorganic ‘struts’ are linked by organic ‘beams’ to give extended structures with surface areas greater than 5000 m2/g. Their ultra-high surface area is useful in storing hydrogen and natural gas, and for capturing carbon dioxide. Recently we have shown that MOFs can be quite effective as air purification and capture of harmful gases. This presentation will highlight the milestones and future prospects of this new field.

12:27PM Q38.00003 Chemical tools for creating energy-relevant nanomaterials, RAYMOND SCHAAK, Pennsylvania State University — An important pre-requisite for using nano scale materials in energy-related applications is the ability to make them on-demand and to rigid and pre-determined standards. For example, creating nanoscale solids with controllable composition, crystal structure, size, morphology, and surface chemistry is necessary for optimizing and fine-tuning their properties, as well as spatially organizing them and interfacing them with other components in a device. This talk will summarize our efforts to controllably and rationally synthesize shape-controlled nanocrystals of complex multi-element metallic and semiconducting materials. Collectively, these results provide reliable and predictable guidelines for designing and synthesizing complex nanomaterials of solids that are typically viewed as challenging to make. The focus will be on applying these ideas to energy-relevant nanomaterials, including nanostructured superconductors with high critical fields, metal hydrides for hydrogen storage applications, nanoparticle catalysts relevant to fuel cells, and metal-based compounds for thermoelectric, battery, and photovoltaic applications.

1:03PM Q38.00004 Structural and electrochemical properties of V2O5 and Ag,V2O5 nanowires prepared by template assisted method, M.B. SAHANA, C. SUDAKAR, R. NAIRK, Department of Physics and Astronomy, Wayne State University, Detroit, MI 48201, V.M. NAIRK, Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, MI 48128 — Vanadium pentaoxide and silver vanadium oxides are promising cathode materials for lithium ion battery as it allows easy intercalation/deintercalation of Li+. The ultra-high surface area is useful in storing hydrogen and natural gas, and for capturing carbon dioxide. Recently we have shown that MOFs can be quite effective as air purification and capture of harmful gases. This presentation will highlight the milestones and future prospects of this new field.

1:15PM Q38.00005 Stable Room Temperature Hydrogen Storage in Titainum-Doped Silica, JASON SIMMONS, TANER YILDIRIM, NIST Center for Neutron Research, AHMAD HAMAED, DAVID ANTONELLI, Department of Chemistry and Biochemistry, University of Windsor — The optimum conditions for viable room temperature hydrogen storage require materials that possess isoteric heats of adsorption in between that of standard physisorbers and chemisorbers, typically in the ~20-30 kJ/mol regime. It has been theoretically predicted that transition metal atoms incorporated onto high surface area materials could enable significant room temperature storage; herein we demonstrate a possible experimental proof of these predictions. Titanium(III) complexes are grafted onto porous silica hosts, then activated to generate sites for dissociative adsorption of hydrogen atoms. Using a combination of sorption measurements and inelastic neutron scattering, we show that the activated titanium provides strong hydrogen binding sites at room temperature and that adsorbed hydrogen is stable for long periods of time at ambient conditions. Further, the hydrogen can be desorbed under mild processing conditions. Neutron vibrational spectra agree well with theoretically predicted vibrational modes of the Ti—H complex. These results represent an important step towards reversible room temperature hydrogen storage.

1:27PM Q38.00006 Universal Behavior of Core-Shell Preferences in Transition-Metal Nanoparticles1, LIN-LIN WANG, DUANE D. JOHNSON, Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign — Transition-metal, core-shell nanoparticles are becoming ubiquitous from (electro-) catalysis to biomedical applications, due to control of size, performance, biocompatibility, and cost. We investigate 66 binary core-shell nanoparticle systems (groups 8 to 11 in the periodic table) using density functional theory (DFT) and systematically explore their segregation energies to determine core-shell preferences. We find that core-shell preferences are described by two simple factors: (1) cohesive energy (related to vapor pressure) and (2) atomic size (quantified by Wigner-Seitz radius). Core-shell preferences determined from DFT segregation energies agree with all available observations, and predict others, which can be used for design purposes. We then provide a universal description of core-shell preference via tight-binding band-energy differences that (i) quantitatively reproduces the DFT segregation energies and (ii) confirms the electronic origins for core-shell behavior.

Funding is through the Department of Energy Catalysis (DEFG02-03ER15476), Energy (DEFC36-05GO15064) with Sandia Metal-Hydride Center of Excellence, and BES (DEFG02-03ER46026)
1:39PM Q38.00007 Catalytic Gold Nanoparticles on an Iron Oxide Surface: A Scanning Tunneling Microscopy/Spectroscopy Study , KWANG TAEG RIM, DAEJIN EOM, LI LIU, ELENA STOLYAROVA, JOAN RAITANO, SIU-WEI CHAN 1, Columbia University, MARIA FLYTZANI-STEPANOPLOUS, Tufts University, GEORGE FLYNN, Columbia University — We present a Scanning Tunneling Microscopy/Spectroscopy study of a model catalyst system consisting of supported gold nanoparticles on a reduced Fe3O4(111) surface in ultrahigh vacuum. Gold forms two electrically distinct types of nanoparticles on an iron oxide surface upon annealing a multilayer Au/Fe3O4(111). STS measurements show that large nanoparticules (~8nm) are metallic while single gold adatoms are bonded to the oxygen sites on the Fe3O4(111) surface. Site-specific adsorption at oxygen surface atoms and the size sensitive nature of the electronic structure (Coulomb blockade) suggest that Au adatoms are positively charged. When this Au/Fe3O4(111) catalyst system is dosed with CO at 260K, there is evidence for CO adsorption at gold adatom sites. These observations are consistent with the proposal that nonmetallic, positively charged, “invisible” Au particles are the catalytically active species for the water-gas-shift reaction on Au/metal oxide surfaces. http://clippercontrols.com/info/dielectric_constants.html

1swncyc@gmail.com

1:51PM Q38.00008 Intercalation dynamics in rechargeable batteries1 , LIAM STANTON, Northwestern University, MARTIN BAZANT — We consider the ion intercalation of rechargeable battery electrode particles during charging (or discharging). We have developed a general phase-field model which incorporates entropic, enthalpic and elastic effects within the particle as well as the nonlinear chemical reactions at the particle-electrolyte interface. It is shown through linear stability analysis and numerical simulations that particle size and elastic effects will decrease or even eliminate both the spinodal region and the miscibility gap in the phase diagram.

1Supported by US NSF RTG grant # DMS-0636574.

2:03PM Q38.00009 Nanowire-based solar cell fabricated by nanosphere lithography , OKI GUNAWAN, SUPRATIK GUHA, IBM T.J. Watson Research Center — Nanowire (NW) structures have been predicted to provide performance enhancement for solar cells due to improved light absorption [1] and (for radial p–n junction geometry) improved carrier collection [2]. We report the development of NW-based solar cells fabricated using nanosphere lithography. This method provides a simple, scalable, low cost and high throughput technique to define large scale NW structures. The fabricated NW solar cells (0.25 μm diameter and 1.3 μm tall) on a p-Si (100) substrate show ~30 % higher short-circuit current and ~4 % higher open circuit voltage compared to the control cells (without any NWs) with baseline efficiency of 6.2 %. The reflectance and quantum efficiency spectra reveal some advantages and shortcomings of the NW-based solar cell. This work marks some progress in the development of a scalable nanowire-based solar cell and highlights some key issues such as conformal-junction formation, surface passivation, and contact formation. [1] L. Hu and G. Chen, Nano Lett. 7, 3249 (2007). [2] B. M. Kayes et. al., J. Appl. Phys. 97, 114302 (2005).

Wednesday, March 18, 2009 2:30PM - 5:30PM —
Session T36 DCP DCOMP: Frontiers in Electronic Structure Theory 408

2:30PM T36.00001 New approach on calculating Green’s functions in Full-Potential Multiple Scattering Methods.1 AURELIAN RUSANU, Oak Ridge National Laboratory, YANG WANG, Pittsburgh Supercomputing Center, G. M. STOCKS, Oak Ridge National Laboratory, JOHN S. FAULKNER, Florida Atlantic University — The most common methods of computing Green’s functions in modern full-potential multiple scattering applications rely on solving Schrödinger (Dirac) equations for regular and irregular solutions of a single-site scatterer over an energy contour in the complex plane. While, for spherical potentials, the standard formulae for calculating the Green’s function are numerically stable they often result in unphysical behavior for non-spherical potentials, particularly close to the nucleus and for large angular momentum quantum numbers. Here we use a new analytical and numerical method that does not require calculation of the irregular solution, to which the numerical instability can be traced. The new approach results in the correct analytic behavior and numerical stability.

1Research sponsored by the Division of Materials Science and Engineering, U.S. DOE, Oak Ridge National Laboratory with UT-Battelle, LLC.

2:42PM T36.00002 Local excitations in charge-transfer insulators: a super atom approach via Wannier functions1, CHI-CHENG LEE, WEIGUO YIN, Brookhaven National Laboratory, WEI KU, Brookhaven National Laboratory and SUNY Stony Brook University — Local excitations in strongly correlated charge-transfer insulator are very often tied to the rich functionalities of these materials. However, these tightly bound local excitations prove to be difficult to calculate from first-principles. In particular, the strong local interactions render the typical first-principles perturbation approach (via diagrammatic Bethe-Salpeter equation) inapplicable to describe the multiplets. In this talk, our recent progress in evaluating the local excitations in NiO will be presented. Utilizing the gauge freedom of the Wannier functions, the oxygen (charge-transfer) degrees of freedom can be integrated into a “super atom”, in which the strong local interactions can be incorporated on the equal footing as the strong coupling between the oxygen p- and Ni d- orbitals. Our results lead to good agreement with recent non-resonant inelastic X-ray scattering data [1] and the cluster calculation [2] for both q-dependence and excitation energies. Finally, extension to propagation of the local excitation will be addressed to include the dispersion in momentum space. [1] B. C. Larson et al, PRL 97, 026401 (2005). [2] M. W. Haverkort et al, PRL 99, 257401 (2007).

1Supported by DOE-CMSN

2:54PM T36.00003 Self-healing diffusion quantum Monte Carlo algorithms: Theory and Applications1, F.A. REBOREDO, P.R.C. KENT, M.L. TIAGO, Oak Ridge National Laboratory, R.Q. HOOD, Lawrence Livermore National Laboratory — We present a method to obtain the fixed node ground state wave function from an importance sampling Diffusion Monte Carlo (DMC) run. The fixed node ground state wave function is altered to obtain an improved trial wave-function for the next DMC run. The theory behind this approach will be discussed. Two iterative algorithms are presented and validated in a model system by direct comparison with full configuration interaction (CI) wave functions and energies. We find that the trial wave-function is systematically improved. The scalar product of the trial wave-function with the CI result converges to 0 even starting from wave-functions orthogonal to the CI ground state. Similarly, the DMC total energy and density converges to the CI result. In the optimization process we find an optimal non-interacting nodal potential of density-functional-like form. An extension to a model system with full Coulomb interactions demonstrates that we can obtain the exact Kohn-Sham effective potential from the DMC data. Subsequently we apply our method to real molecules such as benzene and find that we can improve the ground state energy as compared with the single determinant result even starting from random wave-functions. Results for other molecular systems and comparison with alternative methods will be presented.

1Sponsored the Division of Materials Sciences and the Division of Scientific User Facilities U.S. DOE.
3:06PM T36.0004 Removal of residual nonspherical self-interaction error in LDA+U, FEI ZHOU, VIDUVDS OZOLINS, UCLA — In the established LDA+U method, the electron self-interaction, which is generally nonspherical and orbital-dependent, is removed in a mean-field way. This results in residual self-interaction errors, particularly pronounced for f-electrons. An alternative double counting scheme that modifies the exchange, not Hartree, energy of LDA is proposed as a remedy. We show that LDA+U with our approach preserves the expected degeneracy of f'- and f''-states in free ions and the correct ground states in the PrO2 solid.

3:18PM T36.0005 The f-electron challenge: localized and itinerant states in lanthanide oxides united by GW@LDA+U, MATTHIAS SCHEFFLER, HONG JIANG, RICARDO I. GOMEZ-ABAL, FHI, Berlin, Germany, PATRICK RINKE, UC Sant Barbara, CA 93106 — Understanding the physics of f-electron systems, characterized by the competition between itinerant (delocalized) and highly localized f-states, is regarded as a great challenge in condensed-matter physics today. As a first step towards a systematic ab initio understanding of f-electron systems, we apply many-body perturbation theory in the G0W0 approach based on LDA+U ground state calculations (G0W0@LDA+U) to a selected set of lanthanide oxides (CeO2 and Ln2O3 (Ln=lanthanide series)). These compounds have important technological applications, in particular in catalysis and microelectronics. We demonstrate good agreement between the G0W0 density of states (DOS) and experimental spectra for CeO2 and Ce2O3. For the whole Ln2O3 series G0W0@LDA+U reproduces all main features found for the optical experimental band gaps. Inspection of the DOS reveals that the relative positions of the occupied and unoccupied f-states predicted by G0W0 confirm the experimental conjecture derived from phenomenological arguments.

3:30PM T36.0006 Self-interaction correction in multiple scattering theory — Application to transition metal oxide, MARKUS DAENE, Oak Ridge National Lab, WOLFRAM HERGERT, Martin Luther University Halle, Germany, ARTHUR ERNST, Max Planck Institute for Microstructure Physics, Halle, Germany, MARTIN LUEDERS, ZDZISLAWA SZOTEK, WALTER TEMMERMAN, Daresbury Laboratory, UK — In this work we study the electronic structure of 3d-transition metal oxides as obtained with the self-interaction-corrected-local spin density approximation method, implemented within multiple scattering theory. We briefly describe the formalism and discuss important technical issues of its implementation within the KKR band structure method. We present results of such important properties as lattice constants, local magnetic moments, band gaps and discuss them in comparison with the LSD and the experimental values.

3:42PM T36.0007 Computational Modeling of Actinide Complexes Pertinent to Environment, KRISHNAN BALASUBRAMANIAN, Lawrence Livermore National Lab — We discuss computational projects relevant to actinide separation, complexes and the possibility of actinide sequestration by engineered mesoporous materials We have carried out computational studies on a number of actinide complexes in aqueous solution; as such complexes are of considerable importance in our understanding of behavior of actinide species in the environment and high level nuclear waste, especially experimental-theoretical collaboration on curium (III) complexes with multi-dentate ligands with Nitsche and coworkers at LBNL. Cu(III) complexes with phosphonic acid (PPA) were studied for assessing relative binding strengths of the two ligands with varying pH. Possible isomers of CmH2PPA2+ complexes with phosphonic acid (PPA) were studied for assessing relative binding strengths of the two ligands with varying pH. Possible isomers of CmH2PPA2+ and CmHPPA+ complexes were computed both in the gas phase and aqueous solution and the results of spectra and geometry will be discussed. The effects of the aquo solvent in the configuration preferences of CmH2PPA2+ and We have also studied aqueous complexes of U(VI), Np(VI) and Pu(VI) with OH-. We will discuss the results of our extensive ab initio computations on the equilibrium structure, infrared spectra, and bonding characteristics of a variety of hydrated NpO2(CO3)m− complexes by considering the solvent as a polarizable dielectric continuum as well as the corresponding anhydrite complexes in the gas-phase. The work at CSU Eastbay was supported in part by Office of Basic Energy Sciences of DOE, and the work at LLNL was carried out under contract number W-7405-Eng-48.

3:54PM T36.0008 The converse approach to NMR chemical shifts from first-principles: application to finite and infinite aromatic compounds, T. THONHAUSER, Wake Forest University, D. CERESOLI, N. MARZARI, MIT — We present first-principles, density-functional theory calculations of the NMR chemical shifts for polycyclic aromatic hydrocarbons, starting with benzene and increasing sizes up to the one- and two-dimensional infinite limits of graphene ribbons and sheets. Our calculations are performed using a combination of the recently developed theory of orbital magnetization in solids; and a novel approach to NMR calculations where chemical shifts are obtained from the derivative of the orbital magnetization with respect to a microscopic, localized magnetic dipole. Using these methods we study on equal footing the 1H and 13C shifts in benzene, pyrene, coronene, in naphthalene, anthracene, naphthacene, and pentacene, and finally in graphene, graphite, and an infinite graphene ribbon. Our results show very good agreement with experiments and allow us to characterize the trends for the chemical shifts as a function of system size.

4:06PM T36.0009 NMR chemical shifts from first-principles using the converse approach in periodic boundary conditions, DAVIDE CERESOLI, TIMO THONHAUSER, MIT, NICOLA MARZARI — An alternative, converse approach to the first-principles calculation of NMR shielding tensors can be formulated where NMR chemical shift are obtained from the derivative of the orbital magnetization with respect to the application of a microscopic, localized magnetic dipole. We apply here the modern theory of orbital magnetization to validate this formalism to the case of extended systems in periodic boundary conditions, finding very good agreement with established methods and experimental results. These results underscore the advantages of the converse approach over existing methods: (1) it can be applied to either isolated or periodic systems, (2) it avoids any linear response calculation, allowing to treat systems containing hundreds of atoms, and (3) it is not plagued by the gauge-origin problem.

4:18PM T36.0010 MP2 and RPA applied to solid state systems, MARTIJN MARSMAN, Faculty of Physics, University Vienna, ANDREAS GRUENEIS, JUDITH HARL, GEORG KRESSE — We present ab initio total energy calculations at the level of Hartree-Fock + 2nd-order Møller-Plesset perturbation theory (HF+MP2), and the random-phase-approximation within the framework of the adiabatic-fluctuation-dissipation-theorem (ACFDT-RPA), for extended systems under periodic boundary conditions, using plane wave basis sets. We characterize and compare the accuracy of these methods with respect to their description of the lattice constants, bulk moduli, and atomization energies of several archetypical solid state systems. Furthermore we present calculations of HF+MP2 quasiparticle gaps and compare them to results obtained within the GW approximation to the electronic self-energy.

3Supported by the Austrian Fonds zur Foerderung der wissenschaftlichen Forschung (START grant Y218)

4:30PM T36.0011 Bridging the size gap between density-functional and many-body perturbation theory, PAOLO UMARI, CNR-INFM Democritos — The calculation of quasi-particle spectra based on the GW approximation is extended to systems of hundreds of atoms and the calculation of empty states is avoided. This is achieved through an optimal strategy, based on the use of Wannier-like orbitals, for obtaining a basis for the polarization propagator. Then, a Lanczos chain approach permits to calculate the self-energy. Our method is validated by calculating the vertical ionization energies of the benzene molecule and the band structure of crystalline silicon. Its potentials are then demonstrated by addressing the quasi-particle spectrum of models of vitreous materials, as well as large as well as of organic molecules.
4:42PM T36.00012 Quasiparticle properties of DNA bases from GW calculations in a Wannier basis. XIAOFENG QIAN, NICOLA MARZARI, Department of Materials Science and Engineering, MIT, PAOLO UMARI, Theory at Elettra Group, CNR-INFM Democritos, Basovizza (Trieste), Italy — The quasiparticle GW (GW) approach [1] has been recently developed to overcome the size limitations of conventional plane-wave GW calculations. By taking advantage of the localization properties of the maximally-localized Wannier functions and choosing a small set of polarization basis we reduce the number of Bloch wavefunctions products required for the evaluation of dynamical polarizabilities, and in turn greatly reduce memory requirements and computational efficiency. We apply GW to study quasiparticle properties of different DNA bases and base-pairs, and solvation effects on the energy gap, demonstrating in the process the key advantages of this approach. [1] P. Umari,G. Stenuit, and S. Baroni, cond-mat/0811.1453

4:54PM T36.00013 Reliable Prediction of Charge Transfer Excitations in Molecular Complexes, LEEOR KRONIK, Weizmann Institute of Science, Israel, TAMAR STEIN, ROI BAER, Hebrew University of Jerusalem, Israel — We show how charge transfer excitations in molecular complexes can be calculated quantitatively using time-dependent density functional theory (DFT). Predictive power is obtained from range-separated hybrid functionals using non-empirical tuning of the range-splitting parameter. Excellent performance of this approach is obtained for a series of complexes composed of various aromatic donors and the tetracyanoethylene (TCNE) acceptor, paving the way to systematic non-empirical quantitative studies of charge-transfer excitations in real systems.

5:06PM T36.00014 Transcorrelated method applied to solids: numerical assessment of the SCF effect. KEITARO SODEYAMA, University of Tokyo, REI SAKUMA, Chiba University, SHINJI TSUNEYUKI, University of Tokyo — To calculate the electronic structures of solids including electron correlation effects, we have developed the transcorrelated (TC) method which was first proposed by Boys and Handy. In the TC method, the wave function is represented by a correlated wave function $\Phi = \Phi_0 \exp[-\sum_{i<j} u_{ij}]$, where $\Phi_0$ is a single Slater determinant and $F$ is a Jastrow factor, $u_{ij}$ is a two-body function called Jastrow factor. The many-body Hamiltonian $H$ is similarity transformed to an effective Hamiltonian $H_{TC} = F^{-1} HF$ with up-to-three-body interaction. One-electron orbitals and their orbital energies are optimized by solving a set of Hartree-Fock (HF)-like single particle equations derived by minimizing the variance of the $H_{TC}$. In this study, we have investigated the effect of the self-consistent field (SCF) approach which was used in solving the HF-like single particle equations in the TC method. For this purpose, band gaps of Si, SiC, and LiF were calculated as a one-shot perturbation by using the unperturbed LDA orbitals as initial guess orbitals. The difference between the one-shot TC and conventional SCF TC results is small for Si but large for SiC, and especially large for LiF. From this result, we found that the SCF effect was important for strongly polarized solids such as LiF because the initial LDA orbitals were poorly described for such polarized solids.

Wednesday, March 18, 2009 2:30PM - 4:30PM — Session T37 DCP: Focus Session: Structure and Dynamics of Interfacial Water III 409

2:30PM T37.00001 Study of Water Adsorbed on the Cu(110) Surface using Scanning Tunneling Microscopy and Electron Stimulated Desorption Ion Angular Distribution. JUNSEOK LEE, Department of Chemistry, University of Virginia — The structure of water layer on the Cu(110) surface formed via hydrogen bonding has been investigated with scanning tunneling microscopy (STM), electron stimulated desorption ion angular distribution (ESDIAD), and density functional theory (DFT) calculations. STM results revealed 1D chain and 2D island growth at low temperature (∼80 K) and at low coverage regime. ESDIAD results at low coverage indicate that there are two kinds of O-H bonds of water molecules that are pointing out of the surface plane. At higher coverage the two-dimensional islands of water prevail, eventually covering the whole surface at the saturation coverage. Dynamic changes in the structure of the water layer and the local O-H bond direction have also been investigated as a function of annealing temperature. Using DFT calculation, a model of the 1D chain structure will be presented.

3:06PM T37.00002 Theoretical description of excited state dynamics in nanostructures, ANGEL RUBIO, Nano Bio spectroscopy group and ETSF, Universidad del Pais Vasco and Centro Mixto CSIC-UPV/EHU — There has been much progress in the synthesis and characterization of nanostructures however, there remain immense challenges in understanding their properties and interactions with external probes in order to realize their tremendous potential for applications (molecular electronics, nanoscale opto-electronic devices, light harvesting and emitting nanostructures). We will review the recent implementations of TDDFT to study the optical absorption of biological chromophores, one-dimensional polymers and layered materials. In particular we will show the effect of electron-hole attraction in those systems. Applications to the optical properties of solvated nanostructures as well as excited state dynamics in some organic molecules will be used as test cases to illustrate the performance of the approach. Work done in collaboration with A. Castro, M. Marques, X. Andrade, J.L Alonso, Pablo Echenique, L. Wirtz, A. Marini, M. Gruning, C. Rozzi, D. Varsano and E.K.U. Gross.

3:42PM T37.00003 Interfacial water in electric field, ALENKA LUZAR, Department of Chemistry, Virginia Commonwealth University (VCU), D. BRATKO, Department of Chemistry, VCU and Department of Chemical Engineering, UC Berkeley, C.D. DAUB, Department of Chemistry, VCU — As accessible experimental length scales become shorter, the modification of interfacial properties of water using electric field (electrowetting) must come to grips with novel effects existing at the nanoscale. I will briefly survey some of our recent progress we have made in understanding these effects using molecular simulations.

1Supported by NSF
Understanding their properties is crucial for insight into the effect of confinement on aqueous structure, dynamics as well as physical processes associated with solutes in confinement. We perform molecular dynamics simulations for the RM formed by the surfactant Aerosol-OT (AOT) in isooctane (2,2,4-trimethyl pentane) in order to study the effect of reverse micelle size on the aqueous phase. The structure of the RM is quantified in terms of the radial and pair density distributions. Dynamics are studied in terms of the mean squared displacements and various orientational time correlation functions in different parts of the RM so as to understand the effect of proximity to the interface on aqueous dynamics. Shape fluctuations of the RM are also analyzed.

We are grateful to the US National Science Foundation for their support of this research.

4:18PM T38.00004 Phase Space Transition States for Deterministic Thermostats, GREGORY EZRA, Cornell University, STEPHEN WIGGINS, Bristol University — We describe the relation between the phase space structure of Hamiltonian and non-Hamiltonian deterministic thermostats. We show that phase space structures governing reaction dynamics in Hamiltonian systems, such as the transition state, map to the same type of phase space structures for the non-Hamiltonian isokinetic equations of motion for the thermostatted Hamiltonian. Our results establish a general theoretical framework for analyzing thermostat dynamics using concepts and methods developed in reaction rate theory. Numerical results are presented for the isokinetic thermostat.
4:30PM T38.00005 Using invariant manifolds to classify chaotic transport pathways in mixed phase space\(^1\). KEVIN MITCHELL. University of California Merced — We describe how the topological structure of stable and unstable manifolds embedded within a chaotic phase space can be used to extract a symbolic classification of chaotic transport and escape pathways. We pay particular attention to phase spaces that contain a mixture of both chaos and regularity. For such systems, the dynamics in the vicinity of "stable islands" is known to be particularly troublesome to analyze. We describe a technique that utilizes the structure of invariant manifolds in the vicinity of such stable islands to extract a symbolic model for the islands’ influence on the transport process. Though our analysis focuses on Hamiltonian systems of two degrees-of-freedom, we also discuss the extension of our technique to higher dimensional phase spaces.

\(^1\)Supported by NSF grant PHY-0748828.

4:42PM T38.00006 Transition State Theory: Variational Formulation, Dynamical Corrections, and Error Estimates. ERIC VANDEN-EIJNDEN, Courant Institute — Transition state theory (TST) is discussed from an original viewpoint: it is shown how to compute exactly the mean frequency of transition between two predefined sets which either partition phase space (as in TST) or are taken to be well separate metastable sets corresponding to long-lived conformational states (as necessary to obtain the actual transition rate constants between these states). Exact and approximate criterions for the optimal TST dividing surface with minimum recrossing rate are derived. Some issues about the definition and meaning of the free energy in the context of TST are also discussed. Finally precise error estimates for the numerical procedure to evaluate the transmission coefficient \(S_S\) of the TST dividing surface are given, and it shown that the relative error on \(S_S\) scales as \(1/\sqrt{S_S}\) when \(S_S\) is small. This implies that dynamical corrections to the TST rate constant can be computed efficiently if and only if the TST dividing surface has a transmission coefficient \(S_S\) which is not too small. In particular the TST dividing surface must be optimized upon (for otherwise \(S_S\) is generally very small), but this may not be sufficient to make the procedure numerically efficient (because the optimal dividing surface has maximum \(S_S\), but this coefficient may still be very small).

4:54PM T38.00007 The dynamics of a floppy molecule: a case study. XIAOJIANG MAO, Department of Chemistry, West Virginia University — Urea is a simple but interesting molecule. In the solid state it is known to be planar while in gas phase it is non-planar. This difference is attributed to the hydrogen bonding that is present in the solid state. Ab initio quantum calculations suggest that in the gas phase there exist two different non-planar minima: anti- and syn- respectively. In addition to these minima there also exist both rank-one and rank-two saddles separating these minima. In this talk I will discuss topology of the potential energy surface and its implication for the dynamics of the molecule.

Thursday, March 19, 2009 8:00AM - 11:00AM — Session V37 DCP: Chemical Dynamics and Molecular Spectroscopy

8:00AM V37.00001 Laser-excitation of molecular systems within stochastic time-dependent current-density-functional theory\(^1\). HEIKO APPEL, MASSIMILIANO DI VENTRA, Department of Physics, University of California, San Diego — In this talk we investigate the excited electron dynamics of molecular systems due to laser excitation. The system dynamics is described within the recently proposed stochastic time-dependent current-density-functional theory [1,2].


8:12AM V37.00002 Nonlinear Response Functions in Model Dissipative Anharmonic Systems. MOHAMMAD SAHRAPOUR, NANCY MAKRI, University of Illinois at Urbana-Champaign — We report the results of simulations of third order response functions \(\langle R^{(3)}(\tau_3, 0, \tau_1) = \text{Tr} \{ \hat{\alpha} \left[ \hat{\alpha} \left[ \hat{\alpha} (\hat{r}_1), \hat{r}_0 \right] \right] \right\}\rangle\) where \(\hat{\alpha}\) is the polarizability for harmonic, Morse, and anharmonic model systems in a linearly dissipative environment. These simulations are carried out via the iterative path integral methodology developed earlier in our group which delivers efficient, numerically exact long time quantum dynamics. We find that even minor anharmonicity in the potential qualitatively changes the response function; rotating the pattern seen by 45° in the \(\tau_3 - \tau_1\) plane. We also observe that modulations in the \(\tau_3\) direction increase in frequency as we go to a more anharmonic potential. As the temperature is increased, these modulations also appear in the \(\tau_1\) direction. The observed sensitivity of the response function to anharmonicities in the potential can be exploited to construct more accurate molecular potentials once the appropriate non-linear spectroscopic experiments have been performed.

8:24AM V37.00003 Hamiltonian Monodromy: Unexpected behavior of quasi-linear molecules, atoms in traps and of hydrogen in crossed fields. J.B. DELOS, William and Mary, C. SCHLEIF, UC Merced, D. SADOVSKII, G. DHONT, B. ZHILINSKII, U. du Littoral — A system exhibits monodromy if we take the system around a closed loop in its parameter space, and we find that the system does not come back to its original state. Many systems have this property, including quasi-linear molecules, atoms in a trap or a hydrogen atom in crossed fields. Using classical perturbation theory, Sadovskii and Cushman predicted the presence of monodromy in perpendicular fields. It shows up as a defect in the lattice of quantum states. When the fields are tilted from perpendicular, these lattice defects undergo a series of bifurcations. Atoms in a trap can display a newly discovered dynamical manifestation of monodromy. This phenomenon will also occur with oriented dipolar molecules in fields or with quasilinear molecules. (Supported by NSF and Region Nord–Pas-de-Calais)

8:36AM V37.00004 On the internal photorelaxation mechanism of DNA. ERIC BITTNER, University of Houston — We propose a model for the photo-deactivation mechanism for DNA based upon accurate quantum chemical and molecular dynamical evaluations of model Watson/Crick nucleoside pairs and stacked packs. Our results corroborate recent ultrafast experimental studies on DNA oligonucleotides and suggest that following photo-excitation to a local \(n - n^*\) state, the excitation is rapidly delocalized over several (3-4) bases on an ultrafast time-scale. However, this delocalized state is unstable with respect to the motions of the protons involved in hydrogen-bonding between Watson/Crick pairs and rapidly re-localizes to a charge-transfer state on a longer time-scale ranging from 10 to 100 ps. This state, too, is unstable and releases via a conical intersection with the ground state near the geometry of the enol- and imino-tautomeric form. We suggest that this internal deactivation mechanism is responsible for the intrinsic photostability of DNA.
8:48AM V37.00005 Tunneling Splitting in the Rotationally Resolved Electronic Spectrum of 1,3-Benzodioxide1, JESSICA A. THOMAS, LEONARDO ALVAREZ-VALTIERRA, DAVID W. PRATT, University of Pittsburgh — Gas phase rotationally resolved electronic spectra were collected for the origin and several vibronic transitions of 1,3-benzodioxide. For each band, an autocorrelation program identified the presence of two overlapping spectra which were each fit using a least-squares algorithm to determine the rotational constants. Interpretation of these constants and how they change from one band to the next gives information about the physical causes of this splitting, which will be discussed.

1Work supported by NSF (CHE-0615755)

9:00AM V37.00006 Vacuum Ultraviolet Absorption of Supercritical Water, DAVID BARTELS, IRENEUSZ JANIK, Notre Dame University, TIMOTHY MARIN, Benedictine University — The first continuum $\chi \rightarrow A$ peak in the gas phase absorption spectrum of H$_2$O (maximum at 7.4 eV), is ascribed to promotion of a nonbonding valence electron to a dissociative excited state which is an admixture of antibonding sigma and 3s Rydberg orbitals. Due to the large spatial extent of this orbital the $\chi \rightarrow A$ transition is strongly perturbed by the local environment. In liquid water, this peak is notably broadened and shifted to the blue, with an absorption maximum of 8.3 eV at room temperature. An obvious question is how this transition changes as a function of the water density in the supercritical regime as the system transitions from liquid to gas. As density decreases, most water molecules will be located at an interface between large clusters and voids. We will describe an experiment to measure the VUV absorption of the $\chi \rightarrow A$ transition in supercritical water (T>374 °C, P>220 bar) where the density can be tuned continuously. Experimentally this requires over six orders of magnitude detector dynamic range in the vacuum UV and a short path (ca. 1 micron) high temperature/pressure cell with sapphire windows. This has not been accomplished in any previous experiment. Results will be discussed in the light of recent ab initio calculations of the spectrum in large and small clusters.

9:12AM V37.00007 Vibrational Coupling Pathways in the $\nu_3$ CH Stretch Fundamental Region of Methanol as Revealed by Coherence-Detected FTMW-IR Spectroscopy, SYLVESTRE TWAGIRAYEUZ, DAVID S. PERRY, Department of Chemistry, The University of Akron, JUSTIN L. NEILL, MATT T. MUCKLE, BROOKS H. PATE, Department of Chemistry, University of Virginia — Rotational state-selection on the methanol E species transitions $20 \rightarrow 31$, and $21 \rightarrow 30$ is used to record the infrared (IR) spectra of the connected rotational levels of jet-cooled methanol, CH$_3$OH and CH$_3$OD. The observed spectra of CH$_3$OH contain twelve interacting vibrational bands in the interval 2755-2855 cm$^{-1}$, whereas a direct state count gives 14 vibrations in this interval grouped into 6 tiers by coupling order. The isotope dependence of the spectra confirms that the dominant coupling pathway is a third order coupling of the CH stretch to a combination of the COH bend and an HCH bend.

9:24AM V37.00008 Ab Initio Torsion-Wag Surface for the Ethyl Radical, RAM S. BHATTA, DAVID S. PERRY, Department of Chemistry, The University of Akron — The torsion-wag potential of the ethyl radical has a 6-fold barrier to internal rotation and the minimum energy path involves deviations of the CH$_2$ wag angle of 6 to 11 degrees on either side of planar. Partially optimized 2-dimensional surfaces were calculated at the B3LYP, MP2, and CCSD(T) levels with 6-311+G(d,p) and 6-311+G(3df,2p) basis sets and they were fit to a function containing a polynomial in the wag angle $r$ and trigonometric functions of the torsional angle $\alpha$. Comparison is made with the corresponding surfaces for CH$_3$NH$_2$ and CH$_3$OH$^+$. Unlike CH$_3$CH$_2^+$, both have a substantial barrier to inversion. The dominant torsion-wag coupling term in all three cases has the form $r\cos\alpha$.

1The work was supported by the Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy under Grant No. DE-FG02-90ER14151.

9:36AM V37.00009 Terahertz Investigations of Extraordinarily Efficient Conduction in a Redox Active Ionic Liquid, VERNER THORSMOLLE, JAN BRAUER, École Polytechnique Fédérale de Lausanne, GUIDO ROTHENBERGER, Polytechnique Fédérale de Lausanne, DABIN KUANG, Sun Yat-Sen University, SHAIK ZAKEERUDDIN, MICHAEL GRÄTZEL, JACQUES MOSER, Polytechnique Fédérale de Lausanne — Iodine added to iodide-based ionic liquids leads to extraordinarily efficient charge transport, vastly exceeding expectancy for such viscous systems. Using terahertz time-domain spectroscopy, in conjunction with dc conductivity and viscosity measurements we unravel the conductivity pathways in 1-methyl-3-propylimidazolium iodide melts. Applying low temperatures, we demonstrate for the first time conduction entirely due to a Grotthus bond-exchange mechanism at iodine concentrations higher than 3.9 M. The terahertz and transport results are reconciled in a model providing a quantitative description of the conduction by physical diffusion and the Grotthus bond-exchange process. These novel results are of great importance for the fundamental understanding of conduction in molten salts and for applications where ionic liquids are used as charge-transporting media such as in batteries and dye-sensitized solar cells.

9:48AM V37.00010 Investigation of the Order-Disorder Transition in the Hybrid Inorganic-Organic System [(CH$_3$)$_2$NH$_2$]Zn(HCOO)$_2$, by means of $^1$H NMR, T. BESARA, P. JAIN, Department of Chemistry, Florida State University, Tallahassee, FL, USA, A.P. REYES, P.L. KUHNS, National High Magnetic Field Laboratory, Tallahassee, FL, USA, N.S. DALAL, H.W. KROTO, Department of Chemistry, Florida State University, Tallahassee, FL, USA, A.K. CHEETHAM, Materials Research Laboratory, University of California, Santa Barbara, CA, USA — [(CH$_3$)$_2$NH$_2$]Zn(HCOO)$_2$, a hybrid ABX$_3$ perovskite, with A= (CH$_3$)$_2$NH$_2$, B=Zn and X=HCOO, undergoes a paraelectric-ferroelectric transition around 150 K. Synchrotron studies indicate that hydrogen bonding between the H-atoms in the NH$_2$ group and O-atoms from the formate group is involved. The dimethylamine cation is disordered with nitrogen existing in three different positions, but not known whether statically or dynamically. We have investigated it by means of spin-lattice relaxation time $T_1$, using proton NMR. We find that the cation is dynamically disordered and that the transition involves its slowing down. Evidence is seen for tunneling of the CH$_3$ group and for the compound becoming a glass, with the cation displaying several metastable equilibrium geometries ($T_1$ trajectories).

10:00AM V37.00011 High Resolution Cavity Ringdown Spectroscopy of Jet-Cooled Reactive Intermediates, GABRIEL JUST, PATRICK RUPPER, LINSEN PEI, TERRY MILLER, The Ohio State University — Alkyl peroxy radicals long have been well known to be key intermediates in atmospheric chemistry as well as in low temperature combustion. For the last several years, our group has generated a data set for these radicals using room temperature cavity ringdown spectroscopy. We have recently extended our investigations of the peroxy radicals to obtain a high resolution data set of spectra under jet cooled conditions using a quasi-Fourier-transform-limited laser source and a supersonic slit jet discharge. Over the last few years, we have developed our capability to obtain narrow-bandwidth, near infrared (NIR) radiation for performing high resolution cavity ringdown spectroscopy using the post-amplification of a Ti:Sa ring laser. The NIR light can be generated by either stimulated Raman shifting or by difference frequency mixing by combining the second harmonic of a Nd:YAG laser with our post-amplified light in a BBO crystal. Using this apparatus, we have observed isomer and conformer specific spectra of the following species: methyl peroxy, CH$_3$O$_2$, ethyl peroxy, C$_2$H$_5$O$_2$, propyl peroxy, C$_3$H$_7$O$_2$, and phenyl peroxy, C$_6$H$_5$O$_2$. These spectra show rotationally resolved structure with a temperature of ~15 K as well as other structure attributable to spin-rotation interactions, tunneling splittings etc.
Session V38 DCP: Focus Session: The Transition State in Physics, Chemistry, and Astrophysics
Thursday, March 19, 2009 8:00AM - 11:00AM

8:00AM V38.00001 Quantum Transition State Theory
HOLGER WAALKENS — The main idea of Wigner's transition state theory (TST) is to compute reaction rates from the flux through a dividing surface placed between reactants and products. In order not to overestimate the rate the dividing surface needs to have the no-recrossing property, i.e. reactive trajectories cross the dividing surface exactly once, and nonreactive trajectories do not cross it at all. The long standing problem of how to construct such a dividing surface for multi-degree-of-freedom systems was solved only recently using ideas from dynamical systems theory. Here a normal form allows for a local decoupling of the classical dynamics which leads to the explicit construction of the phase space structures that govern the reaction dynamics through transition states. The dividing surface is spanned by a normally hyperbolic manifold which is the mathematical manifestation of the transition state as an unstable invariant subsystem of one degree of freedom less than the full system. The mere existence of a quantum version of TST is discussed controversially in the literature. The key issue is the presence of quantum mechanical tunneling which prohibits the existence of a local theory analogous to the classical case. Various approaches have been developed to overcome this problem by propagating quantum wavefunctions through the transition state region. These approaches have in common that they are computationally very expensive which seriously limits their applicability. In contrast the approach by Roman Schubert, Stephen Wiggins and myself is local in nature. A quantum normal form allows us to locally decouple the quantum dynamics to any desired order in Planck's constant. This yields not only the location of the scattering and resonance contributions based upon the isotopic dependencies of the effective ground state parameters.

8:36AM V38.00002 Transition States in a Noisy Environment
THOMAS BARTSCH, Loughborough University — No abstract available.

9:12AM V38.00003 Statistical Theory of Asteroid Escape Rates
CHARLES JAFFE, Department of Chemistry, West Virginia University — Transition states in phase space are identified and shown to regulate the rate of escape of asteroids temporarily captured in circumplanetary orbits. The transition states, similar to those occurring in chemical reaction dynamics, are then used to develop a statistical semi-analytical theory for the rate of escape of asteroids temporarily captured by Mars. Theory and numerical simulations are found to agree to better than 1%. These calculations suggest that further development of transition state theory in celestial mechanics, as an alternative to large-scale numerical simulations, will be a fruitful approach to mass transport calculations.
9:24AM V38.00004 Exploring remnants of invariants buried in a deep potential well in chemical reactions. TAMIKI KOMATSUZAKI, Hokkaido University — How the reacting system climbs through saddles from one basin to another on potential energy surface has been one of the most intriguing subjects not only in chemistry but also physics and biology. This decade significant progress has been achieved in establishing the concept of the so-called transition state (TS), that is, a hypersurface of co-dimension one through which the system passes through only once from one basin to another [1-3]. However, there exist still open problems to be resolved; 1) how the no-return TS ceases or bifurcates as the energy increases [4, 2) how the stable/unstable invariant manifolds emanating from the normally hyperbolic invariant manifold wander in deep potential wells in many-degrees of freedom (dofs) systems [5] or how one can generalize the remnant of invariant manifolds [6] to many-dofs systems, 3) how one can generalize the concept of no-return TS besides the region of first-rank saddles. Related to the problem 2), most of all the chemical reaction theories assume that all of the available energy redistributes statistically through the dofs of system in the reactant well before the reaction takes place. It is implicitly expected that the ratio of the measure occupied by tori in phase space to that of the ambient space decreases exponentially as the dimensionality of the system increases. Here we present a novel technique to scrutinize the remnant of invariants buried in chaos in many-degrees of freedom systems [7]. This is regarded as the remnants of a destroyed invariant manifold that may dominate the transport in phase space even at high energy regions where most of all tori vanish. We demonstrate the potentiality of our technique for HCN isomerization, where the conventional procedure based on a finite order truncation in the coordinate transformation of canonical perturbation theory prevent us from detecting remnants of invariants.

References:

1T.K. acknowledges financial support from JSPS and Grant-in-Aid for Research on Priority Area “Molecular Theory for Real Systems.”

10:00AM V38.00005 Intramolecular energy transfer, driving mechanisms, and reaction rates for collective motions of clusters. TOMOHIRO YANAO, California Institute of Technology — Conformational transitions of molecules, clusters, and biopolymers are typically large-amplitude collective motions that involve a large number of degrees of freedom in a coherent manner. One of the major challenges in modern molecular science is to understand the general mechanism for such collective motions. This talk highlights a novel dynamical mechanism for conformational transitions of atomic clusters in terms of intramolecular energy transfer and the driving forces for large-amplitude collective motions. First, we introduce a method of hyperspherical mode analysis, which generally classifies the (3n-6) internal modes of an arbitrary n-atom molecule into three gyration-radius modes, three twisting modes, and (3n-12) shearing modes. This hyperspherical mode analysis reveals that the gyration-radius modes are the primary collective modes that need to be activated in order for the system to achieve large-amplitude conformational transitions. Moreover, it illustrates how the twisting modes and the shearing modes critically initiate and trigger the conformational transitions by inducing the essential driving forces that activate the gyration-radius modes via mode coupling. Finally, we characterize this driving mechanism for conformational transitions from the viewpoint of the phase space geometry of the low-dimensional dynamical system of the gyration-radius modes. This reduced phase space geometry clearly accounts for the origin of non-statistical reaction rate processes of the clusters. The present method of hyperspherical mode analysis as well as the driving mechanism for collective motions could be widely applicable to conformational dynamics of complex molecular systems.

References:

1This work was supported by ONR, NSF, DOE and HPCMO.

10:36AM V38.00006 Collective coherent control: Synchronization of polarization in ferroelectric PbTiO$_3$ by shaped THz fields. TINGTING QI, YOUNG-HAN SHIN, KA-LO YEH, NELSON KEITH, RAPPE ANDREW, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA TEAM, DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY TEAM — Coherent optical control over ultrafast molecular behavior including chemical reactions has been explored in recent years, spurred by the application of optimal control theory and related methods by the development of femtosecond pulse shaping techniques through which complex optical waveforms have been generated and tested on isolated molecular responses. Here we propose and model theoretically the extension of coherent control to collective structural change. We show that properly shaped terahertz fields, resonant with selected lattice vibrational frequencies, could be used to move ions in ferroelectric crystals from their positions in an initial domain orientation along well defined collective microscopic paths into the positions they occupy in a new domain orientation. Collective coherent control will enable direct observation of fast highly nonlinear material responses and far-from-equilibrium structures that can be harnessed in electro-optic devices and non-volatile computer memory.

This work was contributed by ONR, NSF, DOE and HPCMO.

10:48AM V38.00007 Classical-Quantum correspondence in isomerization dynamics: quantum eigenstates and classical Arnold’\textsuperscript{d} web. S. KESHAVAMURTHY, IIT Kanpur, India — Recently, there has been a renaissance of sorts in chemical dynamics with researchers critically examining the validity of the two pillars of reaction rate theory - transition state theory and the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. Since both theories have classical dynamics at their foundation, advances in our understanding of nonlinear dynamics and continuing efforts to characterize the phase space structure of systems with three or more degrees of freedom are beginning to yield crucial mechanistic insights into the dynamics. This talk focuses on a mechanistic understanding of the deviations from RRKM theory for a model isomerization problem with three degrees of freedom. Several studies have established that such systems are prime candidates for observing non-RRKM behavior. We try to answer two of the questions posed in this early work by studying the intramolecular vibrational energy flow in the system from both classical and quantum viewpoints. Using a wavelet-based local frequency analysis it is possible to construct a useful representation of the classical phase space (Arnold’\textsuperscript{d} web) highlighting the important dynamical structures. Insights into the dynamics originate from the various nonlinear resonances and phase space traps which potentially result in quantum eigenstates of varying degree of localization.

References:

Thursday, March 19, 2009 11:15AM - 2:03PM – Session W37 DCP: Theoretical Methods and Algorithms 409
11:15AM W37.00001 X-ray absorption spectra of ice and water: a first principles study with the GW method1, XIUFAN WU, WEI CHEN, ROBERTO CAR, Princeton University — We calculated the X-ray absorption spectra of ice and liquid water by adopting an approach based on the GW method to describe the excited electron in presence of a frozen core hole. We used the static Coulomb-hole and screened exchange approximation for the self-energy and used Maximally Localized Wannier functions to make GW calculations feasible in the large supercell needed to model a disordered system like water. The calculated spectra considerably improve the agreement with experiment, compared with previous DFT calculations. In particular, the three main features observed in experiments are well reproduced in terms of position and intensity for both ice and water. We also find that the difference between the ice and water spectra can be understood in terms of the electronic structures of these systems, manifested by a distorted, tetrahedral hydrogen bond network in the liquid.

1This work is partially supported by NSF under the PCCM-MRSEC program with award number: NSF DMR 02-13706.

11:27AM W37.00002 Iterative Monte Carlo for Quantum Dynamics1, VIKRAM JADHAAO, NANCY MAKKRI, University of Illinois at Urbana-Champaign — We present a fully quantum mechanical methodology for calculating complex-time correlation functions by evaluating the discretized path integral expression iteratively on a grid selected by a Monte Carlo procedure [1]. Both the grid points and the summations performed in each iteration utilize importance sampling, leading to favorable scaling with the number of particles, while the stepwise evaluation of the integrals circumvents the exponential growth of statistical error with time.

1This work is supported by the National Science Foundation under Award Nos. ITR 04-27082, CHE 05-18452, and CRIF 05-41659

11:39AM W37.00003 Resonating Valence Bond wave function with molecular orbitals: first application to dimers1, SANDRO SORELLA, SISSA and DEMOCRITOS, Via Beirut n.2 34014, Trieste, Italy., SAM AZADI, SISSA, Via Beirut n.2 34014, Trieste, Italy., MARIAPA MARCHI, SISSA and DEMOCRITOS, Via Beirut n.2 34014, Trieste, Italy., MICHELE CASUAL, Centre de Physique Théorique, Ecole Polytechnique, CNRS, 91128 Palaiseau, France — We introduce a method for accurate quantum chemical calculations based on a single determinant wave function, the Antisymmetrized Geminal Power (AGP), and a real space correlation factor (the so called Jastrow factor), that can be efficiently sampled by means of standard quantum Monte Carlo techniques. This allows to obtain a very accurate description of the chemical bond even in extremely difficult cases (such as Be2, N2 and C2) where strong dynamical correlations and/or weak vdW interactions are present. The method is based on a constrained variational optimization, obtained with an appropriate number $n$ of molecular orbitals in the AGP wavefunction. It is shown that the most relevant dynamical correlations are correctly reproduced, once $n$ is univocally determined by the requirement to have size consistent results upon atomization to correlated Hartree-Fock Slater determinants in presence of the Jastrow factor. We apply this method to the Iron dimer molecule and obtain an accurate description of the ground state energy and excitations of this molecule, which is compatible with the experimental findings.

1We acknowledge support by MIUR COFIN07.

11:51AM W37.00004 ABSTRACT WITHDRAWN —

12:03PM W37.00005 Representing quantum environments, MICHAEL ZWOLAK, Los Alamos National Laboratory — Understanding dissipative and decohering processes is fundamental to the study of non-equilibrium systems and quantum computing, and such processes can even induce quantum phase transitions. A typical construction is to have a system connected to a continuum environment, which acts as the source of dissipation or decoherence, or as a reservoir of particles. If the connection is strong or the environment has long-range correlations in time, the system dynamics is not easily separated from the dynamics of the environment. To study this situation numerically, one option is to simulate both the system and environment. This is a viable option so long as an efficient finite representation of the environment can be constructed. We will discuss recent results on constructing finite representations of environments for use in computational simulations.

12:15PM W37.00006 ABSTRACT WITHDRAWN —

12:27PM W37.00007 Application of the Finite-Element Space-Time Algorithm to Bound States1, CHARLES WEATHERFORD, Florida A&M University, ALBERT WYNN, DANIEL GEBREMEDIHIN, XINGJUN ZHANG, Florida A&M University — The implementation of the Dirac representation is facilitated by the finite element space-time algorithm.[1] Multicenter integral computations are also facilitated by this same algorithm. The present work is the first application of this original algorithm to the computation of bound states of atoms and molecules. The Dirac representation is employed such that $H_0$, the sum of the one-electron operators while the residual $H_1$ is the sum of the two-electron operators. Soft-Coulomb geminals are then used as the basis for the time-dependent calculation of a superposition of the bound states. The eigenstates and eigenvalues are then extracted by filter-diagonalization. An addition theorem is given for the soft-coulomb geminals and the geminals are translated again using the space-time algorithm, so that multicenter integrals may be computed. Several small atoms and molecules are considered as an illustration of the method.


1Supported by the NSF CREST Center for Astrophysical Science and Technology.

12:39PM W37.00008 Test of Current Variational Procedures for Electronic Structures and Properties of Molecular and Solid State Systems by application to Atomic Systems-$H^-$Ion, HARI PAUDEL, ARCHANA DUBY, UCF Orlando, R.H. SCHIECHER, Uppsala University, Sweden, S.R. BADU, R.H. PINK, T.P. DÅS, SUNY Albany — Electronic properties of atomic systems are obtainable using Linked Cluster Many-Body Perturbation Theory(LCMBPT) with high accuracy and excellent agreement with experiment, using complete sets of states obtained by differential equation procedures [1,2]. Unfortunately such procedures are not practicable for multi-center molecular and solid state problems and variational procedures have to be used for obtaining the occupied and excited one electron states to work on electronic properties of the latter systems. With the aim to assess the accuracies of the latter procedures with Gaussian basis states, like the first principles Hartree-Fock procedure together with many body perturbation theory, and density functional based procedures, we are testing them for both energy and wave function dependent properties of atoms. Results will be presented for $H^-$ ion, where Hartree-Fock theory predicts instability with respect to auto ionization to H atom and electron correlation effects obtained by the LCMBPT procedure [3] restore stability, providing nearly exact experimental affinity for $H^-$.[1] Alfred Owusu et al., Phys. Rev. A56, 305(1997) [2] T.Lee et al., Phys. Rev. A44 1410(1991) [3]C.M. Dutta et al., Phys. Rev. A2, 2269(1970)
12:51PM W37.00009 Computation of Nonlinear Impedance Spectra in Samaria Doped Ceria
FRANCESCO CIUCCI, California Institute of Technology — Samarium Doped Ceria (SDC) electrodes are currently of great interest for solid oxide fuel cells (SOFC) applications. For example, ceria-containing anodes can be operated directly on hydrocarbons without coking, and in addition can be used at lower temperatures than Ni/YSZ. In order to design, optimize, and characterize electrodes, it is very useful to have models to aid in interpreting experimental results. In this work, we present a non-linear, time-dependent model for the study of SDC. This model allows us to compute species concentrations, electric potential and currents under medium bias conditions. A regular perturbation of the drift diffusion equations and Poisson’s equation is used to derive the model for the behavior of bulk of the material. We also include the kinetics of reactions occurring at the SDC-gas surface where the SDC is exposed to a spatially uniform hydrogen-water-argon mixture at fixed total pressure. The numerical procedure allows for fast computations and for the direct determination of fast and rate limiting steps. Impedance spectra are computed in the 2D case and a quantitative comparison between experimental (symmetric cell) and numerical results is presented. Our model can be naturally extended to the non-symmetric case, i.e. the case under which the two sides of the SDC assembly are exposed to different atmospheres.

1:03PM W37.00010 An Analytical Approach to Computing Biomolecular Electrostatic Potential
ANDREW FENLEY, JOHN GORDON, ALEXEY ONUFRIEV, Virginia Tech — Analytical approximations to fundamental equations of continuum electrostatics on simple shapes can lead to computationally inexpensive prescriptions for calculating electrostatic properties of realistic molecules. Here, we derive a closed form, analytical approximation to the Poisson equation for an arbitrary distribution of point charges and a spherical dielectric boundary. The simple, parameter-free formula defines continuous electrostatic potential everywhere in space and is obtained from the exact infinite series (Kirkwood) solution by an approximate summation method that avoids truncating the infinite series. We show that keeping all the terms proves critical for the accuracy of this approximation, which is fully controllable for the sphere. We apply the approximation to 580 biomolecules under realistic solvation conditions, where the effects of mobile ions are included at the low-Hückel level. The accuracy of the approximation as applied to the biomolecules is assessed through comparisons with numerical Poisson-Boltzmann (NPB) reference solutions. For each structure, the deviation from the reference is computed for a large number of test points placed near the dielectric boundary (molecular surface). The accuracy of the approximation is within 1 kT per unit charge for 91.5% of the individual test points.

1:15PM W37.00011 Ab Initio Study of Atomic and Molecular Polarizabilities
IGOR VASILIEV, New Mexico State University, JAMES R. CHELIKOWSKY, The University of Texas at Austin — We calculate the static electric dipole polarizabilities for a variety of atoms and molecules using a finite field method implemented in the framework of an ab initio density functional formalism. Our calculations employ several different representations of the exchange-correlation potential, including the local density approximation, generalized gradient approximation, and asymptotically correct functionals introduced by Leeuwen-Baerends [1] and Casida-Salabur [2]. We observe that the computed values of polarizabilities are strongly influenced by the asymptotic behavior of the density functional exchange-correlation potential. The accuracy of theoretical atomic and molecular polarizabilities is substantially improved by the use of asymptotically correct exchange-correlation functionals. This result can be explained in terms of electronic excitation energies and the polarizability sum rule.

1:27PM W37.00012 Theoretical predictions of the impact of nuclear dynamics and environment on core-level spectra of organic molecules
DAVID PRENDERGAST, Molecular Foundry, Lawrence Berkeley National Laboratory, CRAIG SCHWARTZ, JANEL UEJIO, RICHARD SAYKALLY, Chemical Sciences Division, Lawrence Berkeley National Laboratory — Core-level spectroscopy provides an element-specific probe of local electronic structure and bonding, but linking details of atomic structure to measured spectra relies heavily on accurate theoretical interpretation. We present first principles simulations of the x-ray absorption of a range of organic molecules both in isolation and aqueous solution, highlighting the spectral impact of internal nuclear motion as well as solvent interactions. Our approach uses density functional theory with explicit inclusion of the core-level excited state within a plane-wave supercell framework. Nuclear degrees of freedom are sampled using various molecular dynamics techniques. We indicate specific cases for molecules in their vibrational ground state at experimental conditions, where nuclear quantum effects must be included. Prepared by LBNL under Contract DE-AC02-05CH11231.

1:39PM W37.00013 Efficient free energy calculations of quantum systems through computer simulations
ALEX ANTONELLI, Universidade Estadual de Campinas, RAFAEL RAMIREZ, CARLOS HERRERO, Instituto de Ciencia de Materiales de Madrid, EDUARDO HERNANDEZ, Institut de Ciencia de Materiales de Barcelona — In general, the classical limit is assumed in computer simulation calculations of free energy. This approximation, however, is not justifiable for a class of systems in which quantum contributions for the free energy cannot be neglected. The inclusion of quantum effects is important for the determination of reliable phase diagrams of these systems. In this work, we present a new methodology to compute the free energy of many-body quantum systems [1]. This methodology results from the combination of the path integral formulation of statistical mechanics and efficient non-equilibrium methods to estimate free energy, namely, the adiabatic switching and reversible scaling methods. A quantum Einstein crystal is used as a model to show the accuracy and reliability the methodology. This new method is applied to the calculation of solid-liquid coexistence properties of neon. Our findings indicate that quantum contributions to properties such as, melting point, latent heat of fusion, entropy of fusion, and slope of melting line can be up to 10% of the calculated values using the classical approximation. [1] R. M. Ramirez, C. P. Herrero, A. Antonelli, and E. R. Hernandez, Journal of Chemical Physics 129, 064110 (2008).

1:51PM W37.00014 Applications of a novel QM/MM method incorporating a polarizable force field.
CHRISTOPHER WILLIAMS, JOHN HERBERT, Ohio State University — In conventional QM/MM methods the MM region is modeled by a force field that uses a set of point charges to represent the electrostatics. However, recently developed force fields use multipole expansions combined with polarizable sites to represent electrostatic interactions. A novel algorithm is presented to interface this class of force fields with a QM region by allowing the QM region and the MM region to polarize each other self-consistently. It is implemented using the QChem electronic structure code and the AMOEBA force field as implemented in the software package TINKER. The algorithm is general and can be used with a variety of QM methods including MP2 and DFT. Examples of both ground state and excited state calculations are presented, including the investigation of the effectiveness of many-body expansions in modeling the solvation of charged species and the effect of charged environments on biomolecules.

Thursday, March 19, 2009 11:15AM - 2:03PM –
Session W38 DCP: Focus Session: Ion Channel Physics and Chemical Physics I 410
We gratefully acknowledge support from AFOSR grant #FA9550-05-1-0186 and #FA9550-07-1-0151.

11:15AM W38.00001 Numerical modeling of fast gate-coupled ion permeation in ClC channels

MARY H. CHENG, Department of Chemistry, University of Pittsburgh — We have developed a three dimensional Brownian dynamics (BD) and discrete-state model to couple ion permeation to the motion of a putative fast gate in the ClC channels. The model channel is designed so as to represent certain essential features of ClC chloride channel, in which a glutamate side chain moves from an open state to a closed state (blocking the channel pore at a position which also acts as a binding site for Cl\(^-\) ions moving through the channel). Both BD and the discrete-state model generate results in qualitative agreement with experimental observations and consistent with the foot-in-the-door mechanism. Furthermore, we have formulated a numerical approach to calculate the discrete rate constants in our model channel using BD. The discrete-state model with the rate constants solved via BD produces results consistent with the (continuous space) multi-ion BD simulations.

Support: DoD/MURI, NSF

1Co-authors: Mamontov AB and Coalson RD.

11:51AM W38.00002 Modeling Ion Solvation and Transport through Chloride Transport Proteins

THOMAS BECK, Univ. of Cincinnati — Ion channels and transporters are membrane proteins that selectively conduct ions either passively (channels) or actively using a chemical gradient of one ion (transporters). The H+/Cl- transporter, first discovered in bacteria, has now been shown to also occur in animals and plants. This talk will discuss computational approaches aimed at understanding the ion transit pathways through the bacterial chloride transporter. A Monte Carlo method (TransPath) that uses the crystal structure as input and exhaustively searches the protein for open pore spaces and favorable electrostatic domains has been developed. The algorithm successfully predicted pathways for the motion of chloride ions and protons. In order to better understanding the free energies along the predicted transport pathways, we have developed a new statistical mechanical approach for computing absolute solvation free energies in restricted environments based on a quasi-chemical approach. Anion free energy results employing the new method will be presented.

1Support: DoD/MURI, NSF

12:27PM W38.00003 Snug-fit, fluctuations, and metal-ion hydration in the selectivity of potassium ion channels

LAWRENCE PRATT, Chemical and Biomolecular Engineering, Tulane University — On the basis of molecular simulation, an identification of a single dominating physical factor responsible for Na\(^+\)/K\(^+\) selectivity of the KcsA channel has been contentious. The potential distribution theorem and quasi-chemical theory cast new light on the factors responsible for Na\(^+\)/K\(^+\) selectivity. In that context, we argue that an alternative definitive formulation of the molecular statistical thermodynamic problem can help in achieving a concensus view of selectivity. We summarize the necessary new theoretical ingredients and published numerical results in working toward that consensus view.

1:03PM W38.00004 Conformational changes in the Glutamate receptor as studied by LRET

VASANTHI JAYARAMAN, University of Texas Health Science Center at Houston — Glutamate receptors are the primary mediators of excitatory neurotransmission in the mammalian central nervous system. Glutamate binding to an extracellular ligand binding domain initiates a series of conformational changes that results in the formation of cation selective transmembrane ion channels that ultimately desensitize. We have used luminescence resonance energy transfer to determine the conformational changes that underlie the allosteric process of glutamate mediated gating in the receptor. These investigations showed that agonist binding induced cleft closure in the ligand binding domain confirming that this change observed in the isolated ligand binding domain of the receptor is one of the mechanisms by which agonist mediates activation. The LRET investigations also allowed a study of the conformational changes between the subunits. The apo state of the protein showed a dimer interface that was open. The dimer interface was brought together only in the activated state, suggesting that cleft closure drives the formation of the contacts at dimer interface, which in turn transiently stabilizes the open channel. At longer times, the stress induced by the transmembrane segments, ultimately drives the breakdown of the interface, leading to channel closure and receptor desensitization.

1:39PM W38.00005 Electric and Molecular Characteristics of Ion Channels

RICHARD DESANTIS, APS — A galvanic cell’s electrolyte is an insulator. A conductive electrode pair would quickly discharge a dry cell’s voltage. Voltage-producing paths within an electrolyte can develop spontaneously. A voltage-producing path must bridge from the anode to the cathode, to export voltage out of the insulating electrolyte. Doubling cathode to anode distance does not decrease the cell’s fixed output voltage. The fixed voltage indicates superconductor-like behavior. Gaps between voltage-producing molecules would isolate the anode from the cathode, preventing superconductor-like behavior. Gating activity within membrane protein complexes can prevent or allow voltage-producing paths. Voltage-producing path is a single molecule containing both anode and cathode reactants. Only combined anode-cathode reactions within a single molecule can produce the cell’s fixed exterior voltage. While within the single molecule, atoms can relocate and react. In a lead acid cell, charging voltage raises the molecule’s energy state. The extra energy allows Pb and PbO\(_2\) to form during the molecule’s collapse. For anode-cathode reactions within a single molecule can produce the cell’s fixed exterior voltage. While within the single molecule, atoms can relocate and react. For discharging, an external circuit provides an outlet for the molecule’s voltage, which lowers the molecule’s energy state to a level that permits PbSO\(_4\) production.

1:51PM W38.00006 Coulombic dragging of molecular assemblies on nanotubes

PETR KRAL, KYAW SINT, BOYANG WANG, University of Illinois at Chicago — We show by molecular dynamics simulations that polar molecules, ions and their assemblies could be Coulombically dragged on the surfaces of single-wall carbon and boron-nitride nanotubes by ionic solutions or individual ions moving inside the nanotubes [1,2]. We also briefly discuss highly selective ionic sieves based on graphene monolayers with nanopores [3]. These phenomena could be applied in molecular delivery, separation and desalination.


Thursday, March 19, 2009 2:30PM - 5:30PM – Session X37 DCP: Spectroscopy and Dynamics of Single Molecules and Nanoparticles

2:30PM X37.00001 Reactivity of Aluminum and Doped Aluminum Clusters

ARTHUR REBER, SHIV KHANNA, Virginia Commonwealth University, PATRICK ROACH, WILLIAM WOODWARD, A. WELFORD CASTLEMAN JR., Penn State University — We examine the reactivity of aluminum cluster anions with water, and other nucleophiles. The clusters reveal size dependent reactivity which primarily results in superconductor-like behavior. Anion free energy results employing the new method will be presented.

1We gratefully acknowledge support from AFOSR grant #FA9550-05-1-0186 and #FA9550-07-1-0151.
2:42PM X37.00002 Multiple Isomers in the Photoelectron Spectra of NbC₆ clusters. IVAN IORDANOV, JORGE SOFO. Department of Physics, Penn State — We calculate the photoelectron spectrum of small NbC₆ clusters (2c-n=7), to identify the atomic structure that best matches experimental photoelectron spectra. We use Density Functional Theory calculations to find all stable isomers. In order to obtain more accurate spectra, we use the Symmetry Adapted Cluster Configuration Interaction method for the smaller clusters where the highly correlated niobium d-orbitals dominate the electronic structure. The most stable isomer configurations are linear and cyclic structures, with the cyclic being the ground state for all but NbC₆. To fully explain all experimental observations we are required to use the combined spectra of both ring and linear structures. This means that both structures must be present in the cluster beam, even in cases where the higher energy isomer is up to 0.5 eV higher than the ground state. This surprising result is confirmed by both DFT and Configuration Interaction.

2:54PM X37.00003 Photoelectron Velocity Map Imaging and Density-Functional Investigation of Bismuth and Lead Anions Solvated in Ammonia. KRISTEN CASALENUOVO, Department of Physics, Virginia Commonwealth University, Richmond VA, 23284, MOHAMED A. SOBHY, Departments of Chemistry and Physics, The Pennsylvania State University, University Park, PA 16802, J. ULISES REVELES, Department of Physics, Virginia Commonwealth University, UIJJWAL GUPTA, Departments of Chemistry and Physics, The Pennsylvania State University, SHIV N. KHANNA, Department of Physics, Virginia Commonwealth University, A.W. CASTLEMAN, JR., Departments of Chemistry and Physics, The Pennsylvania State University, SHIV KHANNA RESEARCH GROUP COLLABORATION, THE CASTLEMAN GROUP COLLABORATION — We present the results of photoelectron velocity map imaging experiments for the photodetachment of small negatively charged Bi₃ and Pb₃ (n = 1-2) clusters solvated in ammonia using a Nd:YLF 527 nm laser. We report the vertical detachment energies of the observed multiple electronic bands and their respective anisotropy parameters derived from the photoelectron images. Density-functional theory calculations with generalized gradient approximation for the exchange-correlation potential were performed on these clusters to determine their molecular and electronic structures. Calculated ammonia binding energies and electronic charge transfers are used to rationalize the observed mass spectra distributions.

3:06PM X37.00004 Dielectrophoresis and Dissociation of Micelles in AC-Electric Fields. VICTORIA FROUDE, YINGXI ELAINE ZHU. University of Notre Dame — Dielectrophoresis (DEP) of natural and synthetic colloids has been explored as a route to rapidly manipulate and assemble colloidal particles in suspensions. Most work has been done with micro to submicron sized particles, yet AC-polarization and dielectrophoretic effects on molecules and nanocolloids remain little understood. In this work, we examine the dynamic responses of micelles to applied AC-electric fields by using fluorescence correlation spectroscopy (FCS) at a single-molecule resolution. We focus on the AC-field induced transport of sodium dodecyl sulfate (SDS) micelles tagged with various fluorescent probes and molecular encapsulates. Micelle concentration and DEP mobility of SDS micelles are examined over a broad range of AC-field frequency (1 kHz -10 MHz) and amplitude (100mV -20V). We observe a strong AC-frequency dependence of micelle concentration, from which the DEP crossover frequency switching between the positive and negative DEP response is determined. Surprisingly, we also observe the AC-field induced dissociation of the micelle structure and the resultant release of fluorescent encapsulates at a characteristic low AC-field frequency of 1-10 kHz; the dissociation frequency can be tuned by encapsulated molecules with a strong dependence of their surface conductivity, which could have a potential application for controlled drug release by AC-electric fields.

3:18PM X37.00005 Raman Correlation Spectroscopy¹. MAKI NISHIDA, EDWARD VAN KEUREN, Georgetown University — We have developed a simple method for measurement of diffusion coefficients of specific components in complex mixtures of nanoparticles in a suspension. As a variation of Dynamic Light Scattering (DLS), this method analyzes temporal fluctuations of Raman scattered light from particles caused by Brownian motion. Due to the different scattering nature of Raman scattering compared to DLS, we observe a strong AC-frequency dependence of micelle concentration, from which the DEP crossover frequency switching between the positive and negative DEP response is determined. Surprisingly, we also observe the AC-field induced dissociation of the micelle structure and the resultant release of fluorescent encapsulates at a characteristic low AC-field frequency of 1-10 kHz; the dissociation frequency can be tuned by encapsulated molecules with a strong dependence of their surface conductivity, which could have a potential application for controlled drug release by AC-electric fields.

3:30PM X37.00006 Nanosphere Templating Through Controlled Evaporation: A High Throughput Method For Building SERS Substrates. KRISTEN ALEXANDER, UNC Department of Physics, MEREDITH HAMPTON, UNC Department of Chemistry, RENE LOPEZ, UNC Department of Physics, JOSEPH DESIMONE, UNC Department of Chemistry — When a pair of noble metal nanoparticles are brought close together, the plasmonic properties of the pair (known as a “dimer”) give rise to intense electric field enhancements in the interstitial gap. These fields present a simple yet exquisitely sensitive system for performing single molecule surface-enhanced Raman spectroscopy (SM-SERS). Problems associated with current fabrication methods of SERS-active substrates include reproducibility issues, high cost of production and low throughput. In this study, we present a novel method for the high throughput fabrication of high quality SERS substrates. Using a polymer templating technique followed by the placement of thiolated nanoparticles through meniscus force deposition, we are able to fabricate large arrays of identical, uniformly spaced dimers in a quick, reproducible manner. Subsequent theoretical and experimental studies have confirmed the strong dependence of the SERS enhancement on both substrate geometry (e.g. dimer size, shape and gap size) and the polarization of the excitation source.

3:42PM X37.00007 Resolving Single Molecular Dynamics with a Point-Functionalized Single-Walled Carbon Nanotube. DANNY W. WAN, ISSA S. MOODY, BRETT R. GOLDSMITH, JOHN G. CORONEUS, GREGORY A. WEISS, PHILIP G. COLLINS. Departments of Physics and Astronomy, Chemistry, Molecular Biology and Biochemistry, University of California, Irvine, CA 92697-4566 — Outside of fluorescence measurements, there are currently few means of observing characteristic time constants of individual molecules. We describe the development of a single molecule technique utilizing a point-functionalized SWCNT electronic circuit [1]. Time-dependent components of the SWCNT conductance reveal real-time interactions between a covalently attached protein and the immediate electrolytic environment. We will demonstrate electronic transduction of protein-substrate interactions with single molecule resolution. On-line analysis based on normalization of the power spectrum helps to enhance the resulting signals, even to the extent of providing the user with real time feedback regarding the experiment status. [1] B. Goldsmith et al, Science 315 77 (2007)

3:54PM X37.00008 Auger Rate Quenching in Nanocrystals. GEORGE E. CRAGG, Naval Research Laboratory, Washington, DC 20375, XIAOYONG WANG, MEGAN A. HAHN, Department of Chemistry, University of Rochester, Rochester, NY 14627, SARAH MACCAGNANO-ZACHER, JOHN SILCOX, School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14853, TODD D. KRAUSS, Department of Chemistry, University of Rochester, Rochester, NY 14627, ALEXANDER L. EFROS, Naval Research Laboratory, Washington, DC 20375 — Single nanocrystal (NC) photoluminescence (PL) blinking is believed to arise from a photoionization event, resulting in a charged NC state made dark by the dominance of the non-radiative Auger rate. Suppression of the Auger rate has been suggested as the underlying mechanism for the non-bleeding PL observed in soft-configuration, single CdZnSe/ZnSe NCs. To probe the interplay between the confinement geometry and the PL, we employ a coupled, two-band NC model which is analyzed with numerical routines based on the propagation matrix formalism. The results obtained will verify whether smooth confining potentials mitigate the Auger process, thereby eliminating blinking by allowing NCs to photoluminesce even in their charged state.

This material is based upon work supported by the National Science Foundation under Grant No. DMR 0348955.

This research has been partly supported by NSF (ECCS-0802077, DMR-0801271) and NIH (NCI-CA133592).
4:06PM X37.00009 Dynamical charge and structural strain in MoS2 and MnO nanoparticles \(^1\), QI SUN, XIAOSHAN XU, JANICE MUSFELDT, University of Tennessee, RESHEF TENNE, Weizmann Institute of Science, ALLA ZAK, Weizmann Science Park, SHEILA BAKER, ANDREW CHRISTIANSON, Oak Ridge National Laboratory — We measured the far infrared vibrational properties of bulk and nanoscale MoS2 and MnO in order to investigate finite length scale effects and chemical bonding in these materials. From an analysis of frequencies, oscillator strengths, and the high frequency dielectric constants, we extract Born and local effective charges for both materials. In the intralayer direction of MoS2, we find that the Born effective charge of the nanoparticles is decreased significantly compared to the layered bulk, a result that we attribute to structural strain (and resulting change in polarizability). Preliminary results on the 7 nm MnO nanoparticles suggest that structural strain impacts both polarizability and depolarization field.

\(^1\)This work is supported by the U.S. Department of Energy and the JDRD Program at the University of Tennessee.

4:18PM X37.00010 Ultrafast electronic energy redistribution in hollow gold nanoparticles, KENNETH KNAPPENBERGER\(^2\), Florida State University, ADAM SCHWARTZBERG, LBNL — Nanostructured materials offer great potential for novel ways to generate, utilize, store and transport energy. These unique opportunities arise because nanoclusters often portray strikingly different chemical and physical properties than their bulk counterparts, and, perhaps more intriguingly, these vary widely with cluster size and shape. Here we report on the redistribution of electronic energy to thermal phonons in a series of hollow gold nanoparticles using femtosecond transient absorption. Qualitatively, the relaxation processes are similar to those of solid nanoparticles, however distinct differences are observed, likely owing to the unique properties of the hollow structures. In particular, a larger excitation power density is required to observe coherent vibrational oscillations in hollow gold nanoparticles than is needed for solid particles following electronic excitation. This effect is systematically studied over a range of hollow and solid particles, including multiple diameters and wall thicknesses. Models will be presented to account for the different relaxation mechanism observed for hollow and solid gold nanoparticles.

\(^2\)corresponding author

4:30PM X37.00011 Optical spectra with spin-orbit effects on gold nanostructures \(^1\), ALDO ROMERO, CINVESTAV, México, ALBERTO CASTRO, Institutt fur Theoretisk Physik, Freie Universitat Berlin, MIGUEL MARQUES, Université Lyon, France, MICAEL OLIVEIRA, University of Coimbra, Portugal, ANGEL RUBIO, ETSF, Universidad del Pais Vasco, Spain — The quest for more efficient optoelectronic devices requires a thorough understanding of the intrinsic properties of the metallic nanostructures such as the optical spectra. Many optoelectronic devices are based upon gold nanostructures but even though, there is a large set of experimental studies, little is known theoretically. Between the concerns, it is important to identify where the spin-orbit effect has influences on the optical spectra on those nanostructural materials. We report here the analysis of the effect of the spin-orbit interaction on the shape of the photoabsorption cross section of small gold clusters (Au\(_n\), \(n \leq 8\) and \(n = 20\)) and small nanowires \((n \leq 7)\). As it is shown, the spin-orbit coupling has a strong effect on the absorption spectra mainly for nanowires and much less effect on static properties such as the dipole static polarizability. This has strong implications on transport calculations where spin-orbit effects are considered.


4:42PM X37.00012 First-principles studies of surface-enhanced Raman scattering: Benzene thiol on Au \(^1\), ALEXEY ZAYAK, Department of Electrical Engineering and Computer Science, UC-Berkeley, CA, JEFFREY NEATON, Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA — First-principles calculations based on density functional theory are used to investigate how chemisorption of organic molecules on metal surfaces affects their Raman spectra. Experiments have long reported Raman intensity enhancements of many orders of magnitude for molecules on rough metal surfaces or near nanofabricated metallic tips. The goal of this work is to explore “chemical” effects that may contribute to this enhancement, specifically hybridization and charge transfer between the molecule and its metallic substrate. We consider benzene thiol chemisorbed on extended Au(111) surfaces and finite Au and Ag clusters. Using a finite-difference scheme, we compute the absorption site, molecular orientation, and coverage dependence of Raman-active phonon modes and their intensities. We also examine how the electronic structure of the molecule is modified in each case, and discuss implications for the strength of Raman processes.

\(^1\)This work was supported by DARPA and in part by the DOE under Contract No. DE-AC02-05CH11231

4:54PM X37.00013 ABSTRACT WITHDRAWN

5:06PM X37.00014 Photoluminescence anti-blinking of single CdZnSe/ZnSe nanocrystals, XI-AOYONG WANG, Department of Chemistry, University of Rochester, XIAOFAN REN, KEITH KAHEN, Eastman Kodak Company, MEGAN HAHN, Department of Chemistry, University of Rochester, MANJU RAJESWARAN, Eastman Kodak Company, SARA MACCAGNANO-ZACHER, JOHN SILCOX, School of Applied and Engineering Physics, Cornell University, GEORGE Cragg, ALEXANDER EFROS, Naval Research Laboratory, TODD KRAUSS, Department of Chemistry, University of Rochester, UNIVERSITY OF ROCHESTER TEAM, EASTMAN KODAK COMPANY COLLABORATION, CORNELL UNIVERSITY COLLABORATION, NAVAL RESEARCH LABORATORY COLLABORATION — We have synthesized soft-confinement nanocrystals (NCs) of CdZnSe/ZnSe that on the single particle level exhibit complete elimination of photoluminescence (PL) blinking. These continuously emitting NCs have a very short PL decay lifetime of 5 ns. Moreover, single CdZnSe/ZnSe PL spectra are highly unusual with three distinct peaks. These unique and remarkable optical properties are collectively explained by the radiative recombination of a trion due to suppressed Auger processes in a NC. Upon deformation of the soft-confinement potential, the PL intensity of a single CdZnSe/ZnSe NC switches between two bright states, but still never turns off. Possible mechanisms for this PL anti-blinking behavior will be discussed.

5:18PM X37.00015 Single-Electron Spectroscopy of Quantum Dots using Vertically Self-aligned Electrode Structure, RAMKUMAR SUBRAMANIAN, PRADEEP BHADRACHALAM, VISHVA RAY, SEONG JIN KOH, The University of Texas at Arlington — We demonstrate single-electron tunneling spectroscopy of individual quantum dots using new vertical electrode structure, where the source and drain electrodes are vertically self-aligned and separated by a thin dielectric spacer. A quantum dot placed on the periphery between the source and the drain electrodes forms a double barrier tunnel junction, allowing for single-electron spectroscopy measurements. CMOS compatible fabrication allows many quantum dot units to be fabricated in parallel processing. This technique not only provides an accurate electronic structure of a “single” quantum dot, but such measurement can be made for many of individual quantum dot units fabricated in a single batch process. Thus, this simple procedure provides accurate energy level measurement of “single” quantum dots over the entire quantum dot population. The band gap \((E_g)\), charging energy \((E_c)\) and energy level spacing \((\Delta E)\) were measured directly from the current-voltage and differential conductance spectra for colloidal CdSe quantum dots \((\sim 6.5\text{nm})\). The band gap was measured to be \(E_g \sim 1.75-1.85\text{eV},\) charging energy \(E_c \sim 60\text{meV}\) and the ‘s’ to ‘p’ level separation \((\Delta E)\) was measured to be \(\sim 60-100\text{meV}\). (Supported by NSF CAREER ( ECS-0449958), ONR (N00014-05-1-0030), and THECB ARP (003656-0014-2006)).
site-to-site variations in the vibrational reorganization energy barriers in the interfacial ET systems.

Recent ensemble-averaged studies have indicated inhomogeneous and complex dynamics of interfacial ET reaction. To characterize the inhomogeneity and the complex mechanism, we have applied single-molecule spectroscopy and correlated AFM/STM imaging to study the Interfacial ET dynamics of dye molecules adsorbed to the TiO$_2$ nanoparticle surface. The fluctuation dynamics were found to be inhomogeneous from molecule to molecule and from time to time, showing significant static and dynamic disorders in the dynamics. Furthermore, we have applied site-specific AFM-Raman spectroscopy on analyzing ET associated mode-specific vibrational fluctuations.

We observe a reduction in activating tension, substantial changes in MscS kinetics and complete removal of gating hysteresis. The kinetic treatment of channel traces recorded in response to steps of tension suggested the occurrence of events that leads to the channel opening implying that pore hydration and dewetting are the rate-limiting steps in MscS transitions.

The methods we employ include finite-size scaling (FSS), multicanonical histogram reweighting and Gibbs ensemble methods. We show that, as expected, all three cases belong to the universality class. The scaling fields and critical point parameters are obtained in the thermodynamic limit of infinite system size by extrapolation of our FSS results.

We are investigating the dynamics of channel clusters at the single molecule level using particle tracking with nanometer accuracy in live cells. Here, the cluster structure and individual channels are imaged simultaneously in a total internal reflection microscope. While most Kv2.1 channels in the cell are labeled with green fluorescent proteins (GFP), only a few individual channels are tagged with red quantum dots. This approach allows us to track single molecules and probe their interaction with the cluster perimeter. Different models for the molecular mechanism that localizes Kv2.1 clusters on the cell surface and the implications of our data will be discussed.

We obtain accurate fluid-fluid coexistence curves for a recent simple model of interacting nanoparticles that includes the effects of ion-dispersion forces. It has been proposed that these ion dispersion forces provide at least a partial explanation for the Hofmeister effect [Phys. Rev. Lett., 87:168103, 2001]. We study a model of aluminum oxide nanoparticle [Colloids and Surfaces A, 319:98-102, 2008] for three different electrolyte solutions with added salt type being sodium chloride, sodium iodide and a non-polarizable salt. We observe that partial explanation for the Hofmeister effect [Phys. Rev. Lett., 87:168103, 2001]. We study a model of interacting nanoparticles that includes the effects of ion-dispersion forces. It has been proposed that these ion dispersion forces provide at least a partial explanation for the Hofmeister effect [Phys. Rev. Lett., 87:168103, 2001]. We study a model of aluminum oxide nanoparticle [Colloids and Surfaces A, 319:98-102, 2008].

We are investigating the dynamics of channel clusters at the single molecule level using particle tracking with nanometer accuracy in live cells. Here, the cluster structure and individual channels are imaged simultaneously in a total internal reflection microscope. While most Kv2.1 channels in the cell are labeled with green fluorescent proteins (GFP), only a few individual channels are tagged with red quantum dots. This approach allows us to track single molecules and probe their interaction with the cluster perimeter. Different models for the molecular mechanism that localizes Kv2.1 clusters on the cell surface and the implications of our data will be discussed.

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<td>2:30PM</td>
<td>X38.00001 Dynamics of Kv2.1 channel cluster formation in mammalian neurons.</td>
<td>DIEGO KRAPF, Electrical and Computer Engineering and School of Biomedical Engineering, Colorado State University — Kv2.1 are potassium channels that play an important role in multiple organs and tissues. In particular, in mammalian neurons Kv2.1 channels have an enormous neuroprotective function attained by their ability to form large clusters on the surface of the neuronal cell body. The regulation of Kv2.1 channel clusters is a key factor in protecting the brain, particularly under sudden ischemic conditions such as those encountered in stroke. It is speculated that this kind of stimulus induces channel de-clustering in order to increase neuronal excitability (seizures). However, the physical mechanism that forms and maintains Kv2.1 clusters has remained largely unknown. We are investigating the dynamics of channel clusters at the single molecule level using particle tracking with nanometer accuracy in live cells. Here, the cluster structure and individual channels are imaged simultaneously in a total internal reflect</td>
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8:24AM Y37.00003 Prediction of Zeolite Framework Types by a Machine Learning Approach
SHUJIANG YANG, MOHAMMED LACH-HAB, IOSIF VAISMAN, ESTELA BLAISTEN-BAROJAS, Computational Materials Science Center, George Mason University, Fairfax, VA 22030 — Zeolites are microporous crystalline materials with highly regular framework structures consisting of molecular-sized pores and channels. Characteristic framework types of zeolites are traditionally determined by the combined information of coordination sequences and vertex symbols. Here we present a machine learning model for classifying zeolite crystals according to their framework types. An eighteen-dimensional feature vector is defined including topological descriptors and physical/chemical properties of zeolite crystals [Microporous and Mesoporous Materials 117, 339 (2009)]. Trained with crystallographic data of known zeolites, the new model can predict the framework types of unknown zeolite crystals with up to 98 % accuracy. Compared with conventional methods, the machine learning model is more robust handling crystal disorder and/or crystal defects in a more effective manner. This model can be adapted for classifying and clustering other crystalline species.

1Supported by NSF grant CHE-0626111

8:36AM Y37.00004 Site-specific polarizabilities as predictors of optimal binding sites of H₂O on Naₙ clusters
LI MA, KOBLAR JACKSON, Physics Dept., Central Michigan University, Mount Pleasant, MI 48859, JULIUS JELLINEK, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne IL 60439 — We have used density functional theory (DFT), in the generalized gradient approximation, to study the adsorption of water molecules on sodium clusters, Naₙ, for n = 7, 12, 18, and 25. These clusters span a range of sizes and surface topographies. In each case, we conduct an extensive search to identify the optimal binding site of the ad-molecule on the cluster. We analyze the results within the framework of cluster polarizabilities, making use of a new methodology for partitioning the cluster polarizability into atomic components (Jackson et al., J. Chem. Phys. 129, 144309 (2008)). We show that the most favorable adsorption sites are at surface atoms that have the largest atomic polarizabilities. We will compare and contrast these results with corresponding findings for the adsorption of O₂ and NH₃ molecules on Naₙ clusters.

2This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, U. S. Department of Energy under grant number DE-FGO2-03ER15489

8:48AM Y37.00005 Effect of adsorbates on the isomer stability of Ir₄ clusters
VLADAN STEVANOVIC, ITPEPFL and IRRLA, CH-1015 Lausanne, Switzerland, ZELJIKO SLJIVANCANIN, IRRLA, CH-1015 Lausanne, Switzerland, ALFONSO BALDERESCHI, ITPEPFL and IRRLA, CH-1015 Lausanne, Switzerland and Dipartimento di Fisica Teorica, Università di Trieste, I-34014 Trieste, Italy — The relative stability of Ir₄ isomers, both in the gas phase and on MgO(100) substrate, is studied using density functional theory. The square Ir₄ is the most stable in both cases. The metastable tetrahedral isomer, which experimental data suggest as the most stable form of Ir₄ on MgO(100), is highly distorted by the strong Ir–O interactions. The relative stability of Ir₄ isomers is strongly altered by adsorption of a single C atom since the binding energy of the C adatom to tetrahedral and butterfly Ir₄ is much larger (~1.7 eV) than that to the square one, both in the gas-phase and on MgO(100). After carbon adsorption, the most stable structure of Ir₄ is the butterfly geometry for free clusters and the “tetrahedral” one for Ir₄/MgO(100). The C adatom binds in a bridge configuration in all cases and reduces the distortions produced by the MgO substrate. Energetics and equilibrium atomic geometries will also be discussed for the adsorption (i) one H or O atom and (ii) one CO molecule.

9:00AM Y37.00006 Control and manipulation of Au nanocatalysis: effects of metal oxide support thickness and composition
BOKWON YOON, School of Physics, Georgia Institute of Technology, CHRIS HARDING, VAHIDEH HABIBPOUR, SEBASTIAN KUNZ, ADRIAN NAM-SU FARBACHER, UELI HEIZ, Lehrstuhl fur Physikalische Chemie, Technische Universität München, Germany — At the Nanostructured Interfaces Laboratory, School of Physics, Georgia Institute of Technology — Control and manipulation of the catalytic oxidation of CO by gold clusters deposited on MgO surfaces grown on molybdenum, Mo(100), to various thicknesses, are explored through temperature programmed reaction measurements on mass selected 20-atom gold clusters and via first-principles density-functional theory calculations. Dependencies of the catalytic activities and microscopic reaction mechanisms on the thickness and stoichiometry of the MgO films, and on the dimensionalities and structures of the adsorbed gold clusters are demonstrated and elucidated. Langmuir-Hinshelwood mechanisms and reaction barriers corresponding to observed low and high temperature CO oxidation reactions are calculated and analyzed. Along with the oxidation reactions on stoichiometric ultra thin MgO films we also study reactions catalyzed by Auₙₐ clusters adsorbed on relatively thick defect-poor MgO films supported on Mo, and on defect-rich thick MgO surfaces containing oxygen vacancy defects.

9:12AM Y37.00007 Role of anharmonic contributions for the elasticity of ice
MIRA Todorova, LARS ISMER, JÖRG NEUGEBAUER, Max-Planck-Institut fuer Eisenforschung GmbH, Duesseldorf — Water, one of the simplest molecules in chemistry, forms a liquid and solid phase with features essential to live and environment. Many of these can be attributed to hydrogen bonding, but that does not mean that they are fully understood. Ice should be an easier material to understand, because its molecules are arranged on a regular lattice. Yet even the determination of such basic properties as the bulk modulus and the elastic constants proves to be a challenge. Using first principles calculations we investigate the bulk properties of hexagonal ice. Our initial density-functional theory calculations (GGA-PBE level) yield values, which are much too high when compared to experiment. Even though the consideration of thermal effects within the quasi-harmonic approximation leads to a qualitative agreement between measured and calculated quantities, such as the linear expansion coefficient, ice remains much too hard. The large overestimation of the ice’ softness demonstrates the importance of anharmonic contributions, which will be shown to be crucial and lead to a dramatic reduction of the bulk modulus and the elastic constants.

9:24AM Y37.00008 An Assessment of Hubbard U Corrections on Manganese Oxide Clusters
ELISE Y. LI, Chemistry, Massachusetts Institute of Technology, DAVIDE CERESOLI, NICOLA MARZARI, DMSE, Massachusetts Institute of Technology — Conventional density-functional approaches often fail in offering an accurate description of the spin-resolved energetics in transition metal complexes, due to spurious self-interaction errors (SIE). Previous studies have shown that a self-consistent DFT + U approach [1] can accurately correct SIE in TM complexes, providing excellent agreement with high-level quantum chemistry calculations. In this work we report a systematic evaluation of DFT + U in a series of small manganese oxide clusters (MnOₙ, n =1-4) and their anions, focusing on structural, electronic and magnetic properties. It is found that DFT + U succeeds in systems where the valence electrons are essentially localized on the TM ion, but progressively worsens when the coordination number increases and more covalency comes into play between the TM center and neighboring atoms, pointing to the importance of choosing the appropriate correlated manifold when Hubbard corrections are added. [1] H. J. Kulik, M. Cococcioni, D. A. Scherlis, and N. Marzari, Phys. Rev. Lett., 2006, 97, 103001.

9:36AM Y37.00009 ABSTRACT WITHDRAWN
9:48AM Y37.00010 Advances in a Joint Density-Functional Theory for Electronic Systems in Contact with Liquid Water: A New Form of Density Functional for Water — JOHANNES LISCHNER, TOMAS ARIAS, Cornell University — We present a framework for studying complex electronic systems, such as biological molecules or electrochemical interfaces, that are dissolved in liquid water. The key ingredient, that renders calculations possible, is the usage of an approximate, yet accurate “classical” density-functional theory, while the electronic system is described by traditional Kohn-Sham theory. The electronic system (e.g. biosolute) is then coupled to the aqueous environment via molecular pseudopotentials. Here, we present a new form of “classical” density functional for water which is the first to properly account for the structure of the molecule in an exact way. We accomplish this by writing the free energy in terms of three effective potentials, one for the oxygen and one for each hydrogen atom, in which fictitious non-interacting water molecules move. In this talk, we will show that the resulting functional correctly reproduces the following properties of water: the linear and nonlinear dielectric response, the site-site correlation functions, the surface tension, the bulk modulus of the liquid and its variation with pressure, the density of the liquid and the vapor phases, and their coexistence.

10:00AM Y37.00011 The AM05 density functional applied to the water molecule, dimer, and bulk liquid — ANN E. MATTSSON, THOMAS R. MATTSSON, Sandia National Labs — We show that the AM05 exchange-correlation density functional (Armiento and Mattsson, Phys. Rev. B 72, 085108 (2005)) yields a H2O dimer binding energy of 4.9 kcal/mol. The result is thus within 0.15 kcal/mol of CCSD(T) level theory (5.02 ± 0.05 kcal/mol). We compare the AM05 results with those of five other functionals: LDA, PBE, PBEsol, RPBE, and BLYP. For liquid water, AM05 yields an O-O pair correlation function that is more structured than the ones of PBE and BLYP, which, in turn, are more structured than the one of RPBE. However, LDA and PBEsol yields more structured water than AM05. We confirm that accuracy in the water dimer binding energy is not a strong indicator for the fidelity of the resulting structure of liquid water. We will also report on the performance of AM05 for other systems and discuss the sub-system functional scheme used in the construction of AM05. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:12AM Y37.00012 Heat capacities of aluminum clusters — ANNE STARACE, BAO-PENG CAO, OSCAR JUDD, MARTIN JARROLD, Indiana University-Bloomington — Clusters of certain elements are known to undergo phase transitions from solid-like to liquid-like states. Aluminum clusters have emerged as a model system for metal cluster phase transitions [1]. We report here the measurement of heat capacities of cationic clusters containing 84 to 127 Al atoms using a multi-collision induced dissociation mass spectrometry method [2]. We find two major changes in the heat capacities with increasing cluster size: (1) the fluctuations in the temperature of the phase transition vary more smoothly and (2) the peaks in heat capacity become sharper. Furthermore, we have found a range of cluster sizes (115-117 atoms) that contain two distinct peaks, separated by baseline, in their heat capacities. The origin of the extra peaks in the heat capacity, which is suspected to be due either to a pre-melting transition or to a solid-to-solid transition prior to the melting transition, will be further investigated by means of annealing experiments. The current work extends prior work on singly charged Al cluster cations having 16-83 atoms [2, 3]. [1] Breaux, G. A.; Neal, C. M.; Cao, B.; Jarrold, M. F. Physical Review Letters 2005, 94. [2] Neal, C. M.; Starace, A. K.; Jarrold, M. F. Journal of the American Society for Mass Spectrometry 2007, 18, 74-81. [3] Neal, C. M.; Jarrold, A. K.; Jarrold, M. F. Physical Review B 2007, 76. [4] This work is supported by NSF.

10:24AM Y37.00013 From Atomic Clusters towards Nano-Materials with Controlled properties — S.N. KHANNA, M.C. QIAN, A.C. REBER, J.U. REVELES, R. ROBLES, P.A. CLAYBORNE, S.V. ONG, K. CASALENUOVO, Virginia Commonwealth University, A.W. CASTLEMAN JR., A. SEN, P.W. WEISS, H. SAAVEDRA, A. UGRINOV, N. CHAIK, Pennsylvania State University — One pathway towards the synthesis of nanomaterials with controllable properties is to assemble solids using chosen clusters as the building blocks. The talk will outline a new protocol that enables synthesis of nanomaterials from clusters and highlight how the character of the cluster emerges in the assembled material. Through studies on assemblies involving polyvalent anions As7− and As11− and alkali based cations, we will show how the studies can provide novel ways of controlling the bandgap through energy level of the counterion and the degree of charge transfer. The theoretical predictions will be compared with experimental findings.

The authors are grateful to the Army Research Office for supporting this work through a MURI grant (Grant # W911NF-06-1-0280).

Friday, March 20, 2009 8:00AM - 11:00AM — Session Y38 DCP: Surfaces, Interfaces, and Colloids 410

8:00AM Y38.00001 Aqueous Solutions on Silica Surfaces: Structure and Dynamics from Simulations — ALBERTO STRIOLO, DIMITRIOS ARGYRIS, NAGA RAJESH TUMMALA, University of Oklahoma, MOLECULAR SCIENCE AND ENGINEERING AT OU I-TEAM — Our group is interested in understanding the properties of aqueous electrolyte solutions at interfaces. The fundamental questions we seek to answer include: (A) how does a solid structure perturb interfacial water? (B) How far from the solid does this perturbation persist? (C) What is the rate of water reorientation and exchange in the perturbed layer? (D) What happens in the presence of simple electrolytes? To address such topics we implemented atomistic molecular dynamics simulations. Recent results for water and simple electrolytes near silicon dioxide surfaces of various degrees of hydroxylation will be presented. The data suggest the formation of a layered aqueous structure near the interface. The density profile of interfacial water seems to dictate the density profiles of aqueous solutions containing NaCl, CaCl2, CsCl, and SrCl2 near the solid surfaces. These results suggest that ion-ion and ion-water correlations are extremely important factors that should be considered when it is desired to predict the distribution of electrolytes near a charged surface. Our results will benefit a number of practical applications including water desalination, exploitation of the oil shale in the Green River Basin, nuclear waste sites remediation, and design of nanofluidic devices.

1Department of Energy

8:12AM Y38.00002 Formation of Organic Peroxides and Ethers at Post-Discharge Plasma Plume-Liquid Interfaces — MILAN BEGLIARBEKOV, STEVEN KOTOWICH, VLADIMIR TARNOVSKY, Stevans Institute of Technology — A direct current (DC) micro-hollow cathode plasma source operating in a mixed glow-streamer regime was used to generate an atmospheric pressure N2 discharge. The post-discharge plume / afterglow was interfaced with a target liquid-phase solution, and caused a change in the chemistry of the target solution. In the present work we study the interaction of an N2 plume with a mixture of 2-methyl-1-propanol and hexane, which results in the formation of organic peroxides and ethers at the plume-liquid interface. The presence of the peroxide and ether functional groups is established by 1H-NMR, FTIR, and Raman spectra of the reaction products. Fast Atom Bombardment (FAB) mass spectrometry is also used to further characterize the reaction products.
Deducing 2D Crystal Structure at the Solid/Liquid Interface with Atomic Resolution by Combined STM and SFG Study

8:24 AM Y38.00003 ARTHUR MCCLELLAND, University of Michigan, Applied Physics Program, SEOKHOON AHN, ADAM J. MATZGER, ZHAN CHEN, University of Michigan, Chemistry Department — Supplemented by computed models, Scanning Tunneling Microscopy (STM) can provide detailed structure of 2D crystals formed at the liquid/solid interface with atomic resolution. However, some structural information such as functional group orientations in such 2D crystals needs to be tested experimentally to ensure the accuracy of the deduced structures. Due to the limited sensitivity, many other experimental techniques such as Raman and infrared spectroscopy have not been allowed to provide such structural information of 2D crystals. Here we showed that Sum Frequency Generation Vibrational Spectroscopy (SFG) can measure average orientation of functional groups in such 2D crystals, or physorbed monolayers, providing key experimental data to aid in the modeling and interpretation of the STM images. The usefulness of combining these two techniques is demonstrated with a phthalocyanine monolayer formed at the 1-phenyloctane/highly oriented pyrolytic graphite (HOPG) interface. The spatial orientation of the ester C=O of the monolayer was successfully determined using SFG.

8:36 AM Y38.00004 William Irvine, Stefano Sacanna, Yaël Rohchman, Andrew Hollingsworth, Mark Elesesser, Center for Soft Matter Research, New York University, Mark Bowick, Physics Department, Syracuse University, David Grier, Paul Chaikin, Center for Soft Matter Research, New York University — We study two-dimensional crystallography on a curved oil-water interface. Charged hydrophobic (PMMA) colloids in an oil phase (cyclohexyl bromide) are attracted, without wetting, by image charge effects to an oil-water interface. The micron size spheres form a monolayer on the interface and interact via screened coulomb interactions to form a crystalline lattice. We create a curved oil-water interface by controlling wetting conditions between a water droplet and a substrate or support, to produce interfaces of both constant and varying gaussian curvature with boundary. We simultaneously image and manipulate the flat crystal on the curved surface using a setup capable of simultaneous holographic optical tweezing and confocal imaging. We study the resulting dynamics of topological defects.

8:48 AM Y38.00005 Francisco A. Fernandez-Lima, Veronica Pinnick, Michael Eller, Stanislav Verkhoutourov, Emille Schweikert, Texas A&M University — In an effort to increase the secondary molecular ion signal under ion bombardment, a series of cluster sources have been developed with sputtering yields that deviate from the linear cascade prediction due to the collective cluster beam - surface interaction. In the present talk, the variation of the massive gold Au$_{10}^+$ projectile size (n=1-400) and velocity on the interaction volume and number of desorbed/sputtered particles per impact will be discussed for alkali halide targets. As the projectile size increases, a larger number of clusters $N_{clus}$ is observed, where the secondary ion yield can be described as a decreasing exponential function of the cluster size. Theoretical ab initio calculations show that the relative MS abundences are related to the cluster structure stabilities, defined by a “life” ratio of short and long range interactions between the cluster counterparts. Angular distribution measurements of the secondary ions suggest that under keV bombardment emission normal to the target surface is favored, independent of the cluster ion size. Applications of the massive gold Au$_{10}^+$ projectiles as nanometric imaging probes (<10$^4$ nm$^2$) will be presented.

9:00 AM Y38.00006 Michael Rohlfing, University of Osnabrueck, Thomas Bredow, University of Bonn — We discuss the physisorption of atoms (xenon) and molecules (PTCDI) to a noble-metal surface (silver) within a first-principles approach, focusing on the adsorption energy as a function of distance. Instead of density-functional theory (which fails to describe physisorption) we employ a combination of exact exchange and correlation energies, which we evaluate within the adiabatic-connection fluctuation-dissipation theorem. Correlation accounts for non-local dispersion energy, which is crucial in the present cases. At large distance $Z$ from the surface the correlation causes van der Waals attraction with a characteristic $-C_6/(Z^6)$ asymptotic form. At closer distance the attraction deviates from the asymptotic form, in combination with the repulsive exact-exchange energy, yields an equilibrium of xenon and of PTCDI on the Ag(111) surface in close agreement with experiment.

9:12 AM Y38.00007 Geoffrey Stenuit, CNR-INFM DEMOCRITOS Theory@Elettra Group, Sincrotrone Trieste, in Area Science Park, I-34012 Basovizza (Trieste), Italy, Oksana Plekan, Vitality Feyter, Kevin Prince, Sincrotrone Trieste, in Area Science Park, I-34012 Basovizza (Trieste), Italy — We present a density functional study of the adsorption of adenine molecules on the Cu(110) surface. In agreement with experimental core level photoemission and x-ray absorption data, our calculations predict the existence of two phases: a parallel one at low coverage and a perpendicular one at high coverage. These findings resolve contradictions between calculated geometries and published vibrational spectra, and illustrate the complexity of the interaction between a relatively simple bio-molecule and a metal.

9:24 AM Y38.00008 Bonding of adenine on Cu(110)

9:36 AM Y38.00009 Two-photon photoemission spectroscopy of thiophene/Au(111)

9:48 AM Y38.00010 Interfacial Structure imaging of Pentacene/Si(111) by model- independent method

This work is supported by the US Department of Energy, Office of Basic Energy Science, Division of chemical sciences under contract DE-AC02-98CH10886.

The electronic structure of thiophene adsorbed on Au(111) is investigated by two-photon photoemission (2PPE) spectroscopy and density functional theory (DFT) calculations. The adsorption of thiophene lowers the work function from 5.50 eV for clean Au(111) to 4.62 eV for Au(111) exposed to 4.0 L thiophene, due to the electron donation from the thiophene to the substrate. With thiophene adsorbed on Au(111), the surface state of Au(111) attenuates and a localized $\pi^*$ state is attributed to the $\sigma^*$ antibonding orbital of a Au-S bond and is evidence of an orientational phase transition of adsorbed thiophene. Preliminary 2PPE results will also be presented for aromatic molecules bound to the Au surface via sulfur or other functional groups (e.g., isocyanide).

9:48 AM Y38.00009 Two-photon photoemission spectroscopy of thiophene/Au(111). $^1$ Jing Zhou, Chemistry Department, Stony Brook University, Stony Brook, NY 11794, Nicholas Camillone, Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, Michael White, Chemistry Department, Stony Brook University & Chemistry Department, Brookhaven National Laboratory — The electronic structure of thiophene adsorbed on Au(111) is investigated by two-photon photoemission (2PPE) spectroscopy and density functional theory (DFT) calculations. The adsorption of thiophene lowers the work function from 5.50 eV for clean Au(111) to 4.62 eV for Au(111) exposed to 4.0 L thiophene, due to the electron donation from the thiophene to the substrate. With thiophene adsorbed on Au(111), the surface state of Au(111) attenuates and a localized $\pi^*$ starts to form with increasing thiophene exposure on Au(111). This $\pi^*$ state is attributed to the $\sigma^*$ antibonding orbital of a Au-S bond and is evidence of an orientational phase transition of adsorbed thiophene. Preliminary 2PPE results will also be presented for aromatic molecules bound to the Au surface via sulfur or other functional groups (e.g., isocyanide).

$^1$This work is supported by the US Department of Energy, Office of Basic Energy Science, Division of chemical sciences under contract DE-AC02-98CH10886.
10:00AM Y38.00011 Optical Trapping of Colloidal Nanoparticles by a Weakly Focused Laser Beam , CHUN-YU LIN, HSIA-YU LIN, Lehigh University, SHEAN-JEN CHEN, STEVEN M.T. WEI, H.D. OU-YANG, Lehigh University — We present an analysis of the behavior of an ensemble of colloidal nanoparticles in the focal region of a weakly focused laser beam. Using a mechanical balance of the laser radiation pressure that causes particle migration into the light field and the osmotic pressure of these particles opposing migration, we propose a new method for quantifying the optical trapping potential of individual particles by measuring the increase of the particle concentration as a function of the laser intensity. We find comparable results for the optical trapping potential from this method with values obtained by single particle trapping methods, indicating that radiation-induced particle convection from a weakly focused laser beam does not affect the steady state distribution of the particles in the light field.

10:12AM Y38.00012 Colloidal Crosstalk: Brownian Diffusion of Hydrodynamically Coupled Colloids , STEPHEN ANTHONY, University of Illinois, MINSU KIM, UC San Diego, STEVE GRANICK, University of Illinois — Except at dilute concentrations, the Stokes-Einstein Equation inadequately describes the thermal motion of colloids, due to hydrodynamic interactions between nearby particles. Using single-particle tracking, the rotational and translational motion of hydrodynamically interacting colloids is observed, and deviations from the Stokes-Einstein Equation are readily apparent. The thermal motion of nearby colloids is found to couple in a non-additive fashion, with increasing degrees of non-linearity as particle separation decreases. Similar coupling is observed for colloids near surfaces.

10:24AM Y38.00013 Depletion-Driven Selective Optical Trapping in Nanoparticle Suspensions , YI HU, JOSEPH JUNIO, H.D. OU-YANG, Lehigh University — We report results of an optical trapping study that demonstrates the effects of size-asymmetric particles in suspension on optical trapping efficiency. Using a model colloid system with selective fluorescent dying and particle sizing, we show that the trapping efficiency of nanoparticles can be effectively tuned by adding different sized particles, promoting the use of optical trapping for particle sorting. A variable power IR laser coupled into a high NA objective was used for trapping. For particle detection, we used a 532nm excitation laser aligned to be parfocal with the IR trapping beam through the same objective lens. Fluorescent signals emanating from the focal region common to both beams was band-passed to create a pinhole set to be conjugate to the focal region for confocal detection. In a system composed of 160nm and 63nm particles we demonstrated the synergistic effect of size mixing. Experimental results are also shown for fluorescent particles being driven out of the region by size selective trapping of undyed 160nm particles.

10:36AM Y38.00014 Colloid diffusion on phospholipid membranes is anomalous , BO WANG, STEPHEN ANTHONY, SUNG CHUL BAE, STEVE GRANICK, University of Illinois, Urbana-Champaign — We demonstrate experimentally a simple system in which mean-squared displacement is proportional to time yet the distribution function of displacement probability is exponential, not Gaussian as expected for a classical random walk. This is the case of fluorescent submicron-sized beads that diffuse in one dimension in the smooth potential presented by tubes composed of phospholipid bilayer. A discussion of possible physical origins suggests that a family of physical systems whose few degrees of freedom couple to slow environmental fluctuations may behave analogously.

10:48AM Y38.00015 Determination of Charge Interactions of Nanoparticles by Optical Trapping , JOSEPH JUNIO, H.D. OU-YANG, Lehigh University — We report an experimental study of interactions in colloidal nanoparticles through optical trapping. Using an optical trap with a size much larger than the trapped particles, we were able to create an optical bottle to confine and concentrate the nanoparticles. We measured the highly focused light-induced particle density fluctuation with confocal fluorescent detection. A theory based on a balance between the optical trapping radiation pressure and the osmotic pressure has been developed to calculate the isothermal osmotic compressibility from the forced density fluctuation. The measured osmotic compressibilities of colloidal crystals are then used to determine the surface charge density of the colloidal particle. Comparison of the experimentally determined charge density is compared to that determined by zeta potential measurements. (1)S. Alexander, P. M. Chaikin, P. Grant, G. J. Morales, and P. Pincus, D. Hone, Charge renormalization, osmotic pressure, and bulk modulus of colloidal crystals: Theory, J. Chem. Phys. 80, 5776 (1984)
11:39 AM Z37.00003 Large electric dipole moments and even-odd effects observed in Bi clusters1, JOHN BOWLAN, ANTHONY LIANG, WALTER DE HEER, Georgia Institute of Technology — The electric and magnetic response of BiN2 (N=1-40) produced in a cryogenic molecular beam (15K-30K) shows that these clusters have large electric dipole moments as previously observed in ferroelectric Nb, V, and Ta clusters. The electric deflection profiles are measured as a function of size, field, and source temperature. Bi clusters exhibit the characteristic even-odd oscillations with even N showing an enhanced response. The clusters are paramagnetic but the odd-N clusters have enhanced susceptibilities. These results will be discussed and compared with other work done on low-dimensional bismuth nanostructures.

11:51 AM Z37.00004 Copper nanocluster growth at experimental conditions using temperature accelerated dynamics, C. S. DIAS, GCEP-Centro de Fisica da Universidade do Minho, Braga, Portugal. T-1 Group, MS B268, Los Alamos National Laboratory, Los Alamos, USA, A. F. VOTER, T-1 Group, MS B268, Los Alamos National Laboratory, Los Alamos, USA, — We study the dynamics of vapor phase cluster growth near experimental conditions of pressure at temperatures below 200K. To this end, we carried out temperature accelerated dynamics (TAD) simulations at different vapor pressures to characterize the morphology of the resulting nanoparticles, which leads to a range of values of the flux of impinging atoms at fixed vapor temperature. At typical experimental pressures of $10^{-3} - 10^{-4}$ bar TAD provides substantial boost over regular Molecular Dynamics (MD). TAD is also advantageous over MD, regarding the sampling of the network of visited states, which provides a deeper understanding of the evolution of the system. We characterize the growth of such clusters at different vapor pressures.

12:03 PM Z37.00005 Photoabsorption by Volume Plasmons in Metal Clusters1, CHUNRONG YIN, CHUNLEI XIA, VITALY KRESIN, University of Southern California — Metal clusters exhibit strong photoabsorption resonances in the visible part of the spectrum. These are collective “surface plasmon” excitations which have been extensively investigated. However, the UV part of the spectrum has remained rather unexplored. Some theoretical calculations have predicted that a measurable portion of the delocalized valence electrons’ dipole oscillator strength should be located in this region. This predicted absorption feature has been ascribed to a volume-plasmon type of excitation, which in small particles can couple to light, in contradistinction to the situation in bulk metals. We have carried out a photo-depletion cross section measurement on a pair of prototypical simple-metal nanoclusters, Na25 and Na42, finding that these systems indeed possess a broad volume-plasmon absorption peak centered at $\approx 4$ eV and having an oscillator strength contents of $\approx 15-20\%$ of the total, in good agreement with theoretical calculations. These spectra provide the first experimental confirmation of the existence of optically active volume-type collective electronic excitations in metal nanocluster particles.

1Supported by NSF.

12:15 PM Z37.00006 Atomic Dipole Moments and Polarizabilities of NaX Clusters, N= 2-30, 38, and 551, KOBLAR JACKSON, LI MA, Central Michigan University, Mount Pleasant, MI 48859, MINGLI YANG, Institute for Nanobiomedical Technology and Membrane Biology, West-China Medical School/West-China Hospital, Sichuan University, Chengdu, China, JULIUS JELLINEK, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne IL 60439, USA — The response of NaX clusters, N = 2 - 30, 38, and 55 to a static external electric field is studied using a new method that decomposes the total cluster dipole moment and polarizability into contributions from non-overlapping atomic volumes (Jackson et al., J. Chem. Phys. 129, 144309 (2008)). The atomic dipole moments and polarizabilities are in turn partitioned into local dipole and charge-transfer components, corresponding to dielectric and metallic responses, respectively. Analysis of the atomic polarizabilities indicates a strong dependence on the location of the atoms within the clusters and shows directly the effect of electrostatic screening in the clusters. We show that the relative importance of the charge-transfer component of the cluster polarizability increases with cluster size and approaches the bulk-limit on a per-atom basis for clusters as small as 20 atoms. The charge-transfer component is shown to be responsible for the structure/shape driven variations, and for shape-related anisotropies, in the cluster polarizabilities.

1This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, U. S. Department of Energy under grant number DE-FGO2-03ER15489.

12:27 PM Z37.00007 Magnetic Properties of Arsenic Cluster Assemblies1, MEICHUN QIAN, A. C. REBER, S. N. KHANNA, Dept. of Physics, Virginia Commonwealth University, A. SEN, S. MANDAL, N. K. CHAKI, Depts. of Chemistry and Physics, Penn. State University — Clusters have the potential to serve as building blocks of materials, enabling the tailoring of materials with novel properties. Recently, we synthesized a magnetic cluster assembled material using the ArS7 cluster and cryptated K, which are the elements from main group. X-ray studies show that the As cluster is distorted to accompany two cryptated K. We have investigated the magnetic properties of As cluster assembly using density functional theory. We found the ArS7 cluster has the (-2) valence state and possess one unpaired electron. The magnetic state is stabilized in the crystal and has a lower energy of 90 meV than the nonmagnetic state. The magnetic moments are located on the ArS7 cluster and display antiferromagnetic order in the crystal. We also study the magnetic properties of the As cluster assemblies with transition metal as a linker, and these findings are possible to provide a new kind of magnetic materials.

1Supports from US AFOSR, ARO and DOE.

12:39 PM Z37.00008 Interpreting the magnetic and electric deflections of free metal clusters in molecular beams, ANTHONY LIANG, JOHN BOWLAN, WALTER DE HEER — A short review of the analysis of magnetic and electric deflection data will be presented. Electric and magnetic beam deflection of several metal clusters, including AuN, AlN, NbN3O, NaN4, HoN, CoN, RhN at various temperatures (20K-300K) and field strengths will be presented. The relation between the broadening of the deflected beam and the polarization distribution of the ensemble assuming a classical polar spherical rigid rotor model is demonstrated. Complicating factors including asymmetry effects and residual temperature effects will be discussed.

12:51 PM Z37.00009 Comparative study of metal clusters by Quantum Monte Carlo method1, YUNING WU, HAI-PING CHENG, Quantum Theory Project, Department of Physics, University of Florida, PAUL KENT, CNMS, Oak Ridge National Lab — Lithium and sodium clusters have been studied by fixed-node diffusion quantum Monte Carlo method. This stochastic wave-function-based approach can provide more accurate results and serve as benchmarks against which other techniques may be compared. We studied the binding energies and investigate different geometries to decide the ground state. Our results are compared with those derived from other methods such as DFT and CI methods. Our objective is to validate current quantum Monte Carlo methods for small metal clusters that undergo size dependent geometrical transitions.

1Acknowledgment: DOE/BES DE-FG02-02ER45995: portion of this work at CNMS at ORNL, sponsored by Division of User Facilities, Office of Basic Energy Sciences, US Department of Energy.
the number and positions of the probe and target molecules. Details of their effects will be presented in the paper.

surface tension and strain energy. In this work, we use a molecular approach to describe the entire system. In particular, the solid beam is modeled as a collection of biosensors utilizing nano or micro-sized cantilevers. Through chemical coating of probe molecules that exhibit strong affinity to the target molecules, the cantilever would deflect when the target molecules bind with the probe molecules. Previous simulation studies on these systems often involved the use of a multi-scale approach in which molecular models are used for the probe and target molecules while the cantilever is modeled as a continuum solid beam using surface tension and strain energy. In this work, we use a molecular approach to describe the entire system. In particular, the solid beam is modeled as a collection of molecules connected by lattice springs. The intermolecular interactions between these three types of molecules (i.e., probe, target and cantilever molecules) are modeled using Lennard-Jones potentials. Our results show that the cantilever deflection depend on the combination of the Lennard-Jones parameters as well as the number and positions of the probe and target molecules. Details of their effects will be presented in the paper.

2:17PM Z37.00012 Origin of Structural Stability in Cubic ZrO2 Nanocrystals Studied by EXAFS

Y.L. SOO, S.L. CHANG, National Tsing Hua University, Taiwan, C.L. CHEUNG, R. SABIRIANOV, F. NAMAVAR, W.N. MEI, University of Nebraska, P. CHU, National Central University, Taiwan, J.F. LEE, NSRRC, Taiwan — Local environments surrounding Zr nanocrystalline powders and thin films of cubic zirconia prepared by sol-gel and ion beam assisted deposition (IBAD) methods were investigated by using extended x-ray absorption fine structure (EXAFS) technique. These materials have shown cubic long-range-order structure and high hardness without chemical stabilizers. To understand the origin of structural stability, the short-range-order local structural information obtained from EXAFS measurements is of central importance. Powder samples with different nanoparticle sizes prepared by different sol-gel processes were analyzed. Zr k-edge EXAFS, as well as N K-edge x-ray absorption near-edge structures (XANES), will also be presented to demonstrate the evolution of O vacancies and possible N impurities due to thermal annealing in the IBAD deposited films.

1This work has been supported by NSC in Taiwan.

Friday, March 20, 2009 11:15AM - 2:15PM – Session Z38 DCP: Surfaces, Interfaces, and Colloids II 410

11:15AM Z38.00001 Understanding surface energies of transition metals with density-functional theory

ALOYSIUS SOON, MARTIN FUCHS, MATTHIAS SCHEFFLER, Fritz-Haber-Institut der MPG — Determining index-specific surface energies of metals is, to date, still a non-trivial task, both experimentally and theoretically. Density-functional theory (DFT) calculations within the local-density approximation (LDA) for exchange-correlation (XC) have provided understanding of qualitative trends. Yet, absolute surface energies, in particular of f-elements still exhibit significant uncertainties related to the description of XC: gradient-corrected functionals (GGA) which improve over the LDA for other properties often predict less accurate surface energies. This calls for a careful analysis of XC effects on surface energies, including non-local exchange and/or correlation. Here we analyze the surface energies of 4d-metals with modern GGA functionals (PBEsol, AM05, developed to better describe bulk solids and (jellium) surfaces than the LDA and previous GAGs), using the all-electron FHI-aims code [1]. Relating the bulk cohesive energy and surface energy via a bond cutting model we find modern GAGs can indeed correct the poorer results of the usual PBE-GGA but worsen the bulk cohesive energies of 4d-metals. In addition, we consider hybrid XC functionals, using a cluster correction scheme [2], and discuss the effects of including exact exchange on the calculated surface energies.


11:27AM Z38.00002 The initial stages of NaCl dissolution: Ion or ion pair solvation?

JIRI KLIMES, ANGELOS MICHAELIDES, London Centre for Nanotechnology and Department of Chemistry, University College London — The interaction of water with rock salt (NaCl) is important in a wide variety of natural processes and human activities. A lot is known about NaCl dissolution at the macroscopic level but we do not yet have a detailed atomic scale picture of how salt crystals dissolve. Here we report an extensive series of density functional theory, forcefield and molecular dynamics studies of water clusters at flat and defective NaCl surfaces and NaCl clusters. The focus is on answering seemingly elementary questions such as how many water molecules are needed before it becomes favorable to extract an ion or a pair of ions from the crystal or the cluster. It turns out, however, that the answers to these questions are not so straightforward: below a certain number of water molecules (~12) solvation of individual ions is less costly and above this number solvation of ion pairs is favored. These results reveal a hitherto unknown complexity in the NaCl dissolution process born out of a subtle interplay between water-water and water-ion interactions.

11:39AM Z38.00003 Accelerated Molecular Dynamics of Temperature-Programmed Desorption

KRISTEN FICHTHORN, KELLY BECKER, MARIA MIGNOGLA, Penn State University — The most widely used experimental method for quantifying thermal desorption is temperature-programmed desorption (TPD). Despite its extensive use, interpretation of this experiment can still be controversial. A significant difficulty with interpreting TPD is that this macroscopic experiment offers a limited picture of the underlying microscopic kinetic events. In this work, we use accelerated molecular-dynamics to simulate TPD of n-pentane from the basal plane of graphite, in the first atomistic simulations to probe TPD over laboratory time scales. Although the simulated TPD spectra agree with experiment, a detailed analysis reveals underlying kinetic phenomena that contrast the standard experimental interpretation and opens new possibilities for understanding molecular kinetics at solid surfaces.

1Funded by NSF DMR 0514336
surface potential AFM measurements, however, reveal an apparently anomalous strong dependence of surface potential on the sizes and ratios of CH}\textsubscript{2} of the ionic aqueous solution is important not only for understanding many atmospheric and environmental chemistry processes, JINSUK SONG, MAHN KIM, Physics Department, KAIST — Knowing the interfacial composition for the electrostatic behavior of more complicated organic and biological systems.

contrast to the constant electrostatic potential observed in XPS measurements. Mechanisms underlying these effects will be discussed, with possible implications the proton adsorption, proton desorption, potassium adsorption, and potassium desorption rate coefficients were 45 liter/s equilibrium zeta potential depended on the logarithm of salt concentration, in agreement with a model based on ion exchange reactions. The average values of tion of surface reaction rate constants. The charging of mica in alkaline KCl solutions of arbitrary concentration, however, was too fast for observation. The charging of mica after immersion in water. The zeta potential of freshly-cleaved muscovite mica was recorded within seconds of immersion of Professor, Carnegie Mellon Univ — The advent of a new method for measuring the zeta potential of planar surfaces, the rotating disk, allowed the investigation Au With this in mind we have been investigating the electrostatic properties of simple model systems prepared from self-assembled alkanethiolate monolayers on interest in the use of polar molecules assembled at electrodes for tuning work functions and engineering charge injection barriers in organic electronic devices.

spectroscopy data we observe a consistent shift of the C 1s photoelectron kinetic energies between the top and bottom alkyl segments, defined as -(CH}\textsubscript{2}\textsuperscript{n}, and 0.14/s respectively. Web Page: http://zetaspin.com 1 National Science Foundation under grant CTS 0521719. 2 National Energy Technology Laboratory 12:51PM Z38.00004 Charge Interactions of Unilamellar Vesicles in Aqueous Suspensions . SEONGMIN PARK, KAIST, JOSEPH JUNIO, Lehigh University, MAHN-WON KIM, KAIST, H.D. OU-YANG, Lehigh University — This project reports the results of an experimental optical trapping study of the charge interactions between phosphor-lipid unilamellar vesicles. A 1064nm laser coupled into a high NA objective lens provided the optical trap. Using fluorescently labeled vesicles, we were able to monitor the particle number density by using a 532nm excitation beam aligned to be parfocal with the trapping beam through the same objective. Fluorescent signals from the focal region common to both beams were band-passed to a pinhole for confocal detection. Using the number density of the vesicles in the focal spot as a function of trapping intensity and a force balance model, we were able to calculate the effective trapping energy per vesicle as well as the osmotic virial coefficients for a system of lipid vesicles prepared with DOPG, cholesterol, and Dil. We measured the compressibility of these vesicle suspensions as a function of surface charge and ionic strength of the suspending medium. Compared to conventional scattering methods, this optical trapping method is advantageous, since it can be used for concentrated suspensions, yielding an in situ measurement of colloidal interactions.

12:03PM Z38.00005 Probing colloidal physics on the nanometer length scale . SUNIL SAINIS, Post Doc. Fellow, FRANK VOLLMER, Rowland Junior Fellow — The sharp spectral features associated with ultra-high Q microresonator modes are sensitive to changes in the local environment and surface of the resonator [1]. Microresonator cavities have been used to detect the binding of single molecules [2] and viruses in an aqueous medium. We report on recent experiments that use microresonators to access colloidal physics on the nanometer length scale. We examine shifts in the resonator as a function of bulk ionic strengths and surface adsorption in a colloid.

12:15PM Z38.00006 Effect of boundary condition on the viscosity of olefins: A molecular dynamics study . LING TI KONG, COLIN DENNISTON, MARTIN MUSER, University of Western Ontario, YUE QI, General Motor — The viscosity of hexene was examined by means of non-equilibrium molecular dynamics simulations under different wall-liquid boundary conditions, namely over-smooth wall, more or less realistic wall, and over-adhesive wall. It is found that the wall-liquid interaction plays an important role in the ordering/layering of liquid, and consequently affects the behavior of olefins upon different normal pressures. With the same moving speeds of walls, the shear-rate (the slope of velocity profile) in the liquid is found to decrease with the increasing of normal pressure under over-smooth wall condition, while it is found to increase under the over-adhesive wall condition. The viscosity, in turn, shows a linear dependence on the normal pressure under over-smooth condition while exhibits an exponential dependence under the over-adhesive wall condition. The underlying mechanism of these observations will be presented and discussed in this talk.

12:27PM Z38.00007 Suppressing and Amplifying Depletion Attractions between Surfaces Roughened by Asperities . KUN ZHAO, THOMAS MASON, UCLA — Motivated by recent experiments on roughness-controlled depletion attractions, we study the effect of roughness on depletion attractions between flat surfaces decorated using hemispherical and hemispheroidal asperities. Our calculations show that the depletion attraction between rough surfaces can be either dramatically reduced or amplified depending on the details of the surface morphology. This model also explains the observed self-assembly of rough Janus platelets into dimers and provides quantitative predictions of roughness-controlled depletion attractions for conditions that have not yet been explored experimentally.

12:39PM Z38.00008 The Dynamics of Charging of Muscovite Mica: Measurement and Modeling1 . PAUL J. SIDES, Professor, Carnegie Mellon Univ, DANISH FARUQUI, PhD Student, Carnegie Mellon University, ANDREW J. GELLMAN2, Professor, Carnegie Mellon Univ — The advent of a new method for measuring the zeta potential of planar surfaces, the rotating disk, allowed the investigation of the charging process of mica after immersion in water. The zeta potential of freshly-cleaved muscovite mica was recorded within seconds of immersion of the sample and in fractions of a second thereafter. The zeta potential of mica in water at pH = 5.6 with no added potassium changed by 40 – 50 mV over approximately a minute. A model of adsorption and desorption of potassium ions and protons captured this behavior and provided a framework for determination of surface reaction rate constants. The charging of mica in alkaline KCl solutions of arbitrary concentration, however, was too fast for observation. The equilibrium zeta potential depended on the logarithm of salt concentration, in agreement with a model based on ion exchange reactions. The average values of the proton adsorption, proton desorption, potassium adsorption, and potassium desorption rate coefficients were 45 liter/s ± 15, 0.0014/s ± 0.0006, 58 liter/s ± 5, and 0.14/s ± 0.03, respectively. Web Page: http://zetaspin.com

1 National Science Foundation under grant CTS 0521719. 2 National Energy Technology Laboratory 12:51PM Z38.00009 Effects of Embedded Dipoles on the Electrical Response of Self Assembled Monolayers . P.P. ZHANG, O.M. CABARCOS, T.A. DANIEL, P.S. WEISS, D.L. ALLARA, The Pennsylvania State University — There has been recent interest in the use of polar molecules assembled at electrodes for tuning work functions and engineering charge injection barriers in organic electronic devices. With this in mind we have been investigating the electrostatic properties of simple model systems prepared from self-assembled alkanethiolate monolayers on Au(111) with the incorporation of an embedded ester moiety [-(CO\textsubscript{2})\textsuperscript{n} = E] in the adsorbate molecules. The intrinsic static dipole moment of the ester moiety of ~1 Debye magnitude leads to the formation of a strong, highly organized, planar electric dipole layer in the SAM. From our previous X-ray photoelectron spectroscopy data we observe a consistent shift of the C 1s photoelectron kinetic energies between the top and bottom alkyl segments, defined as -(CH}_{2}\textsubscript{m}E-(CH}_{2}\textsubscript{n}CH\textsubscript{3}, regardless of the relative lengths m and n. This shift correlates well with the value of the electrostatic potential across the E layer. Our recent surface potential AFM measurements, however, reveal an apparently anomalous strong dependence of surface potential on the sizes and ratios of m and n, in contrast to the constant electrostatic potential observed in XPS measurements. Mechanism underlying these effects will be discussed, with possible implications for the electrostatic behavior of more complicated organic and biological systems.

1:03PM Z38.00010 Interfacial Composition of the Ionic Aqueous Solution Studied by the Adsorption of the Cationic Molecules . JINSUK SONG, MAHN KIM, Physics Department, KAIST — Knowing the interfacial composition of the ionic aqueous solution is important not only for understanding many atmospheric and environmental chemistry processes 1 but also for understanding many biological processes because the interaction between biomaterials happens often at the interfacial region such as water-vesicle interface in ionic aqueous solution. In this study, the surface anion density is estimated by measuring the surface density and adsorption angle of the cationic molecule, Malachite Green(MG) adsorbed at the air-ionics aqueous solution interface using the second harmonic generation technique. The anion number density at the interface increases with the increasing concentration of the ions and with the increasing size of the anions for spherical ions. It is consistent with other experimental measurements and simulation results2,3. However, it seems that the anion density depends not only on the anion but also on the cation and shape and chemical composition of the ions. 1 E. Knipping et al., Science 288, 301 (2000) 2 S. Ghosal et al., Science 307, 563 (2005) 3 P. Jungwirth et al., J. Phys. Chem. B 105, 10468 (2001)
Coverage Dependent X-ray Photoemission on Halogenated Benzene on Graphite

KEISUKE FUKUTANI, NING WU, University of Nebraska-Lincoln, PETER DOWBEN, University of Nebraska-Lincoln — We studied the adsorption of isomers of halogenated benzene on graphite. We found difference in the behavior of three different symmetry types, (1,2), (1,3), and (1,4), of diiodobenzene (C\(_6\)H\(_4\)I\(_2\)) and 1,4-bromodiiodobenzene (C\(_6\)H\(_4\)IBr) adsorbed on graphite surface at 95K by X-ray photoemission spectroscopy. Although the molecules are expected to be similar in their electronic structure, the sticking coefficients and the strength of screening effects are considerably different for the different isomers. We find evidence for different intermolecular interactions both in the initial state and in the final state as well. Symmetry, not simply the chemical constituents, play a role in adsorbate chemistry.

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Retardation of ice crystallization by short peptides

JUN SOO KIM, ARUN YETHIRAJ, Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin-Madison — The effect of short peptides on the growth of ice crystals is studied using molecular dynamics simulations. The simulations focus on two sequences (Gly-Pro-Ala-Gly and Gly-Gly-Ala-Gly) that are found in collagen hydrolysate, a substance that is known to retard crystal growth. In the absence of peptides, the growth of ice crystal in the solution with the ice/water interface is observed in at a rate comparable to the experimental data. When peptides are present in the liquid phase, the crystal growth is retarded to a significant extent compared to the pure water. It is found that Gly-Pro-Ala-Gly is more effective (crystallization is up to 5 times slower than in its absence) than Gly-Gly-Ala-Gly (up to 3 times slower) implying that the role of the proline residue is important. The mechanism can be understood in the nature of binding of the peptides to the growing crystal.

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AC Electrowetting of Polymer Aqueous Drops on Parallel Electrodes

LU ZHANG, NISHANT CHETWANI, HSUEH-CHIA CHANG, YINGXI ELAINE ZHU, Department of Chemical and Biomolecular Engineering, University of Notre Dame — We have recently observed the strong field dependence of AC-electrowetting of simple electrolyte aqueous drops on parallel gold electrodes, yet the detailed dynamic process of AC-field induced surface wetting remains unclear. In this work, we use fluorescence labeled DNA aqueous solution as a model system to directly visualize the wetting process of aqueous drops under varied AC electric fields by using combined fluorescence microscopy and contact angle goniometer. The electrowetting behavior of DNA aqueous drops is observed at AC-field frequency greater than the reciprocal of the RC time scale for electrode screening. And the onset of AC electrowetting is accompanied by the observed oscillation in drop contour shape and contact line. In addition, the ejection of nanodrops from the parent aqueous drop is observed when the threshold AC-field amplitude is exceeded. A scaling theory based on electrode interfacial screening is developed to quantify the AC-electrowetting behavior with the dependence of AC-field frequency, strength and medium conductivity.

ABSTRACT WITHDRAWN

Diverging Tolman’s length and asymmetric interfacial density profiles in near-critical fluids

MIKHAIL ANISIMOV, HEATHER ST. PIERRE, DEEPA SUBRAMANIAN, University of Maryland, College Park — The surface tension of a curved surface behaves differently than that of a planar surface; however, the curvature correction to the surface tension - known as Tolman’s length - is commonly ignored in practice. We show that asymmetric fluid phase equilibria result in diverging Tolman’s length at the critical point with the amplitude of the divergence depending on the degree of asymmetry in fluid phase coexistence. The divergence of Tolman’s length originates from the diverging critical fluctuations and does not exist in mean-field theories. However, the amplitude of this divergence (“intrinsic asymmetry”) can be obtained from an appropriate mean-field model. The asymmetry in phase equilibria is especially pronounced in ionic fluids and polymer solutions. In particular, Tolman’s length in polymer solutions may become as large as the thickness of the interface, thus playing a significant role in behavior of micro droplets and confined polymer fluids.

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