

# DIVISION OF PHYSICAL CHEMISTRY

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## The Conduction Band in Liquids and Disordered Solids

### Abstracts

**PHYS 125 [639914]: Electron tunneling resonances in water: signature of conduction band states?**

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Electron transmission through molecular layers is a sensitive probe of the electronic structure of such layers. Its most direct realization relevant to our present discussion is in "underwater" STM experiments. Indeed, the low tunneling barrier observed in electron tunneling through water may indicate the existence of a water "conduction band" substantially below vacuum energy. In this talk I will describe recent theoretical and numerical studies of electron tunneling through molecular layers. In particular, I will focus on several aspects of electron tunneling through water and on the origin of the observed low tunneling barrier in this system. The theoretical finding that electron tunneling through water is a resonance assisted process may provide an important clue regarding the nature of what is perceived as "conduction band" states in this system. The conditions under which such resonances are found and their manifestation in both the deep tunneling regime and near the tunnel barrier will be outlined. I will also discuss the timescale associated with such resonance tunneling processes and its implication for the possible involvement of water nuclear motion in electron transmission through this medium.

**PHYS 126 [638950]: Using photoelectron spectroscopy of hydrated electron clusters to characterize the conduction band of bulk water**

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Full lineshape analysis of the photoelectron spectra of hydrated electron clusters allows these spectra to be extrapolated to bulk. The results bear directly on the extent of electronic delocalization of bulk hydrated electrons, the energetic location of and access to the conduction band, as well as the value of  $V_o$ , the liquid electron affinity of bulk water. These results are assembled into a new energy diagram of bulk water that accounts for the rearrangement of solvent molecules about charge.

**PHYS 127 [643608]: Population-modulated electron attachment spectroscopy: A new way to measure size-selective properties of neutral clusters**

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Size-selected cluster techniques provide a powerful way to determine how the relaxation dynamics and energies of electronically excited states are correlated with network structure. Pure water has proven rather difficult to isolate in a size-selective manner, however, typically requiring difficult deflection methods followed by ionization and mass spectrometric detection. We describe a qualitatively different method where ionization is accomplished by soft electron attachment to a neutral cluster beam. We demonstrate that this can be done in such a way that the anionic cluster is directly and non-destructively traced to a particular neutral. We evaluate prospects for application of this method to map out both the neutral cluster geometries and their electronic states in the vacuum ultraviolet.

**PHYS 128 [643308]: High-pressure index of refraction measurements as a probe of electronic band structure**

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We have developed a new technique for tracking changes in electronic band gaps as a function of pressure in a diamond-anvil cell. We use the inner faces of the diamond anvils to form a Fabry-Perot interferometer, which allows us to measure the index of refraction of the sample as a function of wavelength (240-1000 nm), pressure (0-2 Mbar), and temperature (300-1200 K). The dispersion of the index of refraction is very sensitive to changes in electronic band structure, so we can map out the pressure-induced changes in the electronic band structure and use the temperature dependence of the dispersion to distinguish between direct and indirect band gaps. This technique can be applied to both ordered and disordered phases. We will present preliminary results on the evolution of the band gaps of water and ice, the pressure-induced metallization of solid xenon, and band gap changes in solid and fluid hydrogen.

**PHYS 129 [640675]: Probing the conduction band of disordered atomic and molecular solids with low energy electrons**

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The conduction band density of states (CBDOS) of a disordered solid can be investigated by injecting monoenergetic low-energy electrons into a thin film of the solid, condensed on a metal substrate held at cryogenic temperature in ultra-high vacuum. The number of electrons backscattered from the film, which have lost energy by creating phonons, are analysed as a function of incident electron energy. The excitation function thus obtained is directly proportional to the CBDOS. Results of such experiments will be provided for multilayer rare gas solid and amorphous ice films. The effects of electron resonances, impurities and electronic excitation on the CBDOS will be discussed

**PHYS 130 [643823]: Femtosecond studies of recombination dynamics in liquid water**

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Using femtosecond transient absorption spectroscopy we have investigated recombination processes in liquid water involving both electrons and protons. The new transient absorption spectrometer operates in the UV region from 190 to 400 nm where smaller and thus simpler molecules can be studied. The observed transport and relaxation phenomenas are closely related to the structure of liquid water and the talk will, inspired by the theme of the symposia, aim at relating the chemical processes observed to the dynamics (relaxation and recombination) of electrons in semiconductors.

**PHYS 137 [654650]: Charge injection and transport in molecular organic thin films: What this tells us about the energetics of organic semiconductors**

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Recent models relating to charge injection and transport across organic thin films are discussed. In particular, we focus our discussion on charge injection into organic light emitting devices and photoinduced charge transfer in both single heterojunction and bulk heterojunction solar cells to explore the nature of the energetics in organic materials. For example, we show that organic light emitting device properties are strongly influenced by the density of states at the organic/metal contact interface. Modification of these states, and their origins are considered in detail. Models of exciton transport across bulk and planar heterojunctions in organic solar cells also provide an ideal laboratory for the exploration of charge transport following excitonic photogeneration. These process are modeled and experimentally explored in this talk.

**PHYS 138 [643254]: Modeling the consequences of disorder on the photophysics of conjugated polymers: Do excitons and charges see the same disorder?**

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The amorphous nature of conjugated polymers influences both their photophysical and conductive properties. Our quantum chemistry techniques generate the energy landscape for motion of an exciton in a large disordered system, thereby connecting structural to energetic disorder. We have studied both inner-sphere disorder, arising from the polymer structure itself, and outer-sphere disorder, arising from the surroundings. The experimental change in dipole moment on excitation, which is zero for an ordered sample, allows us to quantify the degree of disorder seen by a photophysical excitation. Such measurements place limits on the characteristics of a random dipole field used to model environmental disorder. Others have used similar dipole fields to explain the field-effect mobility of charge carriers. We will consider the degree to which these two random dipole fields are in agreement, and thus whether a single model can account for both the photophysical and conductive effects of outer-sphere disorder.

**PHYS 139 [641504]: Interpolymer band dispersion in conjugated conducting polymers**

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The energy bands of conducting polymers are highly anisotropic. The bandwidth values perpendicular to the main path of delocalization involve transfer (hopping) integrals,  $t_2$ , that are small and are poorly understood both theoretically and experimentally. The values of these perpendicular transfer integrals affect to what extent band theory is applicable. We present Gaussian and plane wave basis set results using various forms of density functional theory and show that  $t_2$  converges as a function of the basis set size. Experimental validation of the converged transfer integrals will be presented. The variation of  $t_2$  as a function of the relative geometrical orientation of neighboring polymers is very significant also. Applications to large and small bandgap conjugated conducting polymers will be presented.

**PHYS 140 [644421]: Wavelength-resolved ultrafast pump-probe study of photoexcited polaron dynamics in conductive polyaniline**

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Wavelength-resolved ultrafast pump-probe and transient anisotropy methods have been used to study polaron dynamics of primary doped polyaniline in solution. The emeraldine salt form of polyaniline is excited by 800 nm pump pulse resonant with the polaron absorption and is probed from 650 nm to 1025 nm. Three distinct features are observed in the time-resolved transient spectrum: (1) early-time absorption near time zero in the 900 nm to 1025 nm region; (2) transient absorption at the probe wavelengths of 850 to 1025 nm with exponential decay of 10 ps time constant; (3) pronounced oscillatory components with frequencies of 165  $\text{cm}^{-1}$  and 210  $\text{cm}^{-1}$  at most probe wavelengths. The first two features originate from transitions to higher-lying states from the initially excited and conformationally changed intermediate states, respectively. The third is likely to reflect ground state modes, which agree well with recent Raman and IR data. Kinetic simulations were performed to establish a mechanism for the relaxation dynamics. Significant inhomogeneity and vibrational cooling is necessary to adequately model the data.

**PHYS 141 [644848]: Spin polarization mechanisms and optical properties of excess electrons in TiO<sub>2</sub> nanoparticles**

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Steady-state and time-resolved EPR experiments reveal that photoinduced charge separation in surface modified nanoparticles yields interacting electron/hole radical pairs with spectral features indicative of a range of dynamic properties. Fast exchange in the radical pair is indicated by the presence of a central line at the midpoint of electron and hole g-factors. Excess emission is consistent with the triplet character of the exciton precursor. A subset of electron-hole radical pairs exhibits the spin feature characteristic of Correlated Radical Pair Polarization reflecting a weak interaction between photogenerated holes and electrons. Excess electrons in nanocrystalline TiO<sub>2</sub> were studied in bare and dopamine-capped TiO<sub>2</sub> nanoparticles using electron-beam pulse radiolysis. Reaction of hydrated electrons results in injection of electrons into the conduction band of TiO<sub>2</sub> nanoparticles. Bare particles have shown two preferential optical transitions with energies in the visible region ( $\lambda_{\text{max}}=670$  nm and  $\lambda_{\text{max}}=900$  nm) indicative of presence of deep trapping sites. In contrast, optical absorption spectra of injected excess electrons in dopamine-capped nanoparticles display monotonic featureless wavelength dependence up to 1800 nm. The dependence of the

absorption coefficient on the wavelength does not show a characteristic exponential Drude behavior expected for free carrier absorption. This result suggests that the overall spectrum is a consequence of either (i) superposition of the multiple absorption features created from broad distribution of energies of shallow trapping states in disordered particles or (ii) superposition of free carriers and inter subband absorptions in indirect semiconductors.

**PHYS 142 [643302]: Conductivity in disordered solids: What can THz spectroscopy tell us?**

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Terahertz spectroscopy emerged about 14 years ago with the demonstration that nearly single cycle pulses of far-infrared (FIR) radiation could be generated, sent through free space, and subsequently detected in the time-domain. Since then, THz spectroscopy has become an active area with studies ranging from condensed matter physics to gas-phase spectroscopy to biomedical imaging. One of the most unique aspects of THz spectroscopy is that the pulses are of sub-picosecond duration, and it is possible to characterize the time-dependent ac conductivity in the FIR on a ultrafast timescales. That is, it is a non-contact electrical probe with sub-picosecond temporal resolution. We have applied TRTS to novel systems such as low-temperature grown GaAs, semiconductor quantum dots, and sintered colloidal TiO<sub>2</sub>. This talk will describe the transient photoconductivity in CdSe quantum dots and nanocrystalline TiO<sub>2</sub> as a function of size and morphology.

**PHYS 172 [644540]: Role of defect configuration in the excitation and ionization of condensed water**

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We have examined the dissociation and autoionization dynamics of low-temperature (80-180 K) water interfaces using quantum-resolved measurements of the neutrals desorbed during low-energy electron and ultraviolet/vacuum ultraviolet photon impact. The threshold energy for desorption and dissociation is  $6.3 \text{ eV} \pm 0.5 \text{ eV}$ . We correlate this energy with formation and decay of Frenkel-type excitons containing primarily  $1b_1^{(-1)}4a_1^{(1)}$  character. These excitons either dissociate or form trapped ion-pair states involving  $\text{H}_3\text{O}^+$  or  $\text{H}_5\text{O}_2^+$  and  $\text{OH}^-$ . The dissociation and ionization branching ratio and efficiency are examined as a function of phase, defect density, porosity and temperature. The increased yields with porosity and temperature are explained in terms of reduced perturbations of  $a_1$  character and the return of atomic p-character to the exciton.

**PHYS 173 [638983]: Excited states of solvated electrons**

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The electronic states characterizing solvated electrons in a number of environments will be discussed. These include bulk liquid water and methanol, as well as molecular clusters. The discussion will emphasize characteristics of the density of electronic states, as well as their time evolution in non-equilibrium cases. These characteristics include the existence of bound states, their energetic proximity to the onset of delocalized states, and the dependence of these features on solvent relaxation.

**PHYS 174 [644962]: Probing ionization in liquid water with 25fs resolution**

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Phase-matched four-wave mixing in gas-filled capillary waveguides, used as a new source for broad bandwidth ultraviolet pulses, opens up a variety of new capabilities for femtosecond transient absorption studies, in particular, generation of tunable ultrashort ( $\sim 25 \text{ fs}$ ) pulses in 218-300 nm range. This source has been first applied to the two-photon photophysics of liquid water. In combination with a very narrow stable water jet, pump-probe experiment employing, for example,  $2 \times 267 \text{ nm}$  (9.3 eV) as excitation and 400nm and 800nm probe pulses have been performed to probe the ionization channel near the onset of the conduction band. Results at a range of different excitation energies will be compared that span the transition from localized to delocalized excited state wavefunction of liquid water.

**PHYS 175 [644498]: Generation and thermalization of electrons in the liquid water conduction band**

**Robert A. Crowell**, Rui Lian, Ilya Shkrob, and Dimitri Oulianov, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439, Fax: 6302524993, rob\_crowell@anl.gov

The generation, thermalization, and geminate recombination of electrons injected  $\sim 3\text{eV}$  above the water band edge has been studied. A total excitation energy of  $12.4\text{eV}$  has been achieved using both  $2 \times 6.2\text{eV}$  and  $4 \times 3.1\text{eV}$  multi-photon absorption. Simulations of the picosecond geminate kinetics indicate a thermalization is the same in  $\text{H}_2\text{O}$  for both excitation methods while for  $\text{D}_2\text{O}$  the thermalization distance is larger for  $4 \times 3.1\text{eV}$  ionization. Initial interpretation suggests that an excited state of water may play a role in the  $2 \times 6.2\text{eV}$  process whereas for the  $4 \times 3.1\text{eV}$  process a nonvertical mechanism in which some of the photon energy is converted into kinetic energy of the electron in the conduction band is more likely. Relaxation of the conduction band electrons are being studied through the subpicosecond transient spectrum measured over the  $.5\text{-}1.7\mu\text{m}$ . Over this spectral region three forms of the pre-thermalized electrons are observed.

**PHYS 176 [672500]: Localized electrons in polar liquids and molten alkali metal-alkali halides: A femtosecond study**

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Solvated electrons in polar liquids are key intermediates in chemistry and biochemistry. The understanding of their optical response after excitation is of central importance. However, despite being first discovered as a metastable species in metal-ammonia solutions, the relaxation of solvated electrons has only been studied in polar liquids like water or alcohols. On the other hand, metal-molten salt solutions can be regarded as prototype systems to study the influence of topological disorder on the metal-nonmetal transition in condensed matter. One of the best studied examples are alkali metal-alkali halide melts.

Here, we present both the first femtosecond pump-probe studies of (i) solvated electrons in liquid  $\text{NH}_3$  and (ii) localized excess electrons in molten  $\text{KCl}$  at low metal concentrations at  $10^{-4}\text{ mol/l}$  for ammonia and  $10^{-2}\text{ mol/l}$  for molten  $\text{KCl}$ . The ultrafast near-infrared excitation of solvated electrons in liquid ammonia can be understood in terms of a simple temperature jump which red-shifts within our time resolution the electronic resonance into the mid-infrared spectral region. A subsequent blue-shift of the time-dependent absorption spectrum indicates the dynamics of electron "cooling" and occurs on a timescale of 200 fs with no significant isotope effect. This blue-shift is analogous to the solvated electron in water. Strongly localized electrons in molten  $\text{KCl}$  (F-centres) show a transient bleach with a decay time of  $(200 \pm 50)\text{ fs}$  that can be attributed to a hopping process in the electronic ground state. A transient absorption at longer wavelengths, that decays with the same time constant, is an indication of weakly localized electrons (Drude-type electrons). The dynamics of F-centres and Drude-type electrons are governed by the ionic motion of the alkali halide melt.

**PHYS 177 [647478]: Excess electrons in "other liquids"**

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I will address two pivotal questions: Why do some liquids yield solvated electrons upon ionization whereas other liquids, with quite similar properties, do not? And, In what form does the excess negative charge exist in liquids that do not yield these electrons? It will be shown that neither the electron affinity of the solvent nor the stability of molecular anions have much effect on the fate of the excess electron in a given liquid. The prevalent mode of electron stabilization is by the formation of a multimer anion in which the electron density is divided between several molecules. The solvated electron is an extreme case of such an anion; in fact, this idealized species may not exist. Several "unusual" modes of electron thermalization will be considered, including acetonitrile and supercritical carbon dioxide studied at Argonne. These systems illustrate that there are many different ways for the electron to stabilize in a liquid. What happens in water and alcohols is not representative of liquids (even polar liquids) as a class.

**PHYS 205 [636856]: Excited state relaxation and dynamics in organic light emitting diodes**

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The recombination of electron-hole pairs injected in extended conjugated systems is modeled as a multi-step internal conversion relaxation in a monoexcited electronic state-space mediated by electron-phonon coupling. The computed triplet-to-singlet ratio of exciton formation times  $r = \tau_t/\tau_s$  increases from 0.9 for a model dimer to 2.5 for a 32-unit chain, in excellent agreement with experiments. Therewith we rationalize recombination efficiency in terms of spin-dependent interstate vibronic coupling and spin- and conjugation-length-dependent exciton binding energies. We also rationalize the observed linear scaling relation between  $r$  and effective conjugation-length through a simple model consisting of vibronic relaxation through a density of states and the variation of correlation energy with chain length.

**PHYS 206 [641483]: Exciton and polaron dynamics in polymeric semiconductors: The influence of interchain order**

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We address the question posed in this symposium for disordered organic electronic materials by exploring polaron generation and recombination dynamics. We present combined results of femtosecond transient photoluminescence, femtosecond transient absorption, and quasi-steady-state photoinduced absorption spectroscopy on polymeric semiconductors. By control of interchain order via the choice of the side-chain substituents, we have investigated its effect on exciton and polaron dynamics in model electronic materials. We show that interfaces between ordered and disordered domains play a significant role in the photophysics. At high photoexcitation fluence, a high yield (~10%) of polarons is only observed in the ordered semiconductor. This process arises from two-step photoexcitation, first to the lowest exciton, and then to a high-energy state of opposite symmetry. In contrast, triplet exciton population is generated via sequential excitation with smaller yield (<1%) in both ordered and disordered materials. In the low fluence regime, triplet excitons are found to arise from evolution of polarons generated with low efficiency (also <1%) by diffusion-limited processes. The triplet generation yield is strongly dependent on order, with the disordered material displaying a higher yield. Polaron decay is found to be thermally activated, with a higher activation energy and lower room-temperature recombination rate in ordered materials.

**PHYS 207 [642615]: Photo-excitation in polyfluorene: Excitation density and probe wavelength dependent ultrafast pump-probe measurements**

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Excitation density and probe wavelength dependent ultrafast pump-probe measurements are used to characterize the excited state dynamics in pristine polyfluorene film and the photo-induced electron transfer dynamics in a polyfluorene/C60 blend. At low excitation densities, the initial excitation in pristine polyfluorene appears to be a neutral exciton. At high excitation densities, a secondary species is created at times delayed from the initial formation of excitons. We interpret the high excitation density results in terms of the generation of charge separated pairs via a two-step exciton-exciton annihilation process. In the polyfluorene/C60 blend, the decay of the neutral excited state and the growth of the ionic excited state have been time resolved. The photo-induced charge transfer reaction from polyfluorene to C60 occurs with a time constant of approximately 3 ps.

**PHYS 208 [644735]: Effects of aggregation and disorder on the electronic properties of materials used to make organic LED's**

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MEH-PPV and its structurally related oligomers are highly fluorescent conjugated species that have found applications in light-emitting diodes, electronics displays, and as analyte detectors. In order to optimize these materials for applications, a number of important photo-physical issues must be addressed. These include

determining how conformation, degree of aggregation, and aggregate morphology affect the emission properties of the system. Here we present some data on using total internal reflection fluorescence microscopy (TIRF) to compare the fluorescence properties of a variety of aggregate morphologies of PPV oligomers, formed by casting from different solvents, to the properties of isolated single molecules. In addition, Stark spectroscopy is used to characterize the degree of disorder via the measurement of non-zero difference dipole moments in nominally centrosymmetric structures. These results are modeled using semi-empirical calculation in a random solvent field to uncover the molecular source of the disorder.

**PHYS 209: The roles of localized states in electron transfer between molecular adsorbates and semiconductor nanoparticles**

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Interfacial charge transfer dynamics play important roles in many devices that are based on semiconductor nanomaterials, such as dye-sensitized nanocrystalline thin film solar cells and molecular electronics. In this paper we will discuss our recent effort in understanding the nature and role of localized semiconductor states in electron transfer dynamics between molecular adsorbates and semiconductor nanoparticles. Electron transfer dynamics in materials with different density of localized defect states are compared. We also compare electron transfer in molecule-to-nanoparticle charge transfer complex and its intramolecular analogue. The effect of charge delocalization on both electron recombination dynamics will be discussed.

**PHYS 210 [654652]: Real-time atomistic simulation of the ultrafast photoinduced electron transfer from molecular donors to the TiO<sub>2</sub> Acceptor**

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A non-adiabatic (NA) molecular dynamics (MD) simulation of the photoinduced electron transfer (ET) from molecular electron donors to the TiO<sub>2</sub> acceptor will be discussed. The systems under study are typical of the dye sensitized semiconductor nanomaterials used in solar cells, photocatalysis and photoelectrolysis. The electronic structure of the dye-semiconductor system and the adiabatic dynamics are simulated by ab initio density functional theory MD, while the NA effects are incorporated by the quantum-classical mean-field approach. The simulation provides a detailed picture of the ET process. For the systems under study, ET occurs on a 30fs time scale at low temperatures and within 5fs at room temperature, in agreement with the recent ultrafast experimental data. Both adiabatic and NA pathways for the ET are observed. The NA transfer dominates at short times and at low temperatures, and can occur due to strong localized avoided crossing as well as extended regions of weaker NA coupling. Adiabatic ET is the main mechanism at room temperature. The electron acceptor states are formed by the d-orbitals of Ti atoms of the semiconductor and are localized within the first 3-4 layers of the surface. About 20% of the acceptor state density is localized on a single Ti atom of the first surface layer. The simulation predicts a complex non-single-exponential time dependence of the ET process.

**PHYS 448 [639573]: S-state to conduction band spectrum of the hydrated electron**

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The s-state to conduction band (CB) absorption spectrum of the hydrated electron ( $e_{aq}^-$ ) has been determined by a multi-color photo-detrapping experiment. Photo-detrapping has been observed indirectly by monitoring the effect of photo-excitation of  $e_{aq}^-$  on the electron/hole spatial separation, which is inferred from the  $e_{aq}^-$ /hole geminate recombination kinetics following photoionization of neat water. The yield of photo-suppression of geminate recombination ( $Y_{PS}$ ) at 3.10 eV excitation has a high value of 0.92, corresponding to the 1-photon excitation of  $e_{aq}^-$  to the CB of water. The lower energy region of the spectrum (1.55 – 2.07 eV) shows a weaker but measurable  $Y_{PS}$  of ~ 0.18. The results indicate that photo-excitation between 1.55 and 3.10 eV induces migration of  $e_{aq}^-$  by at least 30 Å, involving the CB of water.

**PHYS 449 [639987]: The role of dispersion in the interaction of excess electrons with water clusters**  
**Kenneth D. Jordan**, Dept of Chemistry and Center for Molecular and Materials Simulations, University of Pittsburgh, Pittsburgh, PA 15260, Fax: 412-624-8611, jordan@pitt.edu

It has recently been established that dispersion interactions play an important role to the binding of an excess electron to water clusters. In this talk, the role of dispersion interactions in determining whether an excess electron prefers to be on the surface or interior of the cluster will be examined. In addition, the contribution of dispersion interactions to the excitation energies will be discussed.

**PHYS 450 [644996]: Mapping the conduction band under CTTS Transitions: the photodetachment quantum yield of sodide in THF**

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When small anions are placed in solution, states in the continuum above the gas-phase detachment threshold can be stabilized to below the vacuum level, resulting in strongly allowed charge-transfer-to-solvent (CTTS) bands. Excitation of CTTS bands results in detachment of the electron from the anion, producing a solvated neutral atom or molecule and a solvated electron. By measuring the photodetachment quantum yield for electrons detached from sodium anions in THF, we are able to map out the point at which detachment above the liquid continuum begins. The results suggest the presence of three distinct sub-bands underlying the CTTS absorption spectrum; excitation into the low-energy sub-bands produce solvated Na atom:solvated electron contact pairs, whereas excitation into the highest-energy band results in electron ejection out into the solvent, a hallmark of the conduction band. The ejection quantum yields compare favorably with photoconductivity measurements made on related alkali metal anions by Levanon and co-workers.

**PHYS 451 [672814]: Photoelectron spectroscopy of solute ions in water jets**

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The photoelectron spectrum of bulk liquid solutions is probed at the free vacuum surface of thin, micron size, water jets, using 40 eV to 120 eV tunable photon energy. This allows to cover outer- and inner- valence shell electron bound states of the neat solvent and to measure the vertical ionization energies of solvated anions and cations of simple salt solutions in an extended range of concentrations. The photoelectron spectral intensities can show elevated surface concentration of surface active solutes or ongoing solute reactions. In addition, observed weak secondary spectral peak structures of the neat liquid which seem not to correlate with gas phase features, tentatively, are attributed to water conductance band processes.

**PHYS 452 [644993]: Electron Photodetachment from aqueous halide ions via CTTS States and the bulk conduction band**

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Electron photodetachment from halide anions in aqueous solution has been systematically investigated as a function of excitation energy using femtosecond pump-probe spectroscopy. The excitation energies employed ranged from 4.7 eV to 8.3 eV, enabling us to excite each halide into its various CTTS states and/or the bulk conduction band. Excitation via one- and two-photon mechanisms is carefully verified. The ejection length as a function of detachment energy is mapped using the time-dependent geminate recombination profiles of the solvated electrons produced. The coupling to the bulk conduction band is observed as a higher escape probability of the ejected electron. In this way an action spectrum is generated - this is compared to bulk electronic structure calculations for the spectrum of vertical excited states of halide anions in water.

**PHYS 453 [635604]: Conduction band in nonpolar fluids**

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The existence of a band of states in which the electron is quite mobile and its wave-function is extended is common to all nonpolar liquids. The energy of the lowest state in this band relative to vacuum is designated  $V_0$ . Values of  $V_0$  for nonpolar molecular liquids range from +0.2 to -0.75 eV at room temperature, and  $V_0$  increases with increasing density. The value of  $V_0$  affects such phenomena as the mobility of electrons, the value of the work function of a metal immersed in the fluid, the ionization threshold of molecules in a fluid, and field ionization of Rydberg states of solutes. Consequently, studies of these phenomena provide ways of measuring  $V_0$ . Recent studies provide accurate values of the conduction edge in nonpolar liquids and some results of these studies will be discussed.

**PHYS 476 [637699]: Transition from delocalized states of electrons at interfaces to localized states**

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Femtosecond time and angle resolved two-photon photoemission studies have been used to study electron solvation and localization at interfaces and to directly probe the development of a two dimensional band structure at the interface. This offers a powerful technique for obtaining the electronic structure of the interface. In addition, the energy relaxation measured in the photoemission spectra of molecules adsorbed on metal surfaces is due to a reorientation of the molecular dipole moments in the presence of the excess electron. This dynamical energy shift is a measure of a two dimensional solvation energy that occurs on a timescale of ~200 fs and corresponds to a transition from a delocalized to a localized state. From the time dependence of the square amplitude of the localized electron's wave function in momentum space, the time dependence of the electron's spatial extent in real space can be directly determined.

**PHYS 477 [637314]: Atomically detailed description of metal-dielectric interfaces: The crossover from surface to bulk conducting properties**

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An atomically detailed simulation method designed to be efficacious for modeling conduction properties of closed shell atoms or molecules resident at interfaces that was developed earlier is applied to a metal-dielectric interface of Ag-Xe. The effective mass of conduction electrons resident at Ag-Xe interfaces as a function of the number of layers of xenon present has been measured experimentally by the Harris group at Berkeley. Here a simple yet effective theoretical model of the interface is developed and the effective mass that results is in quantitative agreement with the empirical measurements. The effective mass of a conduction electron is calculated by solving the Schrodinger-Bloch equation using Lanczos grid methods to obtain the Bloch wave vector dependent energies. The metal is treated as a continuum within the effective mass approximation for the purpose of calculating the eigenenergies. This approach shows promise in modeling the conduction properties of more complex interfacial environments.

**PHYS 478 [637967]: Electron-stimulated reactions at the interfaces of amorphous solid water films driven by long-range energy transfer from the bulk**

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The electron-stimulated production of  $D_2$  from amorphous solid  $D_2O$  deposited on Pt(111) is investigated as a function of film thickness. The  $D_2$  yield has two components with distinct reaction kinetics. Using isotopically layered films of  $H_2O$  and  $D_2O$  demonstrates that the  $D_2$  is produced in reactions that occur at both the Pt/amorphous solid water (ASW) interface and the ASW/vacuum interface, but not in the bulk. The *energy* for the reactions, however, is absorbed in the bulk of the films and electronic excitations migrate to the interfaces where they drive the reactions. A model based on the diffusion of electronic excitations to either interface accounts for the principle experimental observations.

**PHYS 479 [644140]: Chemical dynamics of low energy electrons**

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Low energy electrons are ubiquitous in the radiolysis, and the photolysis, of liquids, solids and interfaces. The cross-sections for low energy electrons are strongly dependent on the phase of the medium, for instance, there are differences that are orders of magnitude in size between gaseous and ice water. Stochastic simulations are being used to understand the energy loss properties of low energy electrons in liquids and solids and thereby elucidate their thermalization and physico-chemical properties. Stochastic track structure simulations have been used to determine the energy distribution of daughter low energy electrons produced by ionizing radiation in water. Preliminary calculations of the attenuation of low energy electrons in condensed water are in progress. These calculations have reproduced experimental EELS data for ice and been used to investigate capture of, and ionization and excitation by, low energy electrons. About 53% of low energy electrons are captured with energy greater than 1 eV, about 28% are captured with energy greater than 5 eV, and about 10% with energy between 5eV and 8 eV through a dissociative electron attachment process. The energy distribution of ionizations and excitations is independent of the incident electron energy, except as it affects the maximum energy. The energy distribution of electrons ejected following ionization events is determined by incident electron energy. These findings are of considerable import in determining the effects of low energy electrons (< 25 eV) in the determining radiation damage, for instance the ultra-fast formation of molecular hydrogen.

**PHYS 480 [642776]: Dynamics of photoinjected electrons in amorphous ice layers: Localization, solvation and the conduction band**

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Two-photon photoelectron spectroscopy (2PPE) is used to investigate femtosecond dynamics of electron localization and solvation in amorphous ice layers adsorbed on Cu(111). Electrons, optically excited in the metal, transfer into the conduction band of the ice layer and generate a feature  $e_{CB}$  in the angle-resolved 2PPE spectra. Electrons localize within the first 50 fs to form a state  $e_S$  at 2.9 eV above the Fermi energy. The binding energy of  $e_S$  increases by 270 meV/ps which is attributed to electron solvation. By separating  $e_S$  and  $e_{CB}$  the bottom of the conduction band in the ice layer is determined to occur 1.05 eV below the vacuum level with an effective mass close to the free electron mass. The solvated state  $e_S$  is characterized by an apparently negative dispersion described by an electron momentum distribution with width  $\Delta k_{||}$ . From model calculations we conclude that  $\Delta k_{||}$  changes simultaneously with electron solvation and is determined by the spatial extent of solvated electrons.

**PHYS 481 [644664]: Probing electrical conductivity in liquids and solids by THz time-domain spectroscopy**

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THz time-domain spectroscopy is a measurement scheme that uses ultrafast visible laser pulses to produce and characterize pulses of far-infrared radiation. The technique permits the determination of the complex conductivity of materials over a range of far-infrared (or THz) frequencies. Further, the method can be readily applied to probe non-equilibrium systems. We report here recent results for model liquids and insulating solids. Measurements in photoexcited n- and iso-hexane have provided a direct determination of the scattering time of quasi-free electrons, as well as of the dynamics of carrier recombination. These results will be compared with findings for model photoexcited crystalline insulators, such as sapphire. In these ordered systems, the scattering rate depends strongly on the sample temperature. This reflects scattering by phonons, rather than by the potential fluctuations present in a liquid. The influence of trap states in the liquid and solid samples will also be compared and contrasted.