CPP 33: Molecular Structure

Time: Thursday 15:00–16:45 Location: C 230

CPP 33.1 Thu 15:00 C 230

The structure of liquids studied by soft x-ray emission (XES) and absorption (XAS) spectroscopy — •M. Blum[1], O. Fuchs[1], M. Weigand[1], F. Maier[1], E. Umbach[1,2], L. Weinhardt[3], M. Bär[3], C. Heske[3], M. Zharnikov[4], Y. Zubavichus[4], M. Grunze[4], and J.D. Denlinger[5] — [1]Universität Würzburg, Experimentelle Physik — [2]Forschungszentrum Karlsruhe — [3]University of Nevada, Las Vegas — [4]Angew. Physikal. Chemie, Uni Heidelberg — [5]ALS, Berkeley

Recently, soft x-ray XES and XAS techniques have been employed to probe the electronic structure of liquids. Such experiments represent a technically challenging task, since they require a third-generation synchrotron source and a liquid cell with a thin window separating the liquid from ultra-high vacuum. XES is particularly elaborate in this respect, since it requires a high-efficiency grating spectrometer. With our flow-through liquid cell and a novel high-transmission, high-resolution x-ray spectrometer we have investigated the electronic structure of various liquids including H_2O, D_2O, NaOH, NaOD, acetic acid, amino acids, and various other aqueous solutions under well-defined and reproducible conditions. We will present 2-dimensional resonant inelastic x-ray scattering (RIXS) maps of these liquids, which give unprecedentedly detailed information on the electronic structure. The XES spectra of water show effects that can be correlated with molecular dynamics on the time scale of the core hole lifetime. Moreover, the maps of the aqueous solutions reveal subtle changes in the electronic structure which can be attributed to the influence of the hydration shell and the pH-value.

CPP 33.2 Thu 15:15 C 230

Dipole switching in extended molecular systems: Explicitly time-dependent configuration interaction simulations — •Tillmann Klamroth and Pascal Krause — Institut für Chemie, Theoretische Chemie, Universität Potsdam

We perform laser-driven charge transfer simulations for $Li\text{-}(Ph)_n\text{-}CN$ ($n = 1, 2, 3$) using the TD-CIS (Time-Dependent Configuration Interaction Singles)[1] approach. These molecules serve as systematically extendable model systems. The selectivity, and thus controllability, of an ultra-short laser-induced electronic excitation as a function of the molecular size is investigated. For example, such control may be needed if a small electronic molecular switch is embedded in a larger molecular device.

Using the TD-CIS method within the fixed nuclei approximation, ultra-short π-pulses are employed in order to induce a charge transfer transition. We show that for certain pulse widths the selectivity is lost mainly due to multi-photon transitions and dynamic polarizations of the molecules. The latter processes depends systematically on the molecular size, i.e. it gets more important for larger molecules.

[1] T. Klamroth, Phys. Rev. B 68, 245421 (2003); P. Krause, T. Klamroth, P. Saalfrank, J. Chem. Phys. 123, 074105 (2005); T. Klamroth, J. Chem. Phys.124, 144310 (2006).

CPP 33.3 Thu 15:30 C 230

"Phase"-Transitions in Amorphous Water — •Katrin Winkel[1], Michael S. Elsaesser[2], Erwin Mayer[1], and Thomas Loerting[1,2] — [1]Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck — [2]Institute of Physical Chemistry, University of Innsbruck

An understanding of the anomalies of water is closely linked to an understanding of the phase diagram of the metastable non-crystalline states of ice. Three distinct structural states of amorphous water are known, they are called low- (LDA), high- (HDA) and very high density amorphous ice (VHDA). In our present work decompression of VHDA from 1.1 GPa to 0.02 GPa at 140 K is studied by means of dilatometry and powder X-ray diffraction of quench-recovered states. It is shown that the three amorphous states of ice are reversibly connected to each other. However, while the downstroke VHDA–>e-HDA transition is apparently continuous, the e-HDA–>LDA transition takes place quasi-discontinuously. That is, two amorphous-amorphous transitions of a distinct nature are observed for the first time in a one-component system - a first-order like transition (e-HDA–>LDA) and a transition which is not first-order like but possibly of higher-order (VHDA–>e-HDA). VHDA and e-HDA are established as the most stable and limiting states in the course of the transition. We interpret our

results as evidence disfavouring the hypothesis of multiple first-order liquid-liquid transitions (and the option of a third critical point), but favouring a single first-order liquid-liquid transition (and the option of a second critical point).

CPP 33.4 Thu 15:45 C 230

Effect of compression rate on re-crystallization of hexagonal ice — •Marion Bauer[1], Erwin Mayer[1], and Thomas Loerting[2] — [1]Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck — [2]Institute of Physical Chemistry, University of Innsbruck

We studied the re-crystallization kinetics of ice upon compression under isothermal conditions (170 - 230 K) and characterized the recovered phases by powder X-ray diffraction at 80 K. A competition between crystallization to the thermodynamically stable and a metastable phase was found. The Ice Ih –> Ice II and the Ice Ih –> Ice III transitions are the two competing parallel reactions in the pressure range 0.2 - 0.4 GPa. Stable Ice II is formed at compression rates up to 0.01 GPa/min, predominantly metastable Ice III is formed at compression-rates exceeding 0.1 GPa/min and mixtures of Ice II and Ice III are formed at compression-rates in-between. That is, Ice Ih has two energetically similar ways of adapting the hydrogen bonded network as a reaction to the application of external pressure. Similarly, high density amorphous ice (HDA) shows two parallel ways of crystallization upon heating under isobaric conditions [1]. For both the compression-rate dependent case observed here and the heating-rate dependent case observed earlier [1], the stable ice polymorph shows a slower, albeit earlier growth compared to the metastable polymorph.

[1] Salzmann, Mayer, Hallbrucker, PCCP 6, 5156-5165 (2004).

CPP 33.5 Thu 16:00 C 230

Mixed Quantum-Classical Simulations of Optical Spectra: Pheophorbide-a Butanediamine Dendrimers in Ethanol — •Hui Zhu, Volkhard May, Steffen Hackbarth, and Beate Röder — Institut für physik, Humboldt-Universität zu Berlin, Newtonstraße 15, D-12489 Berlin, Germany

Linear absorbance and time-resolved luminescence spectra are calculated in combining an improved exciton model with classical path approximation npT-ensemble MD simulations [1,2]. The exciton model includes an excitonic coupling based on ab initio electronic structure calculations, single pheophorbide-a excitation energy fluctuations due to solvent dynamics and structure fluctuations of the whole dendrimeric complex, and a separate account for intra chromophore vibrations. All computed spectra are compared with measured data and reproduce the observed trends when increasing the number of included pheophorbide-a molecules from 4 to 32.

[1] H. Zhu, V. May, B. Röder, M. E. Madjet, and Th. Renger, Chem. Phys. Lett. 444 , 118(2007).

[2] H. Zhu, V. May, B. Röder, and Th. Renger, J. Chem. Phys. (submitted).

CPP 33.6 Thu 16:15 C 230

Exact Born-Oppenheimer decomposition of the many-body wavefunction for the complete system of electrons and nuclei — •Ali abedi[1], neepa t.maitra[2], and e.k.u gross[1] — [1]Institut fuer Theoretische Physik, Freie Universitaet Berlin, Arnimallee 14, D-14195 Berlin, Germany — [2]Department of Physics and Astronomy, Hunter College of the City University of New York, USA.

We propose a new set of equations to treat non-adiabatic couplings between electrons and nuclei. The key idea behind the equations is to rewrite the many-body wave-function as a Born-Oppenheimer-type product of the nuclear and electronic wave-function. From the variational principle, we deduce formally exact equations for them. The electronic back-reaction term in the nuclear equation is rigorously contained in a time-dependent vector potential. We illustrate the formalism by performing calculations on one-dimensional diatomic molecule for which the many-body Schr\"odinger equation can be solved numerically.

CPP 33.7 Thu 16:30 C 230

Exact and approximate forces in the diffusion Monte Carlo method — •A. Badinski and R. J. Needs — Theory of Condensed

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The problem of calculating accurate inter-atomic forces within the diffusion Monte Carlo (DMC) method has been a long-standing issue[1-3]. The DMC method is highly successful for calculating ground-state total energies of many-electron systems, but there is still a lack of an accurate and efficient way of calculating forces. Therefore, DMC calculations are usually performed using geometries obtained from either density-functional theory or conventional quantum chemistry methods, or from experiment. In this talk, we present exact expressions for DMC forces and give a practical scheme of estimating them[4]. Equilibrium geometries are derived from DMC forces and compared with those obtained from DMC potential energy curves. Results for four small molecules show that the equilibrium bond lengths obtained from the force and energy calculations are in very good agreement.

[1] C. Filippi, C. J. Umrigar, Phys. Rev. B **61**, 16291 (2000)
[2] R. Assaraf, M. Caffarel, J. Chem. Phys. **119**, 10536 (2003)
[3] A. Badinski, R. J. Needs, Phys. Rev. E **76**, 036707 (2007)
[4] A. Badinski, R. J. Needs, Phys. Rev. B (accepted for publication)