

MO 18: Molecular Dynamics

Time: Thursday 14:00–16:00

Location: V38.02

Invited Talk

MO 18.1 Thu 14:00 V38.02

Excited-states and nonadiabatic dynamics: unveiling mechanistic aspects of ultrafast photoprocesses in nucleobases — ●MARIO BARBATTI — Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany

After UV excitation, all five natural nucleobases composing our genetic code return to ground state without photon emission in the time scale of 1 ps. This ultrafast deactivation, which increases the photostability of the nucleobases, may have been one of the factors contributing to their selection among a number of other possibilities in early biotic history on Earth. In the last years, theoretical simulations along with time-dependent spectroscopy have worked to determine the excited-state mechanisms employed by these molecules in their ultrafast deactivation. In particular, semi-classical nonadiabatic dynamics simulations have revealed a complex scenario, where multiple different reaction pathways are in constant competition between them [1] and whose output is deeply dependent on details of potential-energy surfaces of each nucleobases [2]. In this contribution, the current state of this topic is reviewed and the strengths and limitations of the available theoretical methods to deal with these phenomena are critically appraised.

[1] M. Barbatti, A. J. A. Aquino, J. J. Szymczak, D. Nachtigallová, P. Hobza, and H. Lischka, *Proc. Natl. Acad. Sci. U. S. A.* **107**, 21453 (2010).

[2] M. Barbatti and S. Ullrich, *Phys. Chem. Chem. Phys.* **13**, 15492 (2011).

MO 18.2 Thu 14:30 V38.02

Improvements to the Instanton Method: Tunneling in Large Systems — ●JUDITH B. ROMMEL and JOHANNES KÄSTNER — Institute of Theoretical Chemistry, University of Stuttgart, Germany

Quantum tunneling of atoms has a major impact on chemical reactions, in particular on reactions including hydrogen transfers. The enzyme glutamate mutase catalyzes a radical reaction involving two hydrogen transfers. We found the hydrogen transfers to be rate limiting [1]. The experimentally found kinetic isotope effects ranging from 6 to 30 suggest hydrogen tunneling. An improved path-integral-based instanton approach is used to figure out how the enzyme modulates these effects. The calculation of tunneling rates and kinetic isotope effects in systems with several hundred degrees of freedom like enzymes requires to locate the instanton via an optimization. We found a quadratically converging Newton-Raphson method to be better than mode following methods. The tangent mode method, recently proposed by us, turned out to be the fall-back option [2]. A variable step size formulation of the instanton rate theory allows to distribute sampling points more evenly along the bounce. Therefore, less sampling points are necessary which significantly reduces the computational effort [3].

[1] J.B. Rommel, J. Kästner, *J. Am. Chem. Soc.*, **133**, 10195, 2011.

[2] J.B. Rommel, T.P.M. Goumans, J. Kästner, *J. Chem. Theory Comput.*, **7**, 690, 2011.

[3] J.B. Rommel, J. Kästner, *J. Chem. Phys.*, **134**, 84107, 2011.

MO 18.3 Thu 14:45 V38.02

Fragmentation of the protonated water dimer via non-adiabatic pathways after valence photoionization — ●ZHENG LI¹, ORIOL VENDRELL¹, and ROBIN SANTRA^{1,2} — ¹CFEL, DESY, Notkestr. 85, D-22607 Hamburg, Germany — ²Department of Physics, University of Hamburg, D-20355 Hamburg, Germany

The protonated water dimer, (H₂O)-H⁺-(H₂O), irradiated with the free-electron laser FLASH at DESY (90 eV), undergoes Coulomb-explosion after losing one of its valence electrons via photoionization[1]. The diversity of valence orbitals available for ionization and the large mobility of the central proton lead to increased complexity of its dynamics. The strong two-body dissociation channel H₅O₂⁺ → H₃O⁺ + H₂O⁺ + e⁻ prevails, yet fragmentation channels involving H⁺ and neutral fragments need to be experimentally identified. Because of the closely-lying outer valence orbitals and various conical intersections, non-adiabatic effects are presumably important for the overall dynamics. *Ab initio* potential energy surfaces for the three lowest dicationic states have been computed at the CASSCF(8,11)//Koopmans level. A regularized diabaticization scheme has been used to obtain a diabatic representation of the

Hamiltonian[2]. The quantum dynamics of the photofragmentation has been investigated using the multi-configuration time-dependent Hartree (MCTDH) method[3], the results unravel the underlying mechanism.

[1] L. Lammich *et al.*, *Phys. Rev. Lett.* **105**, 253003 (2010). [2] H. Koeppl *et al.*, *J. Chem. Phys.* **115**, 2377 (2001). [3] M. H. Beck *et al.*, *Physics Reports* **324**, 1 (2000).

MO 18.4 Thu 15:00 V38.02

Ultrafast Dynamics of Photoionized molecules — MOHAMED EL-AMINE MADJET¹, ORIOL VENDRELL¹, and ●ROBIN SANTRA^{1,2} — ¹Center for Free-Electron Laser Science, DESY, Germany — ²Department of Physics, University of Hamburg, Germany

Using a mixed quantum-classical approach, we investigated theoretically the dynamics of acetylene and ethylene after extreme ultraviolet (XUV) photoionization. For acetylene cations produced in the A²Σ_g⁺, we show that the decay of this state occurs via both ultrafast isomerization and non-radiative electronic relaxation [M.E.M. *et al.*, *Phys. Rev. Lett.*, in print (2011)]. We find a time-scale for hydrogen migration and electronic decay of about 60 fs, in good agreement with recent XUV-pump/XUV-probe time-resolved experiments on the same system [Y.H. Jiang, *et al.* *Phys. Rev. Lett.* **105**, 263002(2010)]. Moreover, we predict an efficient vibrational energy redistribution mechanism that quickly transfers excess energy from the isomerization coordinates to slower modes in a few hundred femtoseconds, leading to a partial regeneration of acetylene-like configurations. Preliminary results for ethylene cations will also be presented and discussed.

MO 18.5 Thu 15:15 V38.02

Multi reference perturbation theory for non-adiabatic on-the-fly molecular dynamics: implementation and benchmarking — ●SVEN OESTERLING, ARTUR NENOV, BENJAMIN P. FINGERHUT, and REGINA DE VIVIE-RIEDLE — Ludwig Maximilians Universität München, Department Chemie

Semiclassical on-the-fly dynamics provide a way to simulate molecular processes of moderate sized systems. Treating the nuclei classically, abolishes the need to precompute potential energy surfaces, and thus allows for a full dimensional treatment of the molecular degrees of freedom. The electronic properties are computed with quantum chemical methods, adequate for system-size and nature of the problem. Regarding excited states, major challenges are the accurate, yet cost efficient calculation of the electron correlation, and the precise description of non-adiabatic events. The complete active space perturbation theory (CASPT2) has been shown to resolve the correlation issue, yielding excitation energies close to experimental values.

We implemented an interface for the CASPT2 method, included in the Molpro quantum chemistry package, in the Newton-X dynamics package. As there are no analytical non-adiabatic coupling vectors available in common quantum chemistry programs, a numerical approach, suggested by Tao *et al.*, was used to compute the coupling. The implementation is benchmarked with ethylene, with additional focus on the relevance of Rydberg-states.

MO 18.6 Thu 15:30 V38.02

Surface hopping from accurate quantum-classical correspondence — ●SEBASTIAN MÖBIUS¹, SEBASTIAN WÜSTER¹, MILAN SINDELKA¹, ALEXANDER EISFELD^{1,2}, and JAN MICHAEL ROST¹ — ¹Max Planck Institute for physics of complex systems, Dresden, Germany — ²Department for Chemistry and Chemical Biology, Harvard University, Boston, USA

Mixed quantum-classical treatments of molecular dynamics are well established to study chemical reaction pathways or collision dynamics. The main idea is to evolve nuclear coordinates on classical trajectories, governed by Newton's equation of motion, and the electronic degrees of freedom fully quantum mechanical by Schroedinger's equation. In contrast to Ehrenfest methods, Tully presented a multi-trajectory surface hopping algorithm, which allows for non-adiabatic transitions between adiabatic eigenstates. This algorithm has been proven successful in various cases, studying collision dynamics. While the traditional derivation of the method arguably gives rise to only part of the non-adiabatic coupling terms in the Born-Oppenheimer separated Schroedinger equation, we present a more sophisticated approach

which can reproduce all couplings. Our crucial argument is that only hermitian operators ought to be replaced with a classical variable. We discuss model systems where the newly introduced terms are required in order to match the full quantum calculations. Our extensions of Tully's algorithm opens up new possibilities of application, like spin-orbit coupled systems, atomic Rydberg systems and multidimensional surface intersections (e.g conical intersections).

MO 18.7 Thu 15:45 V38.02

Semiclassical Wigner propagation as a numerical tool in molecular dynamics — ●SERGEI D. IVANOV^{1,2}, THOMAS DITTRICH³, and DOMINIK MARX¹ — ¹Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany — ²Present address: Quantum Dynamics Group, Institut für Physik, Universität Rostock, Rostock, Germany — ³Departamento de Física, Universidad Nacional de Colombia, Bogotá D.C., Colombia

The Wigner function constitutes a one-to-one representation of the

quantum mechanical density operator, including coherences. The state-of-the-art methods based on LSC-IVR readily reproduce static quantum effects already present in the initial state, whereas truly dynamical quantum effects that arise during the time evolution in the presence of nonlinear potentials remain outside reach. Major progress could be achieved through the insight that even quantum coherences can be time-evolved faithfully if the propagation is not based on single but on *pairs* of classical trajectories [1]. Here, we attempt to make an important step ahead towards employing semiclassical Wigner propagation in the molecular dynamics framework; that is to recast the successful grid-based formulation in [2,3] well-suited for low-dimensional problems, into a grid-free representation where all relevant dynamical quantities are evaluated directly as averages over trajectory ensembles.

[1] P. P. de M. Rios and A. M. Ozorio de Almeida., J. Phys. A: Math. Gen., 35:2609, 2002. [2] T. Dittrich and L. A. Pachón., Phys. Rev. Lett., 102:150401, 2009. [3] T. Dittrich, E. Gómez, and L. A. Pachón., J. Chem. Phys., 132:214102, 2010