

MO 20: Theory: Molecular Dynamics

Time: Thursday 14:30–16:45

Location: PH/SR106

Invited Talk

MO 20.1 Thu 14:30 PH/SR106

Controlling charge migration in molecules — ●ALEXANDER I. KULEFF — Theoretische Chemie, PCI, Universität Heidelberg

Exposing molecules to ultrashort laser pulses can trigger pure electron dynamics in the excited or ionized system. In the case of ionization, these dynamics may manifest as an ultrafast migration of the initially created hole-charge throughout the ionized molecule and were termed *charge migration* [1]. Charge migration is solely driven by electron correlation and appeared to be a rich phenomenon with many facets that are rather characteristic of the molecule studied [2]. All this increasingly attracts the attention of the scientific community from both theoretical and experimental sides. Due to the coupling between the electronic and the nuclear motion, the control over the pure electron dynamics offers the extremely interesting possibility to steer the succeeding chemical reactivity by predetermining the reaction outcome at a very early stage. A way to control the charge migration by appropriately tailored [3] femtosecond laser pulses will be presented and the consequences of the application of such a scheme will be discussed.

[1] L. S. Cederbaum and J. Zobeley, *Chem. Phys. Lett.* **307**, 205 (1999).

[2] A. I. Kuleff and L. S. Cederbaum, *J. Phys. B* **47**, 124002 (2014).

[3] N. V. Golubev and A. I. Kuleff, *Phys. Rev. A* **90**, 035401 (2014).

MO 20.2 Thu 15:00 PH/SR106

Dynamics of H_2^+ in intense laser fields: Full-dimensional approximate quantum-mechanical description of dissociation and ionization — ●TOBIAS FIEDLSCHUSTER, JAN HANDT, FRANK GROSSMANN, and RÜDIGER SCHMIDT — Technische Universität Dresden

So far, even for nature's simplest molecule H_2^+ , no exact quantum-mechanical description of the laser-induced dynamics (i. e., simultaneously including vibration, rotation, dissociation and ionization) has been achieved.

In this work, we present a full-dimensional approximate quantum-mechanical treatment. It is based on the extension of a recently developed ab-initio Born-Oppenheimer surface hopping approach (M. Fischer, J. Handt and R. Schmidt, *Phys. Rev. A* **90**, 012525 (2014), *ibid* 012526, *ibid* 012527) to hopping between Floquet surfaces.

The obtained results for dissociation and ionization are in very good agreement with recent experimental data (J. McKenna et al., *Phys. Rev. A* **85**, 023405 (2012)).

The extension of the method to many-electron molecules is discussed.

MO 20.3 Thu 15:15 PH/SR106

Influence of vibrations on the energy transfer in Fenna-Matthews-Olson complex — ●XIAOMENG LIU and OLIVER KÜHN — Institut für Physik, Universität Rostock, D-18051, Germany

We have numerically calculated the effect of vibrational modes on the exciton quantum coherence and energy transfer dynamics of the FMO complex, employing the experimental spectral density from Ref. [1]. The exciton Hamiltonian is restricted to the single excitation space of the seven site FMO model [2]. Particular emphasis is laid on the way, explicit vibrational motions are included. Here, one- (OPA) and two-particle approximations (TPA) are compared. The dynamics is analyzed by means of a Markovian quantum master equation [3]. We examined the influence of vibrations on the populations and coherences, for different values of the Huang-Rhys factor and the temperature. We found that decoherence and equilibration is faster in the TPA, where vibrational motion in the electronic ground state is included.

[1] Wendling, M. et al., *J. Phys. Chem. B* **104**, 5825(2000)

[2] Schmidt am Busch, M. et al., *J. Phys. Chem.* **2**, 93(2011)

[3] Kühn, O. et al., *Chem. Phys.* **204**, 99(1996)

MO 20.4 Thu 15:30 PH/SR106

Transition state spectroscopy of the [H,C,N] molecular system — ●GEORG CH. MELLAU^{1,2}, ROBERT W. FIELD², OLEG L. POLYANSKY^{3,4}, and ALEXANDRA A. KYUBERIS⁴ — ¹Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Germany — ²Department of Chemistry, MIT, Cambridge, MA, USA — ³Department of Physics and Astronomy, University College London, Gower St, London, UK — ⁴Institute of Applied Physics, Russian

Academy of Science, 46 Uljanov Street, Nizhny Novgorod, Russia

In this work we study the molecular eigenstates at the transition state of the $HCN \leftrightarrow HNC$ isomerization using our set of vibrationally assigned ab initio rovibrational eigenenergies. As the vibrational excitation energy approaches the isomerization barrier, the eigenstates show a vibrational angular momentum dependent Dixon-dip like trend [1], which correlates with the semiclassical pattern of the level spacings [2]. Based on this analysis, we can determine the proximity of an eigenstate to the effective isomerization barrier. The barrier proximal "saddle point states" are found to be highly localized in the bending coordinate at the saddle point. Our picture explains why the localization takes place not only for pure bending states but also at higher energies, exactly when the eigenenergies match the effective barrier height corresponding to the extra energy in the excited stretch. Saddle point localized states have been reported in [3]. [1] G. Ch. Mellau, *J. Chem. Phys.* **133**, 7164303 (2010) [2] J. Baraban et al., in prep. (2014) [3] J. R. Henderson et al. *J. Chem. Soc. Faraday Trans.* **88**, 328 (1992)

MO 20.5 Thu 15:45 PH/SR106

Evolving classical nuclei on a single time-dependent potential in electronic non-adiabatic processes — ●FEDERICA AGOSTINI¹, ALI ABEDI², YASUMITSU SUZUKI³, SEUNG KYU MIN¹, NEEPA T. MAITRA², and EBERHARD K. U. GROSS¹ — ¹Max-Planck-Institute of Microstructure Physics, Halle, Germany — ²Department of Physics and Astronomy, Hunter College and the Graduate Center of the City University of New York, USA — ³National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

The Born-Oppenheimer (BO) approximation allows us to visualize dynamical processes in molecular systems as a set of nuclei moving on a single potential energy surface representing the effect of the electrons in a given eigenstate. Yet, this is an approximation, and many interesting phenomena, such as vision or Joule heating in molecular junctions, take place in conditions beyond its range of validity. Nevertheless, the basic construct of the adiabatic treatment, the BO potentials, is employed to describe non-adiabatic processes, as the full problem is represented in terms of adiabatic states and transitions among them in regions of strong non-adiabatic coupling. But the concept of single potential energy is lost. An alternative point of view will be presented: a single, time-dependent, potential [1] arises from the exact factorization of the electron-nuclear wave function, providing the force [2, 3] that drives nuclear motion, also in non-adiabatic situations. [1] Abedi et al., *PRL* **110** 263001 (2013); [2] Agostini et al., *Mol. Phys.* **111** 3625 (2013); Agostini et al., *arXiv:1406.4667 [physics.chem-ph]* (2014); [3] Abedi et al., *EPL* **106** 33001 (2014); Agostini et al., accepted *JCP* (2014).

MO 20.6 Thu 16:00 PH/SR106

On-the-fly Parametrisation of the Frenkel Exciton Hamiltonian — ●PER-ARNO PLÖTZ and OLIVER KÜHN — Universität Rostock, D-18051, Germany

Electronic Excitation Energy transfer in molecular aggregates can be described by the Frenkel exciton approach [1]. Here the problem is separated into local transitions interacting via Coulomb Coupling. The presence of thermal fluctuations implies statistic sampling of these parameters. In a condensed phase this requires to take into account not only intramolecular vibrations and deformations but also solvent contributions.

An efficient method enabling such a description of molecular dynamics and energy transfer on the same footing is density-functional based tight-binding (DFTB). In this contribution we present the recently developed Tight-Binding-Frenkel-Exciton (TBFE) approach [2] and apply it to aggregates of chromophores like porphyrins or perylenes in different environments. This efficient method can provide the input for simulations of exciton dynamics spectroscopy.

[1] V. May and O. Kühn. *Charge and Energy Transfer Dynamics in Molecular Systems* (Wiley-VCH, Weinheim 2011)

[2] P.-A. Plötz, T. Niehaus, O. Kühn, *J. Chem. Phys.* **140**, 174101 (2014)

MO 20.7 Thu 16:15 PH/SR106

Ultrafast Energy Transfer from Solvent to Solute induced by Sub-picosecond Highly Intense THz Pulses — ●PANKAJ

KR. MISHRA^{1,2,3}, ORIOL VENDRELL^{1,3}, and ROBIN SANTRA^{1,2,3} —
¹Center for Free-Electron Laser Science, DESY, Hamburg, Germany —
²Department of Physics, University of Hamburg, Germany — ³Center
for Ultrafast Imaging, University of Hamburg, Germany

Liquid water is the single most important medium in which chemical and biological processes take place. The possibility to generate sub-ps and very intense THz pulses at free-electron lasers in full synchronization with the X-rays (XFEL) opens the possibility to time-resolved investigations of transient state of water and of molecular species dissolved in it. At low intensity, THz light couples to low energy collective modes of the liquid. Here, we investigated the response of liquid water to one and half cycle, 200 fs long THz pulses spectrally centered at about 100/cm (3 THz). The pulse with an intensity of about $5 \cdot 10^{12}$ W/cm² transfers the energy mostly to the translational and rotational modes of the water monomers in a small time-scale when the pulse is about to reach its peak. The intramolecular vibrational energy also follows them after tens of fs during the pulse. Water reaches to a quasi-equilibrium state which is gas like very hot liquid. We also investigated the response of Phenol molecule to such THz pulse in vapor phase and in liquid water environment. Here the single phenol doesn't gain energy due to such pump pulse. But the phenol in liquid water gains significant amount of energy due to strong collision of highly mobile water molecule.

MO 20.8 Thu 16:30 PH/SR106

Auger electron spectroscopy of liquid water: The role of intermolecular electronic relaxation and proton transfer —

•NIKOLAI V. KRYZHEVOI¹, PETR SLAVÍČEK², BERND WINTER³, and LORENZ S. CEDERBAUM¹ — ¹Theoretical Chemistry, University of

Heidelberg, Germany — ²Department of Physical Chemistry, Institute of Chemical Technology, Prague, Czech Republic — ³Joint Laboratory for Ultrafast Dynamics in Solutions and at Interfaces, Helmholtz-Zentrum Berlin, Germany

Electronic relaxation of core-ionized water molecules in liquid is far more diverse and complex than anticipated, and extremely different from that in an isolated water molecule. This has been revealed by simulating Auger electron spectra of normal and heavy liquid water using ab initio and quantum dynamical methods and comparing the theoretical results with the available experimental data [1]. A core-ionized water molecule in the liquid phase, in addition to a local Auger process, relaxes through non-local energy- and charge-transfer, such as Intermolecular Coulombic Decay (ICD) [2] and Electron Transfer Mediated Decay (ETMD) [3]. These intermolecular decay processes play a surprisingly important role, especially ETMD which is considered for the first time in the core-level regime. The electronic relaxation is accompanied by ultrafast proton transfer dynamics [4] which enhances the efficiency of the non-local processes considerably. As a consequence, the double charge forming in the end of the electronic and nuclear relaxation tends to be distributed between different water monomers rather than be localized on a single molecular unit and various reactive oxygen species are created. Our study provides insight into the types and yields of these species. [1] P. Slavíček, B. Winter, L.S. Cederbaum, N.V. Kryzhevoi, J. Am. Chem. Soc. doi: 10.1021/ja5117588. [2] L.S. Cederbaum, J. Zobeley, F. Tarantelli, Phys. Rev. Lett. 79, 4778 (1997). [3] J. Zobeley, R. Santra, L.S. Cederbaum, J. Chem. Phys. 115, 5076 (2001). [4] S. Thürmer, M. Ončák, N. Ottosson, R. Seidel, U. Hergenhan, S.E. Bradforth, P. Slavíček, B. Winter, Nature Chem. 5, 590 (2013).