

MO 6: Posters 1: Novelties in Molecular Physics: Femtosecond Spectroscopy

Time: Monday 16:30–19:00

Location: Empore Lichthof

MO 6.1 Mon 16:30 Empore Lichthof

Vibrational and vibronic coherences in the two dimensional spectroscopy of coupled electron-nuclear motion — ●JULIAN ALBERT¹, MIRJAM FALGE¹, SANDRA GOMEZ², IGNACIO SOLA², HEIKO HILDENBRAND¹, and VOLKER ENGEL¹ — ¹Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Campus Nord, 97074 Würzburg, Germany — ²Departamento de Química Física, Universidad Complutense, 28040 Madrid, Spain

We theoretically investigate the photon-echo spectroscopy of coupled electron-nuclear quantum dynamics [1]. Two situations are treated. In the first case, the Born-Oppenheimer (adiabatic) approximation holds. It is then possible to interpret the two-dimensional (2D) spectra in terms of vibrational motion taking place in different electronic states. In particular, pure vibrational coherences which are related to oscillations in the time-dependent third-order polarization can be identified. This concept fails in the second case, where strong non-adiabatic coupling leads to the breakdown of the Born-Oppenheimer-approximation. Then the 2D-spectra reveal a complicated vibronic structure and vibrational coherences cannot be disentangled from the electronic motion.

[1] J. Albert, M. Falge, S. Gomez, I. R. Sola, H. Hildenbrand, V. Engel, *J. Chem. Phys.* **143**, 041102 (2015)

MO 6.2 Mon 16:30 Empore Lichthof

Two-dimensional femtosecond optical spectroscopy of trapping dynamics in a charge-transfer process — ●MARTIN KESS and VOLKER ENGEL — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Campus Nord, Emil-Fischer-Str. 42, 97074 Würzburg, Germany

We study charge-transfer dynamics monitored by two-dimensional (2D) optical spectroscopy. The often used model consisting of two coupled diabatic electronic states in a single reaction coordinate is used to demonstrate the relation between the vibronic dynamics and the 2D-spectra. Within the employed wave-function approach, dissipation is included via a quantum-jump algorithm with explicit treatment of dephasing. States with long lifetimes which decay slowly due to the interaction with the environment are identified. Using filtered Fourier transforms it is shown that the population of these trap states can be monitored as a function of energy and time.

MO 6.3 Mon 16:30 Empore Lichthof

Theoretical analysis of exciton annihilation in Squaraine-Squaraine Copolymers — ●KILIAN HADER¹, CHRISTOPH LAMBERT², VOLKHARD MAY³, and VOLKER ENGEL¹ — ¹Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Campus Nord, 97074 Würzburg, Germany — ²Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany — ³Institut für Physik, Humboldt Universität, Newtonstr. 15, D-12489 Berlin, Germany

We use a microscopic model [1] to describe exciton annihilation processes in Squaraine-Squaraine Copolymers. Transient absorption traces measured at different laser powers exhibit an unusual time-dependence [2]. The analysis shows that, at shorter times, exciton-exciton annihilation, being effective through the laser excitation of next-neighbor building blocks, determines the excited state decay. At later times, excitations being localized on units which are not directly connected remain so that diffusion or smaller long range interactions are the rate-limiting step leading to a slower decay.

[1] V. May, *J. Chem. Phys.* **140**, 054103 (2014) [2] S. F. Völker, A. Schmiedel, M. Holzapfel, K. Renziehausen, V. Engel, C. Lambert, *J. Phys. Chem. C*, **118**, 17467 (2014)

MO 6.4 Mon 16:30 Empore Lichthof

Sub-One Per Cent Enantiomeric Excess Sensitivity using Femtosecond Photoelectron Circular Dichroism — ALEXANDER KASTNER, CHRISTIAN LUX, TOM RING, ●STEFANIE ZÜLLIGHOVEN, CRISTIAN SARPE, ARNE SENFTLEBEN, and THOMAS BAUMERT — University of Kassel, Institute of Physics and Center for Interdisciplinary Nanostructure Science and Technology (CINSA-T), Heinrich-Plett-Str. 40, D-34132 Kassel, Germany

Photoelectron circular dichroism (PECD) is investigated experimentally on chiral specimen with a varying amount of enantiomeric excess (e.e.). As a prototype we measure and analyze the photoelectron angu-

lar distribution from randomly oriented fenchone molecules in the gas phase resulting from ionization with circularly polarized femtosecond laser pulses. The quantification of these measurements shows a linear dependence with respect to e.e.. In addition, a distinction of differences in the e.e. (denoted as detection limit) below one per cent for nearly enantiopure samples as well as for almost racemates is demonstrated. In combination with a reference the assignment of absolute e.e. values is possible. The present measurement time is a few minutes but can be reduced further. This table-top laser-based approach facilitates a widespread implementation in chiral analysis.

MO 6.5 Mon 16:30 Empore Lichthof

Mass-selective Circular Dichroism after Femtosecond Laser Ionization — ●TOM RING, ALEXANDER KASTNER, STEFANIE ZÜLLIGHOVEN, TOBIAS GRABSCH, CRISTIAN SARPE, CHRISTIAN LUX, ARNE SENFTLEBEN, and THOMAS BAUMERT — Universität Kassel, Institut für Physik und CINSA-T, D-34132 Kassel

Multi Photon Ionization grants access to Circular Dichroism (CD) with circularly polarized laser pulses. The analysis via time of flight mass spectra provides a mass-selective tool to distinguish chiral molecules in the gas phase.[1,2] Hence, mixtures of chiral molecules as well as CD effects on fragments can be investigated.

Introducing a twin mass peak setup allows circumventing shot-to-shot fluctuations in laser pulse intensity, gas density or ion detection. Two foci with a small spatial displacement result in time-separated mass spectra; a change in helicity from focus to focus implements a self-referencing system. The in-line optical setup allows to make use of femtosecond laser pulses, whose broad bandwidth promises new possibilities in chiral control. Besides the advantages of this setup we present first results on different chiral molecules.

[1] Titze et al.: *ChemPhysChem* **2014**, *15*, 2762-2767

[2] Horsch et al.: *Chirality* **2012**, *24*, 684-690

MO 6.6 Mon 16:30 Empore Lichthof

Time-Resolved XUV-induced Electron Solvation Dynamics in Water Clusters — ●RUPERT MICHIELS¹, AARON LAForge¹, CARLO CALLEGARI², MARCEL DRABBELS³, PAOLA FINETTI², OKSANA PLEKAN², KEVIN C. PRINCE², STEFANO STRANGES⁴, MATTHIAS BOHLEN¹, MYKOLA SHCHERBININ¹, and FRANK STIENKEMEIER¹ — ¹Universität Freiburg, Germany — ²Eletra-Sincrotrone, Trieste, Italy — ³EPFL Lausanne, Switzerland — ⁴University of Rome, Italy

The solvation of electrons in aqueous solutions plays a nearly ubiquitous role in biological and chemical systems although a fundamental understanding of its properties (e.g. solvation time, binding energies, solvation shells, and binding motifs) has yet to be fully attained. Here, we report on solvated water clusters induced by XUV ionization followed by electron recapture. The binding energies of the solvated electron were measured in a pump-probe scheme as a function of cluster size in which we found solvation times in the femtosecond to picosecond range.

MO 6.7 Mon 16:30 Empore Lichthof

Deactivation of photo-excited Berenil — ●LENA GRIMMELSMANN, CHRISTIAN SPIES, and PATRICK NUERNBERGER — Physical Chemistry II, Ruhr-University Bochum, Universitätsstraße 150, 44801 Bochum

Berenil is an aromatic diamidin consisting of two amidinophenyl units which are linked by a triazine bridge. It binds well to several molecules, e.g. it can serve as a DNA minor groove binder. The steady-state photochemical behavior of Berenil was analyzed already, but no measurements addressing the dynamical behavior have been performed up to now. We have done steady-state absorption and fluorescence measurements, as well as time-resolved measurements via femtosecond fluorescence upconversion. The fluorescence quantum yield of Berenil in different solvents is very low. The reason is the notable fast decay of the excited-state, which has a lifetime of about 400 fs. Possibly, a rapid internal conversion due to an intramolecular rotation is the reason for the ultrafast decay.

We want to verify the assumption of the fast rotation by binding of Berenil to trypsin and to G-quadruplex DNA to prevent or decelerate the rotation. A slower fluorescence decay when Berenil is bound can

be an evidence for the hindered rotation. As a further approach, investigations of unbound benenil in solvents with different viscosities are performed to analyze the environmental impact on the photo-induced dynamics and hence on the fluorescence lifetime.

MO 6.8 Mon 16:30 Empore Lichthof

Femtosecond Photoelectron and Transient Grating Spectroscopy in the Extreme Ultraviolet Domain — ANDREA BATTISTONI¹, JAKOB GRILJ^{1,2}, MARKUS KOCH^{1,3}, EMILY F. SISTRUNK^{1,4}, THOMAS J. A. WOLF¹, and ●MARKUS GÜHR^{1,5} — ¹PULSE, SLAC National Accelerator Laboratory and Stanford University, 94025 Menlo Park, CA, USA — ²EPFL, Lausanne, CH 1015, Switzerland — ³Experimental Physics, Graz University of Technology, A-8010 Graz, Austria — ⁴Lawrence Livermore National Laboratory, Livermore, CA 94550, USA — ⁵Physik und Astronomie, Universität Potsdam, 14476 Potsdam, Germany

We present ultrafast photoelectron [1] and transient grating spectroscopy [2] using extreme ultraviolet (EUV) pulses from a laser source based on high harmonic generation. For the molecular photoelectron spectroscopy, we compare one-photon to multi-photon probing demonstrating the importance of intermediate resonances in the transient decay [3]. For the transient gratings, we show how broadband EUV continua allow us to distinguish acoustic and electronic effects in a solid VO₂ sample with a light induced insulator-to-metal transition. Permanent gratings, matched to the period of the transient, facilitate heterodyne detection of the (weak) nonlinear response of VO₂ [4].

[1] M. Koch et al., *J. Photoelectr. Spectr. Rel. Phen.* **197**, 22 (2014)

[2] E. Sistrunk et al., *Optics Express* **24**, 4340 (2015)

[3] M. Koch et al., *Phys. Rev. A* **91**, 031403 (2015)

[4] J. Grilj et al., *Photonics* **2**, 392 (2015)

MO 6.9 Mon 16:30 Empore Lichthof

Laser-based THz-field-driven XUV streak camera for time resolved measurements of angular energy distribution of electrons — ●RANKE MARTIN, KARIMI FAWAD, PFAU MARKUS, DIMITRIOU ANASTASIOS, and FRÜHLING ULRIKE — Institut für Experimentalphysik, Universität Hamburg

In this work, we present a novel setup for the study of femtosecond (fs) dynamics in atoms and molecules with the use of a terahertz (THz)-field-driven extreme ultraviolet (XUV) streak camera. High-harmonic generated XUV pulses are synchronized and superimposed with intense single-cycle THz pulses in a gas target. The XUV pulses are used to excite and ionize atoms or molecules. The resulting electrons are accelerated by the electric THz field which directly relates the change of the momentum to the THz vector potential. The kinetic energies of the electrons are measured fully angle resolved by a new velocity map imaging (VMI) spectrometer. The intense THz pulses are generated with a tilted pulse front setup of near infrared laser pulses by means of optical rectification in a nonlinear crystal.

MO 6.10 Mon 16:30 Empore Lichthof

Vibronic spectra of homo- and hetero-dimer aggregates — ●JOHANNES WEHNER, MARTIN KESS, and VOLKER ENGEL — Universität Würzburg, Institut für Physikalische und Theoretische Chemie, Emil-Fischer-Str. 42, Campus Nord, 97074 Würzburg, Germany

We calculate two-dimensional photon-echo spectra of molecular dimers employing different wave-function based approaches. Calculations using perturbative, non-perturbative and phase-cycling methods are compared. The differences in spectra obtained for homodimers and heterodimers are investigated. The two-dimensional spectra are discussed by comparing purely electronic level systems with their vibronic counterparts. In particular, the effect of orientational averaging is addressed.