

MO 9: Femtosecond Spectroscopy I

Time: Wednesday 11:00–13:00

Location: f102

MO 9.1 Wed 11:00 f102

Ultrafast 2D-Vis spectroelectrochemistry — ●JULIA HEITMÜLLER¹, KLAUS ECKSTEIN¹, PASCAL KUNKEL¹, KARL THORLEY², REBECCA RENNER², TOBIAS HERTEL¹, FRANK WÜRTHNER² und TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent 2D spectroscopy is a well established method to investigate dynamic processes with femtosecond time resolution and to observe couplings between different energetic states. Electrochemistry, on the other hand, can be used to generate different oxidized and reduced molecular species in solution. The combination of these two techniques leads to coherent 2D spectroelectrochemistry. For the infrared regime different spectroelectrochemical cells were described and used for 2D measurements in the literature [1,2], but not so far for the visible. We developed a setup using a commercial electrochemical cell (HX-301, Hokuto Denko), which we modified for the experimental requirements. As a model system we investigate a tetraphenoxyperylene bisimide and obtain 2D as well as other spectroscopic measurements of the different redox states *in situ* without requiring oxidizing or reducing agents.

[1] Y. El Khoury, et al., *Rev. Sci. Instrum.* **86**, 083102 (2015)

[2] D. Lotti, et al., *J. Phys. Chem. C*, **120**, 2883 (2016)

MO 9.2 Wed 11:15 f102

Ultrafast excitation energy localization dynamics following delocalized excitation — ●YANG LI, PAVEL MALÝ, JULIAN LÜTTIG, STEFAN MÜLLER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

The efficiency of organic photovoltaic materials, such as conjugated polymers, aggregates and dendrimers, depends on the interplay between molecular architecture and light-induced electronic energy redistribution. The spatial localization of the excitation energy is relevant for conversion efficiency and has been a point of intense research for artificial systems that are designed and synthesized to produce solar fuels. While the delocalized excitation followed by localized emission universally appears in a variety of dendrimers [1], the localization process itself has not yet been probed in real time. In this work, polarization-controlled two-dimensional electronic spectroscopy is applied to track the excitation-wavelength-dependent anisotropy evolution of a molecular heterodimer upon broadband excitation with 11 fs pulses. 2D anisotropy reveals a transient delocalization of the excited-state wave function with Frenkel-exciton character at the moment of excitation. The spatial localization of electronic excitation gives rise to 2D anisotropy depolarization within 200 fs.

[1] D. Aulimer et al., *J. Am. Chem. Soc.* **16**, 5742-5743 (2009).

MO 9.3 Wed 11:30 f102

Ultrafast photo-ion probing of the relaxation processes of 2-Thiouracil. — ●MATTHEW SCOTT ROBINSON, MARIO NIEBUHR, and MARKUS GÜHR — Universität Potsdam, Institut für Physik und Astronomie, Karl-Liebknecht-Straße 24/25, 14476 Potsdam-Golm, Germany

We study the ultrafast relaxation process of 2-thiouracil after UV photo-excitation with the use of multi-photon pump-probe time-of-flight mass spectroscopy, supported by synchrotron-based single-photon vacuum ultraviolet (VUV) photo-ionization studies performed at the Swiss Light Source.

Here we show that most of the observable dynamics are completed 1 ps after excitation, and identify that the parent is primarily produced through 2-photon processes (when using 266 nm photons), whilst all fragments are 3-photon dependent. In addition, through the use of pump and probe beams with different powers we are able to determine if fragments are produced through [1+2] processes or [2+1] processes.

The VUV studies also suggest that the substitution of one of the oxygen atoms of uracil with sulfur to produce 2-thiouracil, introduces a new fragmentation route for the pyrimidine ring, with either CO or HCNH being ejected to produce a 100 amu fragment; the equivalent fragment in uracil (84 amu) is not observed in similar studies. [1]

1. H.W. Jochims, M. Schwell, H. Baumgärtel, and S. Leach, *Chem. Phys.* **314**, 263 (2005).

MO 9.4 Wed 11:45 f102

Effect of External Electric Field on Vibronic and Excitonic Properties of P3HT Studied by Femtosecond Time-Resolved Spectroscopy and Density Functional Theory — ●DEBKUMAR RANA, PATRICE DONFACK, VLADISLAV JOVANOVIĆ, VEIT WAGNER, and ARNULF MATERNY — Jacobs University Bremen, Department of Physics and Earth Sciences, Campus Ring 1, 28759 Bremen

Poly(3-hexylthiophene-2,5-diyl) (P3HT) is of interest for solar cell applications. However, important elementary processes under operational conditions, *i.e.*, in the presence of applied electric fields, are not yet completely understood. In our work, we have used density functional theory (DFT) to evaluate the field-effect on the vibronic properties of P3HT within and beyond the range of typical external electric field strengths. We demonstrate that charge-phonon coupling and hence charge localization increase with field strength. In parallel, we have used femtosecond time-resolved spectroscopy to study the excitonic properties of P3HT thin films in a model P3HT device under operational conditions. We show that polaron-pair (PP) dissociation into charge carriers occurs in the P3HT device more significantly with increasing reverse bias, consistent with the electric field-induced dissociation of oppositely charged species. Moreover, besides PPs directly originating from hot excitons, we experimentally observe PP formation during exciton dissociation via a field-mediated generation process resulting in a slower contribution to the overall decay dynamics. Transient-absorption anisotropy measurements elucidate the excitation polarization memory loss due to external electric fields.

MO 9.5 Wed 12:00 f102

Population of long-lived excited states in 7- and 9-methylpurine probed by femtosecond transient vibrational absorption spectroscopy — ●REBECCA HOLTSMANN, AMKE NIMM-RICH, HENDRIK BOEHNKE, and FRIEDRICH TEMPS — Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Germany

We investigated the photo-induced dynamics of 7- and 9-methylpurine (7-MePur, 9-MePur) as model systems for purine-based DNA building blocks. The ensuing processes upon photoexcitation at $\lambda = 267$ nm were probed by structure-sensitive time-resolved vibrational absorption spectroscopy. After excitation to the $S_2(\pi\pi^*)$ state, the excited-state population is transferred to the $S_1(n\pi^*)$ state by ultrafast internal conversion within $\tau_1 \approx 300$ fs. Aided by ab initio calculations, our results reveal two parallel deactivation pathways from the $1^1n\pi^*$ state for both isomers: Recovery of the ground state associated with vibrational cooling within $\tau_2 \approx 10$ ps and intersystem crossing to a $3^3\pi\pi^*$ state with $\tau_3 = 250$ ps for 7-MePur and $\tau_3 = 480$ ps for 9-MePur, respectively. Exclusively for 9-MePur, an additional deactivation pathway on the nanosecond time scale from the initially populated $S_2(\pi\pi^*)$ state has been identified. In summary, canonical nucleobases like adenine and guanine typically feature excited-state lifetimes of < 1 ps. Consequently, the reported long-lived excited states involved in the electronic deactivation after photoexcitation in 7-MePur and 9-MePur highlight the crucial effects of structural modifications on the dynamics of the purine related nucleobases.

MO 9.6 Wed 12:15 f102

Structural Changes in Metal-To-Ligand Charge Transfer States Investigated by Time-Resolved Vibrational Spectroscopy — ●F. HAINER¹, N. ALAGNA¹, E. DOMENICHINI², M. DARARI³, P. GROS³, S. HAACKE², and T. BUCKUP¹ — ¹Institute of Physical Chemistry, Ruprecht-Karls University Heidelberg, Germany — ²University of Strasbourg, CNRS, IPCMS, Strasbourg, France — ³University of Lorraine, CNRS, L2CM, Nancy, France

Iron(II) complexes with nitrogen-heterocyclic carbene (NHC) ligands are about to become promising chromophores for solar energy applications. In spite of the great interest in these compounds, the assignment of the electronic states involved in the excited state relaxation dynamics is still an open question. In this work, we employed femtosecond transient absorption as well as (pump-)impulsive vibrational spectroscopy to investigate the electronic and vibrational dynamics in the relaxation pathway of such an iron(II)NHC complex. Three contributions are identified and the vibrational dynamics in the low-frequency region is discussed. The photoexcitation of an 1MLCT state is followed by ultrafast intersystem crossing (ISC), which is accompanied by an

intermolecular vibrational redistribution of 100cm^{-1} mode. The vibrational modes appearing below 100cm^{-1} and at 150cm^{-1} correspond to metal-ligand stretch vibrations and are assigned to the electronic excited state manifold. A deformation vibration of the ligand backbone at 350cm^{-1} is found to survive the ISC, indicating that the charge remains on the ligand. The results point to a ground state recovery from a $^3\text{MLCT}$ without a ^3MC state taking part in the dynamics.

MO 9.7 Wed 12:30 f102

High-intensity effects in two-dimensional electronic spectroscopy — ●MARCEL BINZ¹, LUKAS BRUDER¹, LIPENG CHEN², MAXIM F. GELIN³, WOLFGANG DOMCKE⁴, and FRANK STIENKEMEIER¹ — ¹Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany — ²Institute of Chemical Sciences and Engineering, EPFL Lausanne, 1015 Lausanne, Switzerland — ³School of Science, Hangzhou Dianzi University, 310018 Hangzhou, China — ⁴Department of Chemistry, Technical University of Munich, 85747 Garching, Germany

Usually, two-dimensional electronic spectroscopy (2DES) experiments are performed in the regime where perturbation theory holds and the signal can be described by the third-order polarization. However, to measure nonlinear signals, higher laser intensities are generally of advantage as the signal scales with higher order of the incident light fields. Non-perturbative theoretical description of 2DES experiments indicate that compromising effects, such as peak shape distortions and phase shifts, should occur at laser intensities beyond the perturbative limit [1]. Here, we explore these high-intensity effects by studying a simple, clean model system comprising of a rubidium atom vapor in

collinear 2DES experiments, supported by non-perturbative numerical simulations.

[1] L. Chen et al., J. Chem. Phys. **147**, 234104 (2017)

MO 9.8 Wed 12:45 f102

Revealing delocalized states using multiple-quantum two-dimensional spectroscopy — ●FRIEDEMANN LANDMESSER, LUKAS BRUDER, ULRICH BANGERT, MARCEL BINZ, ELENA LEISSLER, DANIEL UHL, and FRANK STIENKEMEIER — Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany

Many-body quantum states are considered to play a crucial role in atomic and molecular systems with respect to dissipation, excitation, and energy transfer (cf. [1]). We aim at investigating collective effects by multiple-quantum coherence experiments, where multiphoton processes can be separated from one-photon transitions [2] and delocalized excitons can be probed with extraordinary sensitivity [3]. We now extend our detection scheme to phase-modulated multiple-quantum two-dimensional coherent spectroscopy [4]. Our focus will lie on the investigation of dilute alkali atom vapors, where we observe dipolar couplings at extremely low densities [3], as well as molecular networks formed on cold rare gas clusters. In the latter system, we previously observed intriguing cooperative processes such as superradiance and singlet fission [5].

[1] F. Fassioli et al., J. Royal Soc. Interface **11**, 20130901 (2014).

[2] L. Bruder et al., Phys. Rev. A **92**, 053412 (2015).

[3] L. Bruder et al., Phys. Chem. Chem. Phys. **21**, 2276 (2019).

[4] S. Yu et al., Opt. Lett. **44**, 2795 (2019).

[5] S. Izadnia et al., J. Phys. Chem. Lett. **8**, 2068 (2017).