

MO 9: Femtosecond Spectroscopy 2

Time: Tuesday 14:30–16:30

Location: PH/HS1

Invited Talk

MO 9.1 Tue 14:30 PH/HS1

Control and Spectroscopy of Chiral Systems in the Condensed Phase — ●TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

Chirality is a fundamental structural property arising from symmetry considerations: A chiral object cannot be superimposed with its mirror image. In this presentation, progress will be shown toward chirally selective control and time-resolved chiral spectroscopy of molecules in the condensed phase. For this purpose, a variety of fundamental and practical issues have to be addressed. Solutions to some of the problems will be discussed. As a means to introduce chirality via light in the most flexible fashion, we have developed vector-field shaping with independent ultrafast control over amplitude, phase, and polarization of an ultrashort pulse as a function of time. Another necessary ingredient is a detection method that provides chiral sensitivity. We have constructed a highly sensitive polarimeter and used it together with accumulative spectroscopy to measure the optical rotation change upon a chirality-modifying photochemical reaction. Thus we achieved all-optical discrimination between racemic and achiral molecular solutions. A second option for chiral detection is to measure photoinduced changes in circular dichroism (CD). Using a new setup for creating "light-pulse enantiomers", we have developed broadband time-resolved CD spectroscopy with shot-to-shot white-light detection. As an example, we investigated oxygen release in hemoglobin.

MO 9.2 Tue 15:00 PH/HS1

Improving Fluorescence Kerr Gating — ●RAMONA MUNDT, GERALD RYSECK, and PETER GILCH — HHU Düsseldorf, Germany

With Kerr gating complete fluorescence spectra as a function of time may be recorded in the femto- to picosecond regime[1]. This advantage over fluorescence up-conversion comes at the expense of an increased background. The background is caused by fluorescence leaking through the polarizers and third harmonic generation of the gate pulses. In the contribution it will be shown that the implementation of reference diodes and a correction procedure greatly increases the data quality.

[1] B. Schmidt et al., Appl. Phys. B, 2003, 76/8, 809-814

MO 9.3 Tue 15:15 PH/HS1

Ultrafast dissociation of molecular oxygen excited at 162 nm wavelength — ●THOMAS GEBERT, DIMITRIOS ROMPOTIS, MAREK WIELAND, FAWAD KARIMI, ARMIN AZIMA, and MARKUS DRESCHER — Institut für Experimentalphysik, Universität Hamburg, Deutschland

Ultrafast dissociation of excited gas-phase oxygen molecules is studied through vacuum-ultraviolet two photon ionization in an interferometric VUV pump-probe experiment. Using powerful fifth harmonic radiation from a Ti:Sa laser with up to 1 uJ pulse energy and a pulse duration of 18 femtosecond at 162 nanometre wavelength a precision of below 2 femtosecond is achieved.

MO 9.4 Tue 15:30 PH/HS1

Jumping and Diffusion of Excitons: Förster transfer drives annihilation in an organic system — ●FRANZISKA FENNEL and STEFAN LOCHBRUNNER — Institut für Physik, Universitätsplatz 3, 18055 Rostock

In many organic materials absorption of light leads to the formation of mobile electronic excitations, i.e. Frenkel excitons. At high excitation densities they can interact with each other resulting in an accelerated decay of the exciton density due to exciton-exciton-annihilation. We investigate the underlying mechanisms and the subsequent steps of annihilation in a disordered organic model system by ultrafast absorption spectroscopy. The time dependent exciton density can be described by two annihilation pathways, the direct energy transfer between two excited molecules and diffusive motion towards a second exciton preceding the annihilation event. It is found that both pathways can be quantitatively understood by applying Förster energy transfer theory to describe the diffusion of the excitons as well as the annihilation step itself. To this end previous formulations of Förster theory are extended to account for the inhomogeneous distribution of the S_0 - S_1 transition energies resulting in an effective diffusion constant. Our

model system consists of dye molecules embedded in a PMMA matrix. This model system allows to tune the exciton diffusion constant via the chromophore concentration [1] and therefore one annihilation pathway can be emphasized with respect to the other.

[1] F. Fennel, S. Lochbrunner, *Phys. Chem. Chem. Phys.* **13**, 3527 (2011)

MO 9.5 Tue 15:45 PH/HS1

Tracking energy flow through the intact photosynthetic apparatus of green sulfur bacteria *in situ*. — ●JAKUB DOSTÁL¹, JAKUB PŠENČÍK², and DONATAS ZIGMANTAS³ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany — ²Faculty of Mathematic and Physics, Charles University in Prague, Ke Karlovu 3, 121 16 Prague, Czech Republic — ³Department of Chemical Physics, Lund University, P.O.Box 124, 221 00 Lund, Sweden

In order to utilize the energy of solar radiation the photosynthetic organisms developed various types of photosynthetic apparatuses. The photosynthetic apparatus of green sulfur bacterium *Chlorobaculum tepidum* consists of chlorosome - a massive light-harvesting antenna, FMO protein - the excitation energy conduit, and the reaction center. All the constituting complexes are clearly distinguishable in the absorption spectrum of the suspension of intact bacterial cells taken at low temperatures (77 K). This opens a possibility to study the light-harvesting processes by means of ultrafast time-resolved spectroscopy *in situ*. In this work we have applied coherent two-dimensional electronic spectroscopy to resolve the excitation energy flow through the entire photosynthetic apparatus.

MO 9.6 Tue 16:00 PH/HS1

Identification of an Ultrafast Triplet Transition Discovered by Pump-Depletion-Probe Experiments — ●JULIA HERZ¹, FABIAN PAULUS², TIAGO BUCKUP¹, UWE BUNZ², and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut — ²Organisch-Chemisches Institut, Ruprecht-Karls-Universität, D-69120 Heidelberg, Germany

Pump-depletion-probe experiments were carried out in order to disentangle the excited state dynamics of TIPS-pentacene. In particular the singlet fission process, in which an excited molecule reacts with a neighbor in its ground state producing two excited triplet species in an overall spin-conserved process, is important. The formed triplet state shows two transitions, one in the visible (T1->T3) and one in the NIR spectral region (T1->T2). Measurements in these two spectral ranges can provide insight into the interplay of the triplet manifold and help to unravel additional singlet fission channels. Applying a depletion pulse resonant with the triplet absorption in the visible leads to a loss of signal in the NIR, however, the evolution of the NIR signal does not follow the dynamics observed in the visible. Our results are explained by an ultrafast relaxation channel (ca. 90 fs) between the triplet states (T3->T2). A rate model simulation of the depletion effect supports this finding and gives further evidence, within our experimental time resolution, that both triplet transitions in the NIR and VIS probe the same triplet state (T1).

MO 9.7 Tue 16:15 PH/HS1

Collinear two-dimensional spectroscopy via fluorescence detection with rapid phase cycling — ●SIMON DRAEGER¹, SEBASTIAN RÖDING¹, ANDREAS STEINBACHER¹, PATRICK NÜRNBERGER^{1,2}, and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Physikalische Chemie II, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum

We present a novel all-collinear setup to perform pulse-shaper-assisted two-dimensional electronic spectroscopy with fluorescence detection. The acousto-optical pulse shaper (Dazzler, Fastlite) allows the variation of the interpulse delays and their relative phases with 1 kHz rate, enabling a rapid scan and shot-to-shot phase cycling. For a four-pulse sequence with variable delay times τ , T and t , the application of phase cycling allows to obtain different nonlinear contributions (e.g. rephasing and non-rephasing photon echo) in one single measurement process. Common laser dyes are used as benchmark molecules to evaluate the setup.