

MO 21: Advanced Time-Resolved Spectroscopy

Time: Thursday 14:00–15:45

Location: PA 2.150

MO 21.1 Thu 14:00 PA 2.150

Broadband fluorescence-detected one- and two-quantum 2D electronic spectroscopy — ●STEFAN MÜLLER, SIMON DRAEGER, XIAONAN MA, MATTHIAS HENSEN, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

We developed a single-beam setup for 2D electronic spectroscopy in the liquid phase using fluorescence as an observable [1]. Collinear femtosecond phase-modulated pulse trains are generated by an acousto-optic dispersive filter on a 1 kHz shot-to-shot basis. Broadband excitation in the visible spectral range is provided by the supercontinuum output of an argon-filled hollow-core fiber. By utilizing phase cycling we demonstrate the simultaneous acquisition of different nonlinear signal contributions such as photon-echo, two-quantum coherence and one-quantum-two-quantum signals without nonresonant solvent response or scattering artifacts that pose a substantial challenge in noncollinear coherence-detected 2D spectroscopy. We show that information about nuclear wave-packet dynamics, doubly excited states as well as coupling between excited states can be received from these nonlinear signals.

[1] S. Draeger, S. Roeding, and T. Brixner, *Opt. Express* **25**, 3259 (2017).

MO 21.2 Thu 14:15 PA 2.150

Diffusion Controlled Singlet Fission of a Tetracene Derivative in Solution — ●NIKOLAUS WOLLSCHIED¹, NICOLÒ ALAGNA¹, JOSÉ LUIS PEREZ LUSTRES¹, TIAGO BUCKUP¹, SEBASTIAN HAHN², UWE BUNZ², and MARCUS MOTZKUS¹ — ¹Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg — ²Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg

Singlet fission (SF) is the process by which one excited singlet state yields two triplet states upon close interaction of two chromophores. This ultrafast photoreaction was first observed in solid state and has strong implications in organic photovoltaics [1]. SF was also reported in concentrated solutions, where the diffusion of the reaction partners extends the dynamics to longer timescales [2]. This eases the identification of the involved species and helps to disentangle the mechanism. In this work, we use ultrafast transient absorption (TA) spectroscopy to investigate concentrated solutions of an aza-substituted tetracene derivative in toluene. Measurements at different concentrations show: a) the correlation between singlet decay and triplet formation and b) acceleration of the reaction dynamics with increasing concentration. Both observations together indicate a diffusion mediated SF process. Spectral analysis suggests a kinetic model involving an intermediate TT state.

[1] M. Smith and J. Michl, *Chem. Rev.*, **110**, 6891, (2010)

[2] B. Walker, A. J. Musser, D. Beljonne, R. Friend, *Nat. Chem.*, **5**, 1019 (2013)

MO 21.3 Thu 14:30 PA 2.150

Exciton diffusion in molecular aggregates characterized by exciton-exciton interaction spectroscopy — ●JAKUB DOSTÁL¹, FRANZISKA FENNEL², FEDERICO KOCH¹, STEFANIE HERBST², FRANK WÜRTHNER², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg

An essential part of natural and artificial light harvesting is the efficient transport of excitation energy. In molecular aggregates it often proceeds as random diffusion of excitons delocalized over several aggregate sites. Random encounters of two excitons lead to a rapid annihilation of one of them due to internal conversion. Tracking the number of such events as a function of population time and excitation intensity can provide valuable information on the timescale of exciton diffusion.

In our contribution we study exciton diffusion in one-dimensional J-aggregates of a perylene bisimide (PBI) dye by means of exciton-exciton interaction 2D spectroscopy (EEI2D). This recently developed spectroscopic technique is able to single out the signal specific to interactions between exciton pairs. We observed that the EEI2D signal of the studied PBI aggregates consists of the diffusion-enabled exciton annihilation and the direct excitation of the two exciton states.

Theoretical modeling of time evolution of the EEI2D signal allowed us to determine the exciton diffusion constant and estimate the exciton delocalization length.

MO 21.4 Thu 14:45 PA 2.150

Optical Properties of Single Mikrometer Dye Crystals — ●CHRIS REHHAGEN, STEFFEN WOLTER, and STEFAN LOCHBRUNNER — University of Rostock, Germany

Dye crystals are of rising interest in opto-electronic applications, especially due to potentially large exciton mobilities. Furthermore, crystals provide stable and regular structures which are well suited for common characterization methods. In this work, small crystals in the range of 10 – 500 μm are prepared from solutions of the dyes TTBC, Coumarin153 and Perylen Orange. To investigate their optical properties a microscope with a resolution of 30 μm is implemented for single-crystal absorption and fluorescence spectroscopy. The setup is also combined with a streak camera in order to investigate the dynamics of electronic excitations. Beyond this, FLIM is used to investigate the lifetime distribution down to a spatial resolution of 200 nm . The results show that there is a connection between the macroscopic structure of the crystals and their optical properties. Especially some TTBC crystals show fluorescence spectra with spectrally narrow components typical for J-type aggregation and a lifetime in the range of tens of picoseconds.

MO 21.5 Thu 15:00 PA 2.150

Structure and dynamics of water at the electrolyte solution-air interface studied with pump-probe SFG — ●MALTE DEISEROTH, SUDIPTA DAS, MISCHA BONN, and ELLEN H.G. BACKUS — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz

Physical and chemical processes occurring at salt-water-air interfaces play a prominent role in a variety of fields ranging from the chemistry of atmospheric aerosols and heterogeneous catalysis to biophysics and biochemistry. Knowledge of the molecular interfacial structure and energy flow dynamics at these interfaces is important, not only for a fundamental understanding of this ubiquitous liquid but also to understand its reactivity.

Here, we report a surface-sensitive sum-frequency generation (SFG) spectroscopy study of the interface of electrolyte solutions with air, aimed at obtaining information about the molecular arrangement of water and ions at the interface, and how this affects energy dissipation at the interface. Time-resolved and 2D pump-probe spectroscopy provide insights into dynamics of interfacial water molecules with sub-picosecond time resolution. Substantial differences are observed between the static SFG spectra obtained from the surface of solutions of Na_2SO_4 , Na_2CO_3 , and pure water, pointing to large variations in the interfacial structure of these different solutions; remarkably, the vibrational dynamics of these systems are indistinguishable. Hence, while electrolytes clearly restructure the interface of water, the vibrational dynamics is unaffected by the structural changes.

MO 21.6 Thu 15:15 PA 2.150

Ultrafast Vibrational Relaxation of Water at the Ice - Air Interface — ●PRERNA SUDERA, JENÉE D CYRAN, ALEJANDRA MARIA SÁNCHEZ, MISCHA BONN, and ELLEN H. G. BACKUS — Max Planck Institute for Polymer Research, Mainz, Germany

For chemical reactions occurring on the ice surface - relevant for e.g. atmospheric reactions - the dynamics of the surface water molecules and energy flow pathways play an important role: following a chemical reaction, the rate of dissipation of excess energy determines the probability of a back-reaction occurring. Here we elucidate the relaxation dynamics of water molecules at the surface of single crystalline hexagonal ice after exciting the O-H stretch vibration and compare our results with the relaxation dynamics of the liquid water-air interface.

To study the vibrational dynamics we apply time-resolved sum frequency generation spectroscopy. With this method, we can vibrationally excite the surface molecules with a femtosecond infrared excitation pulse, and probe the dynamics of the interfacial molecules with the SFG process using a visible and an infrared pulse resonant with the O-H stretch vibrations. This detection scheme ensures that only the interfacial water molecules contribute to the signal; the use of ~ 50

fs laser pulses ensures high time resolution in the experiments.

Our results show that the relaxation dynamics of the O-H stretch mode after excitation at 3100 cm^{-1} at the basal plane of ice is around 70 fs - three times faster than for the water-air interface. We discuss the origins and implications of ultrafast energy dissipation at ice interfaces, compared to the liquid.

MO 21.7 Thu 15:30 PA 2.150

Shaper based infrared spectroscopy in a nonlinear Raman setup — ●NIKLAS MÜLLER, LUKAS BRÜCKNER, and MARCUS MOTZKUS — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg

The infrared and Raman sensitivities differ for a vibrational transition, particularly in molecules with inversion symmetry. Therefore a

combination of both methods yields to more information about the molecules. Combining the established coherent anti-Stokes Raman scattering (CARS) setup [1] with a tunable narrowband infrared light source, we are able to do both CARS and infrared spectroscopy in a single-beam setup. Broadband laser pulses spectrally centered at 800 nm are shaped by a liquid crystal spatial light modulator to generate either background-free coherent anti-Stokes signal in a sample or narrowband tunable infrared light in a birefringent crystal beforehand. The infrared light is generated by difference-frequency generation in a thin LiIO_3 crystal by phase and polarization shaped laser pulses. On the one hand, the large tunability ($>1500 \text{ cm}^{-1}$) is based on the broad phase matching condition of the thin crystal. On the other hand, the narrowband behavior ($<25 \text{ cm}^{-1}$) is achieved by chirped laser pulses yielding to the same instantaneous frequency difference in the crystal. [1] L. Brückner, et al. **JOSA B** 33 1482 (2016)