

MO 21: Coupled Systems

Time: Thursday 14:00–16:00

Location: S HS 001 Biologie

Invited Talk MO 21.1 Thu 14:00 S HS 001 Biologie
Influence of Local and External Electric Fields on the Ultrafast Dynamics of Charge Pairs Photo-Generated in Poly-[3-Hexylthiophene] (P3HT) — DEBKUMAR RANA, TAHIRZEB KHAN, PATRICE DONFACK, VLADISLAV JOVANOVIĆ, VEIT WAGNER, and ARNULF MATERNY — Jacobs University Bremen, Department of Physics & Earth Sciences, Campus Ring 1, 28759, Bremen, Germany

Organic semiconductors have attracted considerable attention in recent years due to their various advantages. However, both stability and efficiency of organic electronic devices still have to be improved. For this purpose, a detailed understanding of basic processes is of great importance. While the investigation of neat semiconductor material will always be the starting point, in the end, more realistic scenarios have to be considered as well. On this account, we have studied the dynamics of charge-pair states in poly-[3-hexylthiophene] (P3HT), a promising organic semiconductor *e.g.* for building solar cells, utilizing femtosecond time-resolved transient absorption spectroscopy influenced by internal and external electric fields. Using sub-diffraction-limited microscopy, we were able to detect the dynamics at the interface between P3HT and a gold electrode. Additionally, in P3HT-only diodes, we have applied external fields in reverse and forward bias. In all cases, we found changes in the observed polaron-pair dynamics compared to the neat-P3HT sample without internal and external electric fields. In our presentation, we will give an overview about the experimental techniques applied as well as the interesting results we have obtained.

MO 21.2 Thu 14:30 S HS 001 Biologie
Exciton migration in multi-stranded J-type aggregates — CHRIS REHHAGEN¹, FRANZISKA FENNEL¹, STEFANIE HERBST², FRANK WÜRTHNER², and STEFAN LOCHBRUNNER¹ — ¹Institut für Physik, Universität Rostock, Albert-Einstein-Str. 23, 18059 Rostock — ²Institut für Organische Chemie & Center for Nanosystems Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg

Understanding the transport mechanisms of electronic excitations in coupled molecular systems is the basis for their application in light harvesting and opto-electronic devices. The exciton transfer properties depend pivotal on the supramolecular structure. Herbst et. al. reported recently a series of perylene bisimides dyes self-assembling into multi-stranded (two to four) J-type aggregates [1]. These aggregates are an ideal model system to study the impact of structural modifications onto the exciton transfer distances. We determine the exciton mobility for these aggregates by analyzing the dynamics associated with exciton-exciton annihilation [2]. Therefore energy dependent pump-probe spectroscopy is applied and a one-dimensional diffusion model is fitted to the obtained data. We compare the exciton mobilities of the different samples with respect to their supramolecular structure. Our results imply that such PBI-aggregates and their molecular engineering are promising for further applications in photonics.

[1] Herbst et. al., Nat. Commun., 9 (2018), 2646.

[2] Wolter et. al., J. Phys. B: At. Mol. Opt. Phys. 50 (2017), 184005.

MO 21.3 Thu 14:45 S HS 001 Biologie
Franck Condon spectra of the 3-tolunitrile dimer — CHRISTIAN HENRICHS and MICHAEL SCHMITT — Institute for Physical Chemistry I, Heinrich-Heine-University, Düsseldorf

The 3-tolunitrile (3-TN) dimer is an example for the class of centrosymmetric homodimers. The investigation of the structure of dimers has been of certain interest with respect to excitonic effects. Therefore, we have to face the question if the homodimer forms J-aggregates or H-aggregates. But not only the structure, but also the question of electronic excitation of the two equivalent chromophores might be interesting. The question is, if the electronic excitation is localized on one of the chromophores, or delocalized over the both. To address these two problems we performed Franck-Condon Fits of the fluorescence emission spectra of the 3-TN dimer and determined the change of the geometry upon electronic excitation via a Franck-Condon fit.

MO 21.4 Thu 15:00 S HS 001 Biologie
Spectroscopic observation of protein influence on charge transfer dynamics in individual YM210W reaction centers

of purple bacteria — PAVEL MALÝ^{1,2,4}, MICHAEL R. JONES³, TOMÁŠ MANČAL¹, and RIENK VAN GRONDELLE² — ¹Charles University, Prague, Czech Republic — ²Vrije Universiteit Amsterdam, The Netherlands — ³University of Bristol, United Kingdom — ⁴present address: University of Würzburg, Germany

In photosynthetic reaction centers (RCs) the energy from sunlight is used to drive charge separation, providing the driving potential for subsequent chemical reactions. Due to the presence of charge transfer (CT) and charge separated (CS) states, the pigments in the RC interact strongly with their protein environment. This sensitivity causes a large dynamic disorder in the RCs due to the protein fluctuations. In this work we report on a first single-molecule spectroscopy study on individual YM210W RC mutants from purple bacterium *Rb. Sphaeroides*. In the single RCs we observe fluorescence (FL) intensity blinking, spectral diffusion and lifetime fluctuations. We obtain both static distributions and dynamic traces, the observed behavior fully agrees with the anticipated dynamic disorder. We find that with increasing FL peak wavelength the spectrum width linearly increases, while the lifetime exponentially decreases. We quantitatively describe the experiments by an excitonic model including charge separation. This model, explaining both bulk and single-RC measurements, shows that the charge separation rate is determined by the fluctuations of the P^+B^- CT state energy, caused by the protein fluctuations.

MO 21.5 Thu 15:15 S HS 001 Biologie
Near field induced speedup of exciton diffusion in light-harvesting arrays — ANDREA MATTIONI, FELIPE CAYCEDO-SOLER, SUSANA HUELGA, and MARTIN PLENIO — Institut für Theoretische Physik and Center for Integrated Quantum Science and Technology IQST, Albert-Einstein-Allee 11, Universität Ulm, 89069 Ulm, Germany

The observation of long-range energy propagation along nano-engineered arrays of bacterial antenna complexes [*Nano Lett.*, **2010**, 10 (4), pp 1450–1457] has been recurrently addressed as a result of ballistic, hence, coherent propagation [*J. Phys. Chem. C*, **2012**, 116 (5), pp 3747–3756]. We show that the experimentally determined quantities relevant for these dynamics hinder the formation of large coherent domains and inevitably lead to classical diffusion in these densely packed arrays, which nevertheless benefit from the spectral complexity of single antenna complexes and near field interactions to result in the propagation observed. We show that the packing density bridges the apparent incompatibility between observed energy transfer rates in bacterial photosynthetic membranes and nano-engineered antenna arrays, which together with exciton delocalization across individual antennas and non-equilibrium transport, provides useful design strategies to optimize energy transfer in the presence of typical room temperature conditions.

MO 21.6 Thu 15:30 S HS 001 Biologie
Broadband Time-Resolved Circular Dichroism Spectroscopy of Monolayer MoS₂ — HEIKO HILDENBRAND¹, ANDREAS STEINBACHER¹, HOPE BRETSCHER², AKSHAY RAO², and TOBIAS BRIXNER¹ — ¹Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg — ²Department of Physics, Cavendish Laboratory, University of Cambridge, 19 JJ Thompson Avenue, Cambridge, CB3 0HE, UK

Circular dichroism (CD) is a common technique for analyzing chiral samples by their difference in absorption of left and right circularly polarized light. Here we present broadband time-resolved CD spectroscopy which is based on the pump-probe technique paired with a setup capable of mirroring an arbitrary polarization state of an ultrashort laser pulse [1]. Hence, by passing a circularly polarized broadband probe pulse through this setup, we can switch between opposite handedness on a shot-to-shot basis. In combination with a chopping scheme, this allows us to simultaneously acquire data of transient CD and absorption changes.

To demonstrate the capabilities of this approach we selectively excite the K and K' valley of a MoS₂ monolayer on a quartz substrate with circularly polarized femtosecond pulses. Since the valley degree of freedom is only accessible via helicity-sensitive techniques, we investigate the ultrafast valley dynamics by time-resolved CD spectroscopy and complement the results with information obtained via transient

absorption spectroscopy of the A and B excitonic bands.

[1] Steinbacher et al., Opt. Express 25, 21736 (2017)

MO 21.7 Thu 15:45 S HS 001 Biologie
variational approaches to quantum impurities: from the Fröhlich polaron to the angulon — ●XIANG LI, GIACOMO BIGHIN, ENDERALP YAKABOYLU, and MIKHAIL LEMESHKO — Institute of Science and Technology Austria, Klosterneuburg, Austria

In this contribution we introduce new variational approaches, termed

as single phonon expansion, coherent state on top of single phonon excitation, and Pekar diagonalization, to quantum impurities and apply them to the Fröhlich polaron, a quasiparticle formed out of an electron (or other point-like impurity) in a polar medium, and to the angulon, a quasiparticle formed out of a rotating molecule in a bosonic bath. We benchmark these approaches against established theories, evaluating their accuracy as a function of the impurity-bath coupling.

[1] X. Li, G. Bighin, E. Yakaboylu, M. Lemeshko, arXiv: 1810.10302