

MO 23: Femtosecond Spectroscopy VI

Time: Thursday 14:00–16:00

Location: F 102

Invited Talk

MO 23.1 Thu 14:00 F 102

Ultrafast Dynamics of Electronic Excitations in Organic Materials and Structures — ●STEFAN LOCHBRUNNER, HENNING MARCINIAK, FRANZISKA FENNEL, and STEFFEN WOLTER — University of Rostock, 18051 Rostock

In future, supramolecular organic structures will be most probably employed in a wide range of photonic devices like organic solar cells and light emitting diodes. Therefore, the behavior of their fundamental electronic excitations, so-called Frenkel excitons, is subject of intense research activities. One key element is the diffusion of excitons which depends sensitively on the degree of order in the organic material. Our femtosecond pump-probe experiments on different systems show that it is possible to discriminate between different relaxation scenarios and to provide absolute numbers for local mobilities.

In a disordered organic material energetic down hill migration within the inhomogeneous distribution of site energies resulting in a low exciton mobility is observed and simulated by Förster transfer processes [1]. In J-aggregates the degree of order is much higher and the excitons are highly mobile throughout their lifetime. Modeling of the observed exciton-exciton annihilation dynamics reveals that the mobility is in this case strictly one dimensional. Contrary, in microcrystalline pentacene three dimensional diffusion is found and traps restrict the mobility of the excitons [2].

- [1] F. Fennel and S. Lochbrunner, *Phys. Rev. B* **85** (2012), 094203.
 [2] H. Marciniak, I. Pugliesi, B. Nickel, and S. Lochbrunner, *Phys. Rev. B* **79** (2009), 235318.

MO 23.2 Thu 14:30 F 102

Singlet exciton size in (6,5) SWNTs revisited — ●CHRISTOPH MANN and TOBIAS HERTEL — Institute of Physical and Theoretical Chemistry, Julius-Maximilian University Würzburg, Germany

Single wall carbon nanotubes (SWNTs) can be thought of as one-dimensional (1D) nanostructures consisting of rolled-up graphene sheets. Because of their unique electronic, mechanical and optical properties, an understanding of the excited-state dynamics in SWNTs is of great interest for both, better insight into fundamental photophysics of 1D systems in complex environments and for optoelectronic applications. The excited state dynamics are dominated by strongly bound Wannier-Mott type excitons. The electron-hole correlation length - i. e. the exciton size - represents one of their most basic photophysical characteristics and is therefore key for a better understanding of a variety of optical properties. The finite volume of the exciton in phase space corresponds to the exciton size and can be directly measured by femtosecond pump-probe spectroscopy and by using the Phase Space Filling model for analysis. Our experiments result in a surprisingly large exciton size compared to earlier experimental and theoretical publications. We discuss possible reasons for this discrepancy.

MO 23.3 Thu 14:45 F 102

Low Temperature Exciton Dynamics in Perylene Bisimide Aggregates — STEFFEN WOLTER, ●FRANZISKA FENNEL, KARL MAGNUS WESTPHAL, and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock

In this contribution a perylene bisimide dye is investigated which assembles into one-dimensional J-aggregates at ambient conditions. It is a promising candidate for photonic applications due to its high quantum yield and exciton mobility. In first temperature dependent experiments, we were able to switch between H-type and J-type aggregates by varying the aggregate length and found, that only in the latter case diffusion driven exciton-exciton annihilation occurs [1]. Our studies focus now on the exciton dynamics at low temperatures to characterize the influence of dynamic and static disorder.

We present stationary and femtosecond pump-probe spectra down to liquid nitrogen temperature using a continuous flow cryostat. They indicate that at low temperatures a certain amount of static disorder remains and prevents the exciton wavefunction from spreading over more than a few molecules. However, the excitons stay mobile and exciton-exciton-annihilation again happens to be a prominent decay mechanism. The mobility seems to be governed by a delicate interplay between static disorder and thermal fluctuations. The exciton diffusion properties at room temperature and at 77 K are compared

with respect to the delocalization length, diffusion constant and static disorder.

- [1] Wolter S., Aizezers J., Fennel F., Seidel M., Würthner F., Kühn O., Lochbrunner S. *New J. Phys.* **14**, 105027 (2012)

MO 23.4 Thu 15:00 F 102

Femtosecond Time-Resolved Characterization of Single PTCDA Nanocrystals — ●TAHIR ZEB KHAN, KHADGA J. KARKI, MAHESH NAMBOODIRI, and ARNULF MATERNY — Research Center for Functional Materials and Nanomolecular Science, Jacobs University, Campus Ring 1, D-28759 Bremen, Germany

The organic semiconductor 3,4,9,10 perylene tetra carboxylic dianhydride (PTCDA) is an important model system, which helps to gain information about the processes playing a role in organic electronic devices. We have investigated thin films formed by PTCDA nanocrystals. Comparing results obtained from transient absorption experiments with different spatial resolution from few micrometers down to sub-100-nanometer resolution, different lifetimes of the photoinduced exciton states could be observed. The high spatial resolution was obtained by using a system combining femtosecond time-resolved spectroscopy with a scanning near-field optical microscope (SNOM). A series of experiments has been performed, which yielded information about the dependence of the exciton dynamics on crystallite size, layer thickness, and exciton density. We demonstrate that the SNOM approach does not only help to avoid structural inhomogeneities, but also yields results with much more well-defined excitation intensity. The latter plays an important role in nonlinear effects and specifically strongly influences the exciton annihilation dynamics in the S_1 state of PTCDA. A short review of the results will be presented.

MO 23.5 Thu 15:15 F 102

Simulation of Laser Induced Fluorescence (LIF) Spectra of Conjugated Polymers — ●RUT VON WALDENFELS, MICHAEL WALTER, and MICHAEL MOSELER — Physikalisches Institut, Universität Freiburg

Conjugated polymers are materials of great interest since they can be used as active semiconductors in optoelectronic devices e.g. light emitting diodes or organic solar cells. In optoelectronic devices these polymers are part of the molecular donor-acceptor complexes which form the active layer for the conversion of light energy into electric current and vice versa. As a part of the conversion charge transfer from the donor to the acceptor molecule takes place which is not fully understood. It is particularly difficult to decide which parameters, like structure, confirmation and distance between donor and acceptor significantly influence the charge transfer process.

We simulated the vibrational resolved spectrum for the transition from the electronic ground state to the first excited state of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and showed that it matches excellently the measured laser induced fluorescence (LIF) spectrum. Due to the helium nanodroplet environment at ultralow temperatures the measurement achieves an outstanding precision compared to other methods and therefore could be used as a benchmark to validate our theoretical model. I also present the application of the method to zinc phthalocyanine (ZnPc), a widely used electron donor material in organic solar cells. Furthermore, we applied our method to a donor-acceptor complex of ZnPc and a C_{60} molecule.

Invited Talk

MO 23.6 Thu 15:30 F 102

Noise-Induced Förster Resonant Energy Transfer between Orthogonal Dipoles in Photoexcited Molecules — ●PETER NALBACH¹, IGOR PUGLIESI², HEINZ LANGHALS³, and MICHAEL THORWART¹ — ¹I. Institut für Theoretische Physik, Universität Hamburg — ²II. Lehrstuhl für BioMolekulare Optik, Ludwig-Maximilians-Universität München — ³Department of Chemistry, Ludwig-Maximilians-Universität München

Förster resonance energy transfer (FRET) has become a process of ubiquitous importance for proximity measurements of light absorbing and fluorescent structures. Recent experiments, however, in a perylene bisimide dyad, where donor and acceptor dipoles are perfectly orthogonal in equilibrium and, thus, FRET should vanish, show energy transfer with near unit quantum yield.

We show [1] that FRET in an orthogonally arranged donor-acceptor

pair can be induced by environmental noise. Environmental fluctuations break the strict orthogonal dipole arrangement and cause effective fluctuating excitonic interactions. Using a scaling argument, we show that interaction fluctuations are coupled to those of the energy levels and are strong enough to induce large FRET rates. We discuss the temperature dependence and predict a modified distance dependence

as compared to standard Förster theory. In summary, our findings show that the basic FRET theory has to be extended and we highlight the importance of environmental fluctuations for energy transfer processes.

[1] P. Nalbach, I. Pugliesi, H. Langhals, and M. Thorwart, Phys. Rev. Lett. 108, 218302 (2012).