

## MO 9: Femtosecond Spectroscopy II

Time: Tuesday 10:30–12:30

Location: V38.03

## Invited Talk

MO 9.1 Tue 10:30 V38.03

**The Interplay between Electron Transfer and Förster Resonant Energy Transfer** — ●IGOR PUGLIESI<sup>1</sup>, PATRICK KÖLLE<sup>2</sup>, REGINA DE VIVIE RIEDLE<sup>2</sup>, HEINZ LANGHALS<sup>2</sup>, and EBERHARD RIEDLE<sup>1</sup> — <sup>1</sup>BioMolekulare Optik, LMU München — <sup>2</sup>Dept. Chemie, LMU München

Energy and electron transfer are two fundamental processes on which the functioning of photoactive biological systems, solar cells and optoelectronic devices is based. The rates of these two processes can be described by Fermi's Golden Rule as they are both mediated by electronic coupling between donor and acceptor. This points to an intimate relation of energy and electron transfer on the electronic level. While energy transfer induced electron transfer has been observed in many artificial and biological systems, the inverse connection has not yet been investigated. Here we present an extended set of perylene diimide dyads with an donor-spacer-acceptor motif undergoing intramolecular FRET. Although the photoexcited donor is initially quenched by electron transfer from the spacer, after back transfer the energy of the donor is surprisingly transferred to the acceptor. Through broadband pump-probe measurements and high level *ab-initio* calculations we show that the donor-spacer electron transfer state itself is responsible for the energy transfer via multipole-multipole interactions with the locally excited state of the acceptor. The dyads presented here are a first example that shows how electron transfer can be connected to energy transfer for the use in novel photovoltaic and optoelectronic devices.

MO 9.2 Tue 11:00 V38.03

**Time-resolved studies on the photoinduced electron transfer in mixed-valence donor-acceptor oligomers** — ●FLORIAN KANAL<sup>1</sup>, STEFAN RUETZEL<sup>1</sup>, HAN LU<sup>2</sup>, CHRISTOPH LAMBERT<sup>2</sup>, and TOBIAS BRIXNER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany — <sup>2</sup>Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Mixed-valence triarylamine-donor-triarylmethyl-acceptor compounds are interesting model systems for investigating photoinduced electron transfers. These compounds possess a broad absorption band in the near infrared spectral region originating from an intervalence charge transfer (IVCT).

Here, we present femtosecond transient absorption experiments on two different alternating donor-acceptor triads consisting of a donor-acceptor-donor and an acceptor-donor-acceptor pattern. For comparison the respective donor-acceptor subunit as well as the subunit dimer were also investigated. By using the output of an amplified Ti:Sapphire femtosecond laser one can pump the systems directly into the IVCT state. The reduced acceptor as well as the oxidized donor show typical transient absorption bands, which are probed with a whitelight supercontinuum. The molecular dynamics are unraveled by a global data fitting procedure. Environment-dependent contributions of the dynamics are identified by performing the experiments in solvents of different polarity.

MO 9.3 Tue 11:15 V38.03

**Impact of High Excitation Densities upon Excitons in Perylene Bisimide Aggregates** — ●MARCUS SEIDEL, STEFFEN WOLTER, and STEFAN LOCHBRUNNER — Universität Rostock, Institut für Physik, Universitätsplatz 3, 18055 Rostock

Transient absorption measurements are performed on substituted Perylene Bisimide Aggregates with intense pump pulses that clearly saturate the ground state absorption of the molecules. The investigated Perylene Bisimides form J-aggregates at room temperature if solved in a nonpolar solvent with sufficiently high concentration [1]. Since the fluorescence quantum yield and the exciton diffusion length of these aggregates are high [1,2], they might be very suitable components for optoelectronic devices such as organic solar cells. Exciton-Exciton-Annihilation has been observed as the dominating interaction at moderately high excitation densities [2]. Although the interaction itself is not known in detail, it is assumed that two- and multi-excitonic states, resp. play an important role in the light induced dynamics of the quasi-particles. In a first approach to detect these multi-excitonic states in fs-pump-probe measurements, intense laser pulses are utilized

to generate high excitation densities. The corresponding transient absorption spectra reveal a fast decaying component, which is considered as a multi-excitonic state signature.

[1] Li X.-Q., Zhang X., Ghosh S., Würthner F., Chem. Eur. J. 14, p.8074 - p.8078 (2008)

[2] Marciniak H., Li X.-Q., Würthner F., Lochbrunner S., J. Phys. Chem. 115, p.648 - p.654 (2011)

MO 9.4 Tue 11:30 V38.03

**Ultrafast emission quenching in a perylene diimide by structure rearrangement induced electron transfer from its substituent** — ●PATRICK KÖLLE<sup>1</sup>, ARTUR NENOV<sup>1</sup>, UWE MEGERLE<sup>2</sup>, PATRIZIA KROK<sup>2</sup>, HEINZ LANGHALS<sup>1</sup>, REGINA DE VIVIE-RIEDLE<sup>1</sup>, and EBERHARD RIEDLE<sup>2</sup> — <sup>1</sup>Ludwig-Maximilians-Universität München, Department Chemie, Germany — <sup>2</sup>Ludwig-Maximilians-Universität München, Lehrstuhl für BioMolekulare Optik, Germany

The ultrafast excited-state dynamics of the fluorescent perylene diimide chromophore and its non-fluorescent amino-functionalized derivative are investigated by transient spectroscopy and quantum chemical calculations. The fluorescent system shows no dynamics in the sub-nanosecond time region. For the functionalized molecule the stimulated emission signal decays rapidly on a sub-picosecond timescale, while the excited state absorption decreases with a time constant of several picoseconds. The theoretical analysis assigns the fast decay to a charge transfer from the amino substituent to the perylene diimide chromophore. The transfer is made possible by a decrease of the N-N distance and a planarization of the substituent as the system moves away from the Franck-Condon point. Experiments in different solvents demonstrate that the dynamics of this fluorescence quenching correlate with the solvation time. The rapid relaxation from the charge transfer state into the ground state is observed on a picosecond timescale and is attributed to a passage through a conical intersection.

MO 9.5 Tue 11:45 V38.03

**Introducing a new concept to understand excited state dynamics in polyenes: The dynamophore** — ●OLIVER SCHALK<sup>1,2</sup>, ANDREY E. BOGUSLAVSKIY<sup>1</sup>, MICHAEL S. SCHURMAN<sup>1</sup>, EBERHARD RIEDLE<sup>2</sup>, and ALBERT STOLOV<sup>1</sup> — <sup>1</sup>SIMS, Ottawa, Canada — <sup>2</sup>BioMolekulare Optik, LMU, München

In organic molecules, UV- and vis-photons are absorbed by a chromophore, which constitutes the part of a molecule where the electronic transition for a given spectral band is localized. However, the dynamics induced by these photons may take place in a distinct region of the molecular framework. We define this region as dynamophore, i.e. the entity where the nuclear dynamics upon light absorption are mainly localized. This concept allows for systematizing recurring patterns in the relaxation pathway of different molecules and provides the possibility to develop a simplified model for the photodynamics. In this presentation, we elaborate on this new concept and show first examples from our time resolved photoelectron studies and *ab initio* calculations on small polyenes such as butadiene, cyclopentadiene [1], and cyclohexa-1,4-diene [2]. These examples emphasize a trend toward the localization of excited state dynamics, and illustrate the importance of Franck-Condon active modes in the selection of a specific dynamophore.

[1] O. Schalk *et al.* J. Phys. Chem. A 114, 4508 (2010).

[2] O. Schalk *et al.* J. Am. Chem. Soc. 131, 16451 (2011).

MO 9.6 Tue 12:00 V38.03

**Reaction Dynamics of a Molecular Switch Unveiled by Coherent Two-Dimensional Electronic Spectroscopy** — ●MARTIN KULLMANN, STEFAN RUETZEL, JOHANNES BUBACK, PATRICK NUERNBERGER, and TOBIAS BRIXNER — Institut für Physikalische und Theoretische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Coherent two-dimensional electronic spectroscopy is usually employed on molecular species with fixed geometric configuration. Here we present two-dimensional Fourier-transform electronic spectra of dissolved 6,8-dinitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline], a photochromic system present in two ring-open forms which differ by a cis/trans configuration of a double bond. Both isomers undergo a photo-induced ring closure.

The two-dimensional spectra, recorded with 20 fs pump pulses centered at 605 nm and a supercontinuum probe covering the complete visible spectral range, allow for a detailed analysis of the photophysics and photochemistry of the two isomers, and directly reveal that cis/trans isomerization among them does not play a major role [1]. This experiment demonstrates the potential of two-dimensional electronic spectroscopy for reactive processes.

[1] M. Kullmann, S. Ruetzel, J. Buback, P. Nuernberger, and T. Brixner, *J. Am. Chem. Soc.* 133, 13074, (2011).

MO 9.7 Tue 12:15 V38.03

**Femtosecond Pump-Probe Scanning Near-Field Optical Microscopy (PP-SNOM): Sub-Wavelength Resolution Chemical Imaging and Local Dynamics** — •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

Femtosecond time-resolved pump-probe (PP) spectroscopy techniques allow for the investigation of ultrafast dynamics of molecules. Scanning near-field optical microscopy (SNOM) is capable of generating images with spatial resolution below diffraction limit. In our work, we have combined these two techniques enabling us to record nanoscale images non-invasively along with chemical specificity and local probing of the molecular dynamics. We present results of PP-SNOM investigations of thin films of the organic semiconductor 3,4,9,10 perylene tetra carboxylic dianhydride (PTCDA). The exciton dynamics of a 160 nm thick PTCDA layer composed of nano-crystals on glass was locally probed with a SNOM tip allowing for 100 nm spatial resolution. Intensity-dependent exciton dynamics observed at exciton densities higher than  $10^{19} \text{ cm}^{-3}$  is attributed to exciton-exciton annihilation. Differences found for the annihilation constant found in far and near-field investigations are discussed.