

## MO 16: Femtosecond Spectroscopy II

Time: Thursday 14:00–16:15

Location: f102

MO 16.1 Thu 14:00 f102

**Sensitized photoswitching by ultrafast electronic energy transfer in a benzimidazole-naphthopyran donor-acceptor dyad** — SHUANGQING WANG, SEBASTIAN MEGOW, MATS BOHNSACK, ●FALK RENTH, and FRIEDRICH TEMPS — Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, 24098 Kiel, Deutschland

The excited-state dynamics of a molecular dyad with a benzimidazole (PPBI) donor and a naphthopyrane (DPNP) photochromic switch as acceptor was studied by static and femtosecond time-resolved spectroscopies and quantum chemical calculations. The static absorption spectrum of the dyad and calculations indicate that the electronic coupling between the donor and acceptor in the electronic ground state is weak. Selective photoexcitation of the PPBI subunit at 310 nm shows a strong quenching of the PPBI fluorescence in the dyad compared to free PPBI. The corresponding transient absorption maps for the dyad and its constituents and measurements of the transient absorption anisotropy decay reveal a quantitative electronic energy transfer (EET) from the PPBI\*-DPNP donor-excited state to the PPBI-DPNP\* acceptor-excited state with a time constant of  $2.90 \pm 0.60$  ps. This reduces the excited-state lifetime of PPBI from 1.4 ns to a few ps and enables ultrafast ring-opening of the DPNP to the merocyanine form. Quantitative modeling assuming Förster resonance energy transfer (FRET) provided an EET time estimate of 1.2–4.2 ps and confirmed FRET as EET mechanism. Our results highlight the feasibility of functional devices utilizing FRET for sensitized photoswitching.

MO 16.2 Thu 14:15 f102

**Ultrafast Triplet Formation and Molecular Vibrations in Halogenated Tetraazaperopyrenes** — ●NIKOLAUS WOLLSCHIED<sup>1</sup>, BENJAMIN BENJAMIN<sup>2</sup>, VAISHNAVI RAO<sup>1</sup>, FELIX BERGER<sup>1</sup>, JOSE L.P. LUSTRES<sup>1</sup>, MARCUS MOTZKUS<sup>1</sup>, SEBASTIAN HÖFENER<sup>3</sup>, JANA ZAUMSEIL<sup>1</sup>, LUTZ H. GADE<sup>2</sup>, and TIAGO BUCKUP<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, Ruprecht-Karls University Heidelberg, Germany — <sup>2</sup>Institute of Organic Chemistry, Ruprecht-Karls University Heidelberg, Germany — <sup>3</sup>Institut für Physikalische Chemie, Karlsruher Institut für Technologie, Germany

Tetraazaperopyrenes are air-stable n-type semiconductors which can be used in organic field effect transistors. By introducing halogen substituents to the aromatic backbone, structure property relationships such as energy levels can be tuned systematically. [1] This allows for a methodical investigation of photodynamics via femtosecond transient absorption in solution and zonecast thin films. In both cases, triplet formation is observed, occurring on vastly different timescales and via two different pathways: In solution, intersystem crossing is observed on the nanosecond timescale, correlating with substituent mass and energy detuning. In thin films, the triplet states are formed by singlet fission in a much faster time scale. Moreover, Raman activity of low frequency vibrational modes during singlet fission is observed and correlated with the formation of the biexcitonic state. Quantum chemical calculations of electronic states energy and spectra are presented. [1] Hahn et al., Chem. Eur. J., 21, 17691, (2015).

MO 16.3 Thu 14:30 f102

**Intramolecular Singlet Fission in Tetraaza-TIPS-Pentacene Oligomers: Triplet formation via the Biexcitonic State** — ●NICOLÒ ALAGNA<sup>1,2</sup>, JOSE L.P. LUSTRES<sup>1,2</sup>, NIKOLAUS WOLLSCHIED<sup>1,2</sup>, QINGQING LUO<sup>1</sup>, JIE HAN<sup>3</sup>, ANDREAS DREUW<sup>2,3</sup>, FLORIAN GEYER<sup>4</sup>, VICTOR BROSIUS<sup>4</sup>, UWE H.F. BUNZ<sup>4</sup>, TIAGO BUCKUP<sup>1,2</sup>, and MARCUS MOTZKUS<sup>1,2</sup> — <sup>1</sup>Physikalisch Chemisches Institut, Ruprecht-Karls University, Germany — <sup>2</sup>Centre for Advanced Materials, University of Heidelberg, Germany — <sup>3</sup>Interdisziplinäres Zentrum für Wissenschaftliches Rechnen, Ruprecht-Karls University, Germany — <sup>4</sup>Organisch Chemisches Institut, Ruprecht-Karls University, Germany

Singlet fission (SF) is a photo-induced process where an excited singlet exciton is converted into two triplet states of nearly half energy. It has been shown for several systems in the liquid phase and in thin films. In this work, we investigate SF in diethynylbenzene-linked tetraaza-TIPS-pentacene dimers with different geometry configurations. Analysis of transient absorption and fluorescence measurements shows an efficient SF ( $\Phi_T > 160\%$ ) in the ortho and meta dimer as well as in the

(1,3,5) trimer. Our results show that the formation of the long-lived triplet state  $T_1$  takes place via an intermediate component, called the correlated triplet pair or biexcitonic state. The long-lived triplet state  $T_1$  formed by SF is, however, only a fraction compared to the total amount of the triplet-pair generated. We show that the  $^1(TT)$  state decays via annihilation and triplet fusion mechanisms.

MO 16.4 Thu 14:45 f102

**Signatures of halogen-bond interactions in time-resolved fluorescence spectroscopy** — ●BASTIAN GEISSLER<sup>1</sup>, SARAH KHANI<sup>2</sup>, ELRIC ENGELAGE<sup>3</sup>, CHRISTOF HAETTIG<sup>3</sup>, STEFAN HUBER<sup>3</sup>, and PATRICK NUERNBERGER<sup>1</sup> — <sup>1</sup>Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg — <sup>2</sup>Center for Theoretical Chemistry, Ruhr-Universität Bochum, 44780 Bochum — <sup>3</sup>Organische Chemie I, Ruhr-Universität Bochum, 44780 Bochum

The formation of non-covalent halogen bonds between a halogenated organic compound and a Lewis base in solution is an active field of research with relevance to various chemical reactions and biological processes. However, the complex spectroscopic behavior of such mixtures and the assignment of (transient) spectroscopic signatures to halogen-bond formation in solution are still rather unexplored.

In this contribution, we focus on benzoimidazolium derivatives serving as halogen bond donors and pyridine derivatives as Lewis base acceptors dissolved in acetonitrile. We identify the impact of additional counterions  $[OTf]^-$  and  $[BAr^F_4]^-$  on the fluorescence properties of these donor-acceptor pairs. In addition to ultrafast transient absorption measurements, we perform time-resolved fluorescence streak imaging studies to scrutinize halogen bonding and competing complex formations. Whereas transient absorption indicates an ultrafast reversible halogen-bond cleavage upon illumination, the fluorescence studies additionally reveal new insights concerning the role of complexation with  $[OTf]^-$  and  $[BAr^F_4]^-$ .

MO 16.5 Thu 15:00 f102

**Understanding ring-closing and ring-opening reaction of photochromic molecule fulgide in bulk crystal** — ●SOUMYAJIT MITRA<sup>1</sup>, SIMON.F BITTMANN<sup>1</sup>, SCOTT MURPHY<sup>2</sup>, AJAY JHA<sup>1</sup>, and R.J.DWAYNE MILLER<sup>1,3</sup> — <sup>1</sup>Atomically Resolved Dynamics Group, Max Planck Institute for the Structure and Dynamics of Matter, CFEL, Luruper Chaussee 149, 22761, Hamburg, Germany — <sup>2</sup>Department of Chemistry and Biochemistry, Research and Innovation Centre, University of Regina, 3737, Wascana Parkway, Regina, SK S4S 0A2, Canada — <sup>3</sup>Departments of Chemistry and Physics, University of Toronto, 80 St. George Street, Toronto, ON M5S3H6, Canada

Coupling of resonant light field with photochromic molecules (also known as molecular photoswitches) changes the orientation within the molecular structure, which gets manifested in differential optical or mechanical properties. The structural understanding of this photo-switching process holds the key to the rational design of next generation molecules. In this work, we are employing ultrafast transient absorption measurements in fulgide crystals to study complex interplay of different electronic states due to the presence of two possible reaction pathways: isomerization and electrocyclization. The role of lattice phonons in directing localized chemical reactions will be discussed. Our work pave the way towards understanding and thereby controlling of reaction pathways in complex molecules with multi-photoswitching centers.

MO 16.6 Thu 15:15 f102

**Simulating the XUV spectra of ultrafast dissociating vinyl bromide** — ●FLORIAN ROTT<sup>1</sup>, MAURIZIO REDUZZI<sup>2,3</sup>, THOMAS SCHNAPPINGER<sup>1</sup>, STEPHEN R. LEONE<sup>2,4,5</sup>, and REGINA DE VIVIE-RIEDLE<sup>1</sup> — <sup>1</sup>Department of Chemistry, LMU Munich, Germany — <sup>2</sup>Department of Chemistry, University of California, Berkeley, USA — <sup>3</sup>ICFO - The Institute of Photonics Sciences, The Barcelona Institute of Science and Technology, Spain — <sup>4</sup>Chemical Sciences Division, Lawrence Berkeley National Laboratory, USA — <sup>5</sup>Department of Physics, University of California, Berkeley, USA

The ultrafast dissociation of vinyl bromide after strong-field excitation is characterized experimentally and theoretically. After a multiphoton excitation of the  $\pi\pi^*$  transition, the relaxation process is illuminated via Attosecond Transient Absorption Spectroscopy (ATAS)

using the bromine M-edge. Using non-adiabatic molecular dynamics at the complete active space self-consistent field (CASSCF) level of theory including singlet and triplet states we simulated the dissociation after excitation to the bright  $\pi\pi^*$  state. For the calculation of the XUV absorption spectra the bromine  $3d$  core-excited states as well as the valence excited states of vinyl bromide were computed using the restricted active space perturbation theory (RASPT2). Combining the structural information from the dynamics simulation with the calculated XUV spectra we are able to simulate the corresponding time-dependent transient absorption spectrum of vinyl bromide. The simulated spectrum shows a good agreement with the experimental ATAS trace in the relevant energy range.

MO 16.7 Thu 15:30 f102

**Ultrafast Dynamics of Fe(II)-based Photosensitizers** — ●AYLA PÄPCKE<sup>1</sup>, JAKOB STEUBE<sup>2</sup>, PHILIPP DIERKS<sup>2</sup>, YANNIK VUKADINOVIC<sup>2</sup>, MATTHIAS BAUER<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institute of Physics and Department of Life, Light and Matter, University of Rostock, 18051 Rostock (Germany) — <sup>2</sup>Institute of Inorganic Chemistry and Center for Sustainable Systems Design (CSSD), University of Paderborn, Warburger Straße 100, 33098 Paderborn (Germany)

Water splitting systems are currently intensively investigated as a potential source for renewable energy. In these systems metal complexes are often used as photosensitizers for absorbing the sunlight. Most of these complexes contain noble metals like iridium and ruthenium. To replace these rare and expensive metals, iron is a promising candidate since it is earth-abundant, inexpensive, environmentally benign, and results in broad absorption bands in the visible spectral region. After absorption of light a metal-to-ligand charge transfer state is populated which should have a long lifetime in the ns-regime to allow for efficient intermolecular interaction. However, in iron(II)-complexes this lifetime is in the fs to ps-range and thereby relatively short. To extend the lifetime several approaches in the design of the complexes are pursued, e.g. the use of strong  $\sigma$ -donating N-heterocyclic carbene or cyclometalating ligands. Here we present ultrafast pump-probe experiments on such complexes. The electronic relaxation path is characterized by means of the transient absorption spectra and the success of the chemical design strategy is assessed on the basis of the observed lifetimes.

MO 16.8 Thu 15:45 f102

**Point-Mutation (W76F) in Anabaena Sensory Rhodopsin Investigated by Femtosecond Time-Resolved Spectroscopy** — ●OSKAR KEFER<sup>1</sup>, REI ABE-YOSHIZUMI<sup>2</sup>, NICOLÓ ALAGNA<sup>1</sup>, HIDEKI KANDORI<sup>2</sup>, and TIAGO BUCKUP<sup>1</sup> — <sup>1</sup>Physikalisch-Chemisches

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ASR is a microbial retinal protein (MRP) that contains two isomeric chromophores, which can undergo ultrafast photo-isomerization. Point mutation inside the retinal pocket of anabaena sensory rhodopsin (ASR) is an efficient way to investigate the structural changes during the isomerization of the retinal protonated Schiff-base (RPSB). Pre-distortion of the conjugated  $\pi$ -framework of retinal is believed to be a major factor in the acceleration of the isomerization rate. This pre-distortion is observable in the ground-state vibrational Raman activity of the  $C_{14}$ -H-out-of-plane (HOOP) mode (around  $800\text{cm}^{-1}$ ) and present in some ASR mutants with accelerated dynamics. Coherent time-resolved vibrational and femtosecond pump-probe experiments were used to investigate the structural changes of RPSB in a W76F point-mutated ASR derivative. By comparing resonant DFWM-measurements with non-resonant DFWM-measurements the vibrational modes of the excited-state manifold can be obtained. This mutant shows no significant HOOP-mode activity in the ground state vibrational Raman spectrum compared to wild-type ASR, further corroborating the role of pre-distortion in the Retinal isomerization.

MO 16.9 Thu 16:00 f102

**Generation of broad bandwidth sub-30 fs deep ultraviolet pulses at high repetition rates** — ●LUKAS BRUDER<sup>1</sup>, LUKAS WITTENBECHER<sup>2</sup>, PAVEL KOLESNICHENKO<sup>2</sup>, and DONATAS ZIGMANTAS<sup>2</sup> — <sup>1</sup>Institute of Physics, University of Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Germany — <sup>2</sup>Department of Chemical Physics, Lund University, P.O. Box 124, 22100 Lund, Sweden

The generation of deep ultraviolet optical pulses featuring broad spectral bandwidth and short pulse durations is a challenging task, especially when using high repetition rate ( $> 100\text{ kHz}$ ) laser systems that provide only low pulse energies ( $< 10\ \mu\text{J}$ ) to drive the nonlinear conversion processes. Yet, high repetition rates are highly desirable in spectroscopic applications to improve statistics. Based on achromatic phase matching [1], we have recently accomplished the generation of 265 nm-pulses with 10-20 nm bandwidth using input pulse energies of  $0.5\ \mu\text{J}$  at a repetition rate of 200 kHz. Despite the low pulse energies, we reach comparable conversion efficiencies (25 %) than in [1]. We currently compress the pulses to 25 fs, but compression to the sub-10 fs regime should be feasible.

[1] P. Baum, S. Lochbrunner, and E. Riedle, *Opt. Lett.* **29**, 1686 (2004).