

## MO 3: Femtosekundenspektroskopie I

Zeit: Montag 14:00–16:00

Raum: 3G

**Hauptvortrag** MO 3.1 Mo 14:00 3G  
**Dynamics and Mobility of Electronic Excitations in Organic Materials** — ●STEFAN LOCHBRUNNER — Institut für Physik, Universität Rostock, Universitätsplatz 3, 18055 Rostock

In organic materials and thin layer systems designed for optoelectronics applications complex energy transport and electronic relaxation processes govern the performance. Since many of them contribute it is difficult to derive a microscopic understanding purely from measuring device parameters. Femtosecond spectroscopy provides complementary information since it probes the primary processes initiated by the absorption of a photon and is predominantly sensitive to local effects. Our pump-probe experiments on different systems with 30 fs time resolution show that it is possible to discriminate between different relaxation scenarios and to provide absolute numbers for the local mobility. For thin microcrystalline pentacene films we find that the originally excited Frenkel excitons decay within 70 fs to a non fluorescing species which is still mobile. Its exact nature is currently under investigation. The subsequent decay of the exciton population can be modeled assuming that diffusion driven exciton-exciton annihilation takes place and a significant concentration of traps exists which can immobilize the excitons. A diffusion constant of  $5 \cdot 10^4 \text{ cm}^2/\text{s}$ , a trap concentration of  $2 \cdot 10^{19} \text{ cm}^{-3}$ , and a lifetime of 850 ps for the trapped excitons are obtained.[1] In unordered polymers the large spreading of site energies restricts the exciton diffusion length. To circumvent this problem perylene bisimide dyes are incorporated in a polymer matrix with a high concentration to allow for exciton migration via Förster energy transfer. A fast transfer of 1.5 ps between the dye molecules is derived from the anisotropy decay indicating efficient exciton migration.[2] However, the lifetime of the excitons is limited due to trapping by dimers. In the next step we want to avoid the dimer formation and to achieve diffusion lengths in the order of the layer thickness. To look into the dynamics of one dimensional systems perylene bisimide aggregates are investigated. Here an ultrafast relaxation associated with weak signal oscillations is found pointing to the formation of excimers. On the picosecond time scale no further signal changes are observed indicating that the excimers are immobile and annihilation processes do not occur.

[1] H. Marciniak, M. Fiebig, M. Huth, S. Schiefer, B. Nickel, F. Selmaier, and S. Lochbrunner, *Phys. Rev. Lett.* **99** (2007) 176402.

[2] M. Schlosser and S. Lochbrunner, *J. Phys. Chem. B* **110** (2006) 6001.

MO 3.2 Mo 14:30 3G  
**Three-Pulse-Spectroscopy in neat water and aqueous solution** — ●MARTIN K. FISCHER, HRISTO IGLEV, and ALFRED LAUBEREAU — Physik-Department E11, Technische Universität München, 85748 Garching, Germany

The ultrafast generation and solvation of electrons in liquids is studied by pump-repump-probe spectroscopy. The application of a third pulse to excite the precursors of the fully hydrated electron leads to the manipulation of the relaxation process.

The technique was applied to study the dynamics in neat  $\text{H}_2\text{O}$ , 15mMol NaBr and 15mMol NaI aqueous solutions. The measured transients are compared to the corresponding pump-probe data. The observed increase in the yield of the long-lived hydrated electrons leads to a novel information about the generation process.

MO 3.3 Mo 14:45 3G  
**Ultrafast thermal melting of bulk ice** — ●STANISLAV PANDELOV, MARCUS SCHMEISSER, HRISTO IGLEV, and ALFRED LAUBEREAU — Physik-Department E11, Technische Universität München, 85748 Garching, Germany

Melting of ice is the most common structural transition and can provide us information about the microstructure of water. The ice-water phase transition after an ultrafast temperature jump is studied in protonated and isotopically mixed ice using 2-color IR spectroscopy [1, 2]. For energy depositions beyond the limit of superheating of the solid phase ( $330 \pm 10 \text{ K}$ ) [3] partial melting is observed. The process occurs in two steps: (i) ultrafast thermal bulk melting of the excited ice lattice within  $5 \pm 2 \text{ ps}$  and (ii) secondary melting at the generated phase boundaries with a time constant of  $33 \text{ ps}$  [3]. The latter process (interfacial melting) is found to consume energy amounts in

agreement with the latent heat of melting and is accompanied by an accelerated temperature and pressure decrease of the residual ice component. This results support a thermally-driven melting mechanism starting with homogeneous nucleation in the bulk.

[1] H. Iglev, M. Schmeisser, K. Simeonidis, A. Thaller, A. Laubereau, *Nature* **439** 183 (2006).

[2] M. Schmeisser, A. Thaller, H. Iglev, A. Laubereau, *New J Phys* **8** (2006).

[3] M. Schmeisser, H. Iglev, A. Laubereau, *J Phys Chem B* **111** 11271 (2007).

MO 3.4 Mo 15:00 3G  
**Direct Femtosecond Observation of Tight and Loose Ion Pairs upon Photoinduced Bimolecular Electron Transfer** — ●KATRIN ADAMCZYK<sup>1</sup>, OMAR F. MOHAMMED<sup>2</sup>, NATALIE BANERJI<sup>2</sup>, JENS DREYER<sup>1</sup>, BERNHARD LANG<sup>2</sup>, ERIK T. J. NIBBERING<sup>1</sup>, and ERIC VAUTHEY<sup>2</sup> — <sup>1</sup>Max Born Institut für Nichtlineare Optik und Kurzzeit-spektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany — <sup>2</sup>Department of Physical Chemistry, University of Geneva, 30 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

Photoinduced bimolecular electron transfer reactions have been subject of intensive chemical dynamics research for many decades [1]. These processes play a key role in many areas of chemistry and biology, among these are photosynthesis, solar energy conversion, ET in proteins and biocatalysis. Generally accepted models suppose that charge separation in polar solvents leads to two geminate ion pairs, namely loose or solvent-separated ion pairs (LIPs) and tight or contact ion pairs (TIPs). We show that monitoring marker modes of the ion products [2] with polarisation-sensitive ultrafast infrared spectroscopy enables a differentiation of the contributions of these distinct ion pairs in the observed kinetics. We find that large exergonic electron transfer reactions predominantly occur in tight donor-acceptor pairs. Tight ion pairs are found to be highly anisotropic, revealing the importance of mutual orientation of the reactants and thus demanding refinement of theoretical models relying on spherical reaction species that solely involve reaction distances. [1] A. Weller, *Pure Appl. Chem.* **54**, 1885 (1982). [2] O. F. Mohammed et al., *J. Phys. Chem. A* **110**, 13676 (2006).

MO 3.5 Mo 15:15 3G  
**Charakterisierung der Femtosekunden Mehrphotonen-Ionisation von  $\text{N}_2$  durch rotationsaufgelöste Fluoreszenzspektroskopie** — ●ANDREAS WIRSING<sup>1</sup>, JÜRGEN PLENGE<sup>1</sup>, CHRISTOPHER RASCHPICHLER<sup>1</sup>, MICHAEL MEYER<sup>2</sup> und ECKART RÜHL<sup>1</sup> — <sup>1</sup>Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin — <sup>2</sup>LIXAM, Centre Universitaire Paris-Sud, Batiment 350, F-91405 Orsay Cedex, Frankreich

Die Wechselwirkung von  $\text{N}_2$  mit Femtosekunden-Laserpulsen wurde in den letzten Jahren eingehend untersucht. Zur Charakterisierung der dabei auftretenden Ionisationsprozesse werden gewöhnlich die gebildeten Ionen oder Photoelektronen detektiert. Ein komplementärer Ansatz beruht auf der Fluoreszenzspektroskopie, die es im Gegensatz zur Photoelektronenspektroskopie aufgrund der höheren Auflösung ermöglicht, die Rotationsverteilung der elektronisch angeregten Stickstoffionen präzise zu ermitteln. Wir präsentieren rotationsaufgelöste Fluoreszenzspektren von  $\text{N}_2^+$  ( $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$  Übergang) nach der Multiphotonen-Ionisation von molekularem Stickstoff mit Femtosekunden-Laserpulsen bei  $\lambda=803,4 \text{ nm}$ . Aus den Fluoreszenzspektren wird die Rotationsanregung von  $\text{N}_2^+$  ( $B^2\Sigma_u^+$ ) ermittelt. Bei der Ionisation mit einem nahezu transformlimitierten Laserpuls wird eine Anregung der Rotationsniveaus  $J^+ = 1$  bis  $J^+ = 32$  des Ions beobachtet. Durch den Einsatz von gechirpten Laserpulsen kann die Rotationsanregung von  $\text{N}_2^+$  ( $B^2\Sigma_u^+$ ) kontrolliert werden. Mögliche Mechanismen der Kontrolle der Rotationsanregung werden diskutiert.

MO 3.6 Mo 15:30 3G  
**Few photon induced dissociative ionization of  $\text{N}_2$  at FLASH** — ●YUHAI JIANG<sup>1</sup>, LUTZ FOUCAR<sup>2</sup>, ARTEM RUDENKO<sup>1</sup>, MORITZ KURKA<sup>1</sup>, CLAUDIUS DIETER SCHRÖTER<sup>1</sup>, THORSTEN ERGLER<sup>1</sup>, KAI UWE KÜHNEL<sup>1</sup>, MARKUS SCHÖFFLER<sup>2</sup>, SVEN SCHÖSSLER<sup>2</sup>, TILO HAVERMEIER<sup>2</sup>, MATHIAS SMOLARSKI<sup>2</sup>, KYRA COLE<sup>2</sup>, THORSTEN

WEBER<sup>2</sup>, REINHARD DÖRNER<sup>2</sup>, STEFEN DÜSTERER<sup>3</sup>, ROLF TREUSCH<sup>3</sup>, PAUL RADCLIFFE<sup>3</sup>, ELKE PLÖNJES<sup>3</sup>, MICHAEL GENSCHE<sup>3</sup>, ROBERT MOSHAMMER<sup>1</sup>, and JOACHIM ULLRICH<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg — <sup>2</sup>Institut für Kernphysik, Universität Frankfurt, D 60486 Frankfurt — <sup>3</sup>DESY, Notkestrasse 85, 22607 Hamburg

The Free electron LASer at Hamburg (FLASH) delivers extreme ultraviolet (XUV) radiation at unprecedented intensities with femtosecond pulse durations. In combination with advanced multi-particle detection systems—the Heidelberg reaction microscope—this opens the door for mapping the dissociative multiple-ionization dynamics of molecules at ultrashort time scales. Multiple ionization of N<sub>2</sub> and in particular the fragmentation channels N<sub>2</sub><sup>2+</sup> → N<sup>+</sup> + N<sup>+</sup> and N<sub>2</sub><sup>3+</sup> → N<sup>+</sup> + N<sup>2+</sup> induced by two and three XUV-photon of 44 eV, respectively, have been studied using our coincidence technique. On the basis of the kinetic energy releases of ionic fragments and the known molecular potential curves of dissociative states, it was found that sequential photoabsorption of N<sub>2</sub><sup>2+</sup> (d<sup>3</sup>Π<sub>g</sub>) → N<sub>2</sub><sup>3+</sup> occurs at a time of about 20 fs after populating N<sub>2</sub><sup>2+</sup> by absorption of two photons from the ground state of

N<sub>2</sub>.

MO 3.7 Mo 15:45 3G

**Effect of Size Quantization on Interfacial Electron Transfer Dynamics in TiO<sub>2</sub> Nanoparticles** — ●HIRENDRA N. GHOSH — Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-85, India — Max-Born Institute for Nonlinear and Short Pulse Spectroscopy, 12489, Berlin, Germany

Interfacial electron transfer dynamics was carried out in alizarin sensitized TiO<sub>2</sub> nanoparticles with quantum size using femtosecond transient absorption (TA) spectroscopy. The TiO<sub>2</sub> nanoparticles have been synthesized by arrested precipitation method. Electron injection dynamics were found to be multi-exponential with time constants of 100 fs, 17 ps and 50 ps. This observation was explained on the basis discreteness of the conduction band levels due to finite size effect. The back electron transfer (BET) dynamics found to be very slow as compared to the bulk system. The result gives us direct proof of non-adiabatic electron transfer reaction in a strong binding dye like alizarin.