MO 52: Femtosecond Spectroscopy IV

Zeit: Donnerstag 14:00–15:45 Raum: 6B

MO 52.1 Do 14:00 6B

Ultrafast Fluorescence Quenching in a Naphthalene Bisimide Dye — Patrizia Krok[1], •Stefan Lochbrunner[1], Alfred Błaszczyk[2], Marcel Mayor[2], and Eberhard Riedle[1] — [1]Lehrstuhl für BioMolekulare Optik, LMU München — [2]Department für Chemie, Universität Basel

Naphthalen bisimide dyes are promising candidates for molecular electronics applications since their electronic structure can be efficiently tuned by substituents. In the case of two phenyl substituted naphthalene bisimide derivatives we find that the fluorescence quantum yield [1] and the emission lifetime of the naphthalene chromophore depend strongly on the number of carbon atoms in the linker between the chromophore and the phenyl substituent. While a benzyl thio substituted derivative emits reasonably strong fluorescence from the S_1 state, the fluorescence of a phenyl thio substituted derivative is reduced by a factor of 16. In a pump-probe experiment the transient absorption of both molecules was studied after selective excitation into the S_1, S_2, or the S_3 state. The experimental traces reveal an ultrafast nonradiative decay of the higher states into S_1. The lifetime of the stimulated emission from the S_1 state is 40 ps for the fluorescent dye and only 6 ps for the nonfluorescent dye. We argue that the fast decay is the result of an electron transfer from the phenyl substituent to the chromophore. The charge transfer state has a similar lifetime of also about 6 ps, which we understand as the time for the charge recombination.

[1] A. Błaszczyk, M. Fischer, C. von Hänisch, and M. Mayor, Helvetica Chimica Acta **89** (2006), 1986.

MO 52.2 Do 14:15 6B

The Fluorescence Signature of an Ultrafast H-Transfer — •Thomas Schmierer, Björn Heinz, and Peter Gilch — Department für Physik, Ludwig-Maximilians-Universität, Oettingenstr. 67, D-80538 München, Germany

Ortho-substituted nitro-arenes find widespread application in biotechnology as photo-labile protecting groups. The primary photo-process in these compounds is believed to be an H-transfer from the *ortho*-substituent to the nitro group. For one nitro-arene, *ortho*-nitrobenzaldehyde (NBA), it has recently been demonstrated that the product of this transfer is formed in ∼ 400 fs [1]. Here, we report on the femtosecond fluorescence signature of this transfer which has been recorded with a Kerr gate set-up [2]. NBA absorbs in the UV and its emission is extremely weak and short-lived. Therefore, special procedures are required to realize time-resolved measurements which will be outlined in the presentation. Implications of these measurements on the mechanism of the H-transfer will be discussed.

[1] S. Laimgruber et al., Angew. Chem. Int. Ed. 44 (2005) 7901
[2] B. Schmidt et al. Appl. Phys. B 76 (2003) 809

MO 52.3 Do 14:30 6B

Mode-selective vibrational energy transfer after infrared excitation of a hydrogen-bonded OH stretching vibration — •Valeri Kozich, Wolfgang Werncke, Jens Dreyer, Satoshi Ashihara, and Thomas Elsaesser — Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Strasse 2A, D-12489 Berlin, Germany

Vibrational energy relaxation in hydrogen bonds is of considerable importance for understanding ultrafast dynamics in many chemical and biological systems. We have studied the relaxation of the hydrogen-bonded OH stretching vibration of 2-(2'-hydroxy-5'-methyl-phenyl)benzotriazole (TINUVIN P) by ultrafast infrared-pump/Raman probe and infrared-pump/infrared probe spectroscopy. We determined a 200 fs lifetime for the OH stretching mode and revealed that intramolecular vibrational energy redistribution occurs through a few major channels that all involve combination and overtone bands of modes with considerable in-plane OH bending character. The most prominent role for the primary relaxation process is played by the mode with the largest OH bending contribution, thus highlighting the important role of energy transfer from stretching to bending motions in hydrogen bonds. Theoretical calculations of vibrational energy transfer rates based on a Fermi golden rule approach are in accordance with these experimental results.

MO 52.4 Do 14:45 6B

Catastrophic melting of ice at the limit of superheating — •Marcus Schmeisser, Hristo Iglev, and Alfred Laubereau — Physik-Department E11, Technische Universität München, 85748 Garching, Germany

Melting of ice is a process of universal relevance and considerable experimental and theoretical efforts have been invested to study this phenomenon. In our recent study of isotopically mixed ice [1, 2] we demonstrated that shock laser heating of bulk ice can overcome the common surface melting, leading to substantial superheating of the ice lattice.

Here, we present an experimental study of bulk melting of protonated and isotopically mixed ice. Using the recently developed ultrafast IR temperature jump technique of ice [1, 2] catastrophic melting of the excited ice lattice and further features were observed for the first time [3]. The partial melting process is accompanied by accelerated temperature and pressure decays of the residual ice component.

[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**, 104+ (2006).
[3] M. Schmeisser, H. Iglev, A. Laubereau, *subm.*

MO 52.5 Do 15:00 6B

Femtosecond dynamics of the reexcited species generated from the CTTS-State in aqueous solution — •Martin K. Fischer, Hristo Iglev, and Alfred Laubereau — Physik-Department E11, Technische Universität München, 85748 Garching, Germany

The dynamics of the atom:electron-pair and the solvated electron in aqueous solution are studied using femtosecond pump-probe and pump-repump-probe techniques. After excitation of 20 mM $I^-_{(aq)}$ with a laser pulse at 200 nm wavelength in the 2nd charge-transfer-to-solvent (CTTS)-band, the resulting electron release and relaxation dynamics are investigated using probing pulses in the range 450 to 3900 nm.

Direct evidence for the second, direct detachment channel is obtained in accordance with theoretical predictions. The quantum yield of hydrated electrons is found to increase drastically as compared to excitation at 242 nm and can be traced back to a new formation channel. We will also report on novel pump-repump-probe experiments observing for the first time the atom:electron pair state predicted by quantum simulations.

MO 52.6 Do 15:15 6B

Ultrafast Excimer Formation in Perylene Bisimide Aggregates — Stefan Schindlbeck[1], •Stefan Lochbrunner[1], Volker Dehm[2], and Frank Würthner[2] — [1]Lehrstuhl für BioMolekulare Optik, LMU München — [2]Institut für Organische Chemie, Universität Würzburg

Perylene bisimide dyes are versatile building blocks in organic electronics and their aggregates represent promising functional units. 1-dimensional aggregates are generated by self-assembly of tridodecylphenyl substituted perylene bisimide molecules [1]. We investigate the electronic structure of these aggregates with femtosecond absorption spectroscopy to provide the underlying knowledge for understanding the behavior of corresponding functional units. The transient spectrum observed after optical excitation into the first electronic absorption band consists of ground state bleach and a broad and structureless excited state absorption. No indications for a reasonable strong stimulated emission are found even at short delay times down to 100 fs. This is surprising since the absorption is associated with a strong transition dipole and points to an extremely fast change in the electronic wavefunction that reduces efficiently the oscillator strength. The results are explained by the formation of excimers and a reduction of the intermolecular distance. The electronic wavefunction exhibits charge transfer character in the potential minimum whereas the S_1 character of the monomer dominates in the Franck-Condon region.

[1] F. Würthner, Z. Chen, V. Dehm, and V. Stepanenko, Chem. Commun. **2006**, 1188.

MO 52.7 Do 15:30 6B

Ultrafast Exciton Dissociation in Micro Crystalline Pen-

tacene Films — •Henning Marciniak[1], Stefan Lochbrunner[1], Martin Huth[2], Stefan Schiefer[2], and Bert Nickel[2] — [1]Lehrstuhl für BioMolekulare Optik, LMU München — [2]Department für Physik und CeNS, LMU München

Micro crystalline thin films of organic molecules are frequently used in organic electronics applications. Their electronic structure and dynamics determine to a large extent the device behavior. We investigate with femtosecond absorption spectroscopy pentacene films prepared by vapor deposition which are used in many prototype applications. They consist of closely packed grains that are microcrystals formed by several monolayers of pentacene molecules [1]. 30 fs long pump pulses are applied to generate singlet excitons in the film. Transient spectra are measured with a white light as probe beam and time traces with compressed pulses resulting in a time resolution of 30 fs. The polarization dependent bleach spectra point to a fairly strong charge transfer character of the primary excitations. We find that the original exciton emission decays within 100 fs indicating that an ultrafast dissociation of the excitons into polarons or triplet excitons takes place. The recovery kinetics exhibits two components. One depends on the excitation energy and can be modeled with annihilation processes. A second component is interpreted as occupied traps which have a limited lifetime.

[1] B. Nickel, R. Barabash, R. Ruiz, N. Koch, A. Kahn, L. C. Feldman, R. F. Haglund, and G. Scoles, Phys. Rev. B **70** (2004), 125401.