

## MO 5: Femtosecond Spectroscopy I

Time: Tuesday 14:00–16:00

Location: F 102

MO 5.1 Tu 14:00 F 102

**Influence of TiO<sub>2</sub>/Perylene Interface Modifications on Electron Injection and Recombination Dynamics** — ●ROBERT SCHÜTZ, ANDREAS F. BARTELT, ANTJE NEUBAUER, RAINER EICHBERGER, and THOMAS HANNAPPEL — Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

Dye sensitized solar cells (DSSCs) operate by injecting electrons from the excited state of a light-harvesting dye into the continuum of conduction band states of a wide bandgap semiconductor. It is well known that the efficiency of DSSCs can be improved by controlling the interface energetics using molecular interface modifiers. Whereas this leads to a beneficial band level shifting, it also affects the interfacial electron injection and recombination dynamics. We used femtosecond transient absorption spectroscopy in the VIS region to demonstrate a retardation of the ultrafast injection and recombination dynamics by coadsorbing inert gases and solvents with increasing dipole moments on a TiO<sub>2</sub>/perylene interface. Model perylene dyes with different electronic couplings to the colloidal TiO<sub>2</sub> films were subject to precisely defined chemical environments. While coadsorption of N<sub>2</sub> and Ar doubled injection times compared to UHV, introduction of solvents led to retardations of up to 2 orders of magnitude which correlates well with the degree of polarity of the chemical species. The ultrafast component of the nonexponential back electron transfer was significantly reduced with coadsorbant polarity.

MO 5.2 Tu 14:15 F 102

**Ultrafast UV/IR spectroscopy of hydrogen bonded photoacid molecules** — ●MIRABELLE PRÉMONT-SCHWARZ<sup>1</sup>, DINA PINES<sup>2</sup>, EHUD PINES<sup>2</sup>, and ERIK T.J. NIBBERING<sup>1</sup> — <sup>1</sup>Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, D-12489 Berlin, Germany — <sup>2</sup>Department of Chemistry, Ben Gurion University of the Negev, P.O.B. 653, Beersheva 84125, Israel

Photoacids are organic molecules which experience a significant decrease in pKa upon electronic excitation, thereby making them much stronger acids in the excited state than in the ground state. This property has been greatly exploited in the last decades permitting dynamical proton transfer and hydrogen bonding research on femtosecond timescales. While their use is now quite well established, the photo-physics leading to this drastic change in pKa remain unclear. Transient UV pump/ IR probe spectroscopy is used in order to characterize the photocycle of diverse photoacids in solvents with increasing hydrogen bonding capability. The OH stretching oscillator is a direct probe for hydrogen bond strength. Indeed, the stronger the hydrogen bond, the larger the frequency red-shift. Therefore, by monitoring the hydrogen stretching oscillators in the excited state, insight into the nature of electronic redistribution in the photoacid molecule is obtained. The ultrafast UV/IR pump-probe experiments show a substantial frequency red shift of the OH stretching oscillator upon photoexcitation. It is found that the magnitude of this shift is correlated with the hydrogen bond accepting capabilities of the solvent.

MO 5.3 Tu 14:30 F 102

**Ultrafast Two-Dimensional IR Photon Echo Measurements of Hydrated DNA** — ●MING YANG, ŁUKASZ SZYC, ERIK T.J. NIBBERING, and THOMAS ELSAESSER — Max Born Institute for Nonlinear Optics and Short Pulse Spectroscopy, Max Born Strasse 2A, D-12489 Berlin, Germany

Biomolecular structure and function are strongly determined by the interactions with the solvent water. The ultrafast dynamical nature of hydration facilitate efficient energy transfer between these biomolecules and the surrounding water shells. We investigate the ultrafast dynamics of NH and OH stretching excitations of an adenine-thymine (A-T) DNA oligomer with two-dimensional infrared photon echo spectroscopy. By controlling the water content of the DNA films we distinguish the contributions of the NH stretching transitions of the DNA bases from the OH stretching vibrations of water. At 0% relative humidity, with only few water molecules present near the phosphate groups, the 2D spectra show diagonal peaks of the NH stretching modes of the A and T bases around 3200 and 3320 cm<sup>-1</sup>. Off-diagonal peaks indicate vibrational couplings between these modes. At 92% relative humidity, where the DNA oligomer is fully hydrated, we observe the

additional water OH stretching contribution, showing spectral diffusion on a time scale of 100 fs. Interestingly, an apparent completion of spectral diffusion for a 500 fs population waiting time suggests the key role of water mediating vibrational energy transfer between the NH stretching modes of DNA and the OH stretching modes of water.

MO 5.4 Tu 14:45 F 102

**Investigation of intramolecular vibrational energy redistribution after overtone excitation of the CH-stretching vibration by femtosecond pump-probe experiments** — ●ALEXANDER KUSHNARENKO, VITALY KRYLOV, EDUARD MILOGLYADOV, MARTIN QUACK, and GEORG SEYFANG — Physical Chemistry Lab., ETH Zürich, Wolfgang-Pauli-Strasse 10, CH-8093 Zürich, Switzerland

Intramolecular vibrational energy redistribution (IVR) is essential for our understanding of intramolecular dynamics and for the theory of chemical reactions. One can derive the time evolution of the wavefunction theoretically from ab initio calculations and experimentally from high resolution IR-spectroscopy [1, 2]. The intramolecular dynamics can be measured directly in femtosecond pump-probe experiments in the gas phase [3], where after near-IR excitation the time dependence of the population of the initially excited level is obtained from the absorption of a delayed IR probe pulse. If a single excited molecular level is coupled to a dense set of background states a simple decay signal is obtained. However, in more complex cases oscillatory signals are measured and a decay may be superimposed. Using a hollow waveguide [3] we have investigated the IVR process for differently deuterated methyl iodides and fluorides and we have observed the phenomena mentioned.

[1] M. Quack, Chapt. 27 in "Femtosecond Chemistry", J. Manz and L. Woeste, eds., Verlag Chemie (Weinheim, 1995) 781. [2] H. R. Dübal, M. Quack, J. Chem. Phys. **81**, 3779 (1984). [3] V. Krylov, A. Kushnarenko, E. Miloglyadov, M. Quack, G. Seyfang, Proc. SPIE **6460**, 64601D-1 (2007).

MO 5.5 Tu 15:00 F 102

**Ultrafast photochemistry in protochlorophyllide-a by femtosecond infrared spectroscopy** — ●MIRIAM COLINDRES<sup>1</sup>, MATTHIAS M. N. WOLF<sup>1</sup>, SONJA SEIDEL<sup>2</sup>, GUDRUN HERMANN<sup>2</sup>, and ROLF DILLER<sup>1</sup> — <sup>1</sup>Fachbereich Physik, TU Kaiserslautern, Kaiserslautern, Germany — <sup>2</sup>Institut für Biochemie und Biophysik, Universität Jena, Jena, Germany

Primary light induced processes of protochlorophyllide-a (PChlide), the precursor in the biosynthesis of chlorophyll, were studied applying transient VIS/mid-IR femtosecond absorption spectroscopy. The light dependent reduction of PChlide is catalyzed by the enzyme NADPH:protochlorophyllide oxidoreductase (POR). We present the first results of ultrafast vibrational dynamics on a sub-ps time scale of the enzyme substrate PChlide in solution. Our results suggest the existence of two reaction pathways after electronic excitation [1]. The shift of the C=O stretch vibration around 1600 cm<sup>-1</sup> indicates the intramolecular charge transfer state in the reactive channel. In the range 1640-1375 cm<sup>-1</sup> C-C and C=C vibrations of the porphyrin backbone dominate the transient vibrational spectra and monitor both the reactive and non-reactive pathway. Our experiments corroborate the model of the primary reaction dynamics of PChlide in solution as presented in ref.[1] and allow for a better understanding of the elementary steps of photochemistry in the enzyme-substrate complex PChlide-POR.

[1] B. Dietzek, S. Tschierlei, G. Hermann, A. Yartsev, T. Pascher, V. Sundström, M. Schmitt and J. Popp, ChemPhysChem 2009, 10, 144-150

MO 5.6 Tu 15:15 F 102

**Isotope labeled riboflavin studied by sub-ps time-resolved infrared spectroscopy** — ●MATTHIAS M. N. WOLF<sup>1</sup>, TATIANA DOMRATCHEVA<sup>2</sup>, KATHARINA CHEVALIER<sup>1</sup>, and ROLF DILLER<sup>1</sup> — <sup>1</sup>Fachbereich Physik, TU Kaiserslautern, D-67663 Kaiserslautern, Germany — <sup>2</sup>Max-Planck-Institut für medizinische Forschung, D-69120 Heidelberg, Germany

Biological blue light receptors as Cryptochromes, AppA or Phototropins utilize the characteristic blue light absorption of Flavin chromophores. In our previous work [1] we investigated excited state vibrational modes and dynamics of Riboflavin in DMSO with sub-picosecond time resolved infrared spectroscopy. Assignment of elec-

tronic ground and first excited state vibrational modes was performed via quantum chemical calculations.

Here we present measurements and calculations of two isotope labeled Riboflavin compounds. The results clarify the assignment of carbonyl vibrations and their involvement in various hydrogen-bonding schemes that might be relevant for native protein systems. In addition variation of excitation wavelength and its effect on picosecond dynamics will be discussed.

[1] M. M. N. Wolf et. al., J. Phys. Chem. B 112 13424-13432 (2008).

MO 5.7 Tu 15:30 F 102

**CRASY: Correlated Rotational Alignment Spectroscopy Resolves Isotopic Structure** — ●CHRISTIAN SCHRÖTER, KYRIAKI KOSMA, INGOLF-VOLKER HERTEL, and THOMAS SCHULTZ — Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin

Femtosecond-pump-probe-spectroscopy is a common tool for the investigation of structure and dynamics of electronic states. Due to the inherent low resolution of femtosecond experiments, this spectroscopy cannot resolve the details of isomeric and isotopic structure. This is a problem, because molecular properties are intrinsically tied to the molecular structure. Here we present CRASY-experiments which simultaneously resolve structural and electronic properties of molecular compounds.

CRASY is a method which combines rotational spectroscopy in the time domain with femtosecond-pump-probe experiments. An IR pulse generates a coherent rotational wave packet by means of non-adiabatic alignment. After a variable delay we probe the wave packet by a UV pulse which excites and ionizes the molecule via a resonant electronic state. If we detect ion-masses (mass-CRASY) the ion signal is modulated by the rotational frequencies encoded in the rotational wave packet. They can be extracted by Fourier-transformation. Since ev-

ery mass-channel supplies its own rotational spectrum mass-CRASY allows to extract rotational frequencies for single isotopes and isomers.

The mass-CRASY method was tested in experiments with CS<sub>2</sub>. Rotational frequencies of rare isotopes can be extracted without synthesizing expensive enriched isotopic mixtures. Results are presented.

MO 5.8 Tu 15:45 F 102

**Influence of structure and morphology of ZnPc:C<sub>60</sub> films on charge carrier dynamics studied by terahertz spectroscopy** — ●CHRISTIAN STROTHKÄMPER, RAINER EICHBERGER, THOMAS HANNAPPEL, and ANDREAS BARTELT — Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

We used optical pump terahertz probe (OPTP) spectroscopy to examine the influence of structure and morphology on the conductivity of thin blended zinc phthalocyanine (ZnPc) C<sub>60</sub> films with a molecular ratio of 1:1. We were able to measure the photoinduced conductivity on sub-ps to ns timescale and on ZnPc:C<sub>60</sub> films with a thickness of 200nm which are comparable to real photovoltaic devices. The decay of the conductivity can be described by a multiexponential fit with the longest decay components on the order of several ns. The morphology and structure can be changed by varying the substrate temperature during evaporation of the components. Recently, the formation of crystalline C<sub>60</sub> and ZnPc domains with increasing substrate temperature was observed with TEM. The decay of the conductivity is correlated to the film morphology and is slowed down with improved sample morphology and structure. Our results suggest that the lifetime of separated charge carriers in the crystalline domains is enhanced due to the reduction of interfacial recombination. No photoconductivity was observed in neat ZnPc and C<sub>60</sub> films, indicating that the interfaces are necessary for the generation of mobile charge carriers.