

## MO 7: Femtosekundenspektroskopie 1

Zeit: Dienstag 10:30–12:30

Raum: VMP 6 HS-F

MO 7.1 Di 10:30 VMP 6 HS-F

**Time-resolved investigation of the ultrafast dynamics of Lycopene using Pump-Degenerate Four Wave Mixing (Pump-DFWM) experiment** — ●MARIE MAREK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalische Chemie, Philipps Universität Marburg, D-35043 Marburg, Germany

Carotenoids are one of the most wide spread class of natural molecules fulfilling a wide range of biological tasks in bacteria and plants. In spite of the importance of carotenoids in Photobiology the dynamics of the excited states are still not clear. In this work we expand our knowledge about the excited states of carotenoids and apply Pump-Degenerate Four Wave Mixing (Pump-DFWM) to an important member of the carotenoid family, lycopene. In this two-dimensional technique, an Initial Pump pulse promotes the system to the excited state, which is then probed by the succeeding DFWM sequence. We focus particularly on the internal conversion between the  $S_2$  and  $S_1$  state with high temporal and spectral resolution. By measuring the evolution of the amplitudes and frequency shifts of the excited state vibrations we show that the symmetric C=C stretching mode plays a dominant role for the internal conversion. Furthermore, similar to our previous study on  $\beta$ -carotene [1], a low-lying vibrationally hot state is also identified for lycopene in solution. Besides that, observation of a low-frequency mode at  $370\text{ cm}^{-1}$  is discussed under the light of lycopene isomers distribution in the ground state.

[1] J. Hauer, T. Buckup, M. Motzkus, JPCA 111, 2007, 10517.

MO 7.2 Di 10:45 VMP 6 HS-F

**Degenerate Four-Wave-Mixing Studies on Bacteriorhodopsin** — ●JAN PHILIP KRAACK, TIAGO BUCKUP, and MARCUS MOTZKUS — Physikalische Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany

Bacteriorhodopsin (bR) is a membrane protein which enables the organism *Halobacterium salinarum* (Hs) to convert visible light into chemical energy. This is driven by a cyclic process on a millisecond timescale, which is initiated by the isomerization of the protein-bound chromophore all-trans retinal on the sub-picosecond timescale. In this work, time-resolved degenerate four-wave-mixing (DFWM) experiments are presented on the light-adapted form of this model system to investigate the photoinduced wave packet dynamics in electronic ground and excited states on the sub-20 femtosecond timescale. It has been shown that this coherent Raman-technique can give insight to electronic population as well as wave packet dynamics. The observed signals are discussed in dependence of the excitation wavelength as well as the effect of time ordering of the three DFWM-pulses generating the signal. It is shown, that low- as well as high-frequency vibrational motion can be observed due to the homodyne signal-generation. The origin of wave packet motion is discussed and an interpretation in terms of the known models for the initial molecular dynamics is given.

MO 7.3 Di 11:00 VMP 6 HS-F

**Ultrafast vibrational dynamics of hydrated DNA** — ●ŁUKASZ SZYC, JASON R. DWYER, MING YANG, ERIK T. J. NIBBERING, and THOMAS ELSAESSER — Max-Born-Institute, D-12489 Berlin, Germany

Determination of the dynamics and interactions of water molecules with DNA is of utmost importance in understanding the structure and function of DNA. Here we use polarization-sensitive two-colour IR pump-probe spectroscopy to discern the vibrational dynamics of N-H stretching excitations of DNA oligomers containing 23 alternating adenine-thymine base pairs from the O-H stretching excitations of solvation shell water molecules, which are strongly overlapping in the linear absorption spectrum. For a DNA film at 0 % relative humidity (r.h.), where the number of water molecules per base pair is typically two, lifetimes of approximately 0.5 ps are found for N-H and O-H stretching modes. The transient pump-probe anisotropies demonstrate the coupling of different N-H stretching modes. Fully hydrated DNA films show similar N-H stretching bands as at 0 % r.h. and two types of O-H stretching responses. An O-H stretching band with maximum at  $3500\text{ cm}^{-1}$ , limited spectral diffusion and population kinetics similar to 0 % r.h. is attributed to water molecules directly interacting with the DNA oligomers. O-H stretching excitations with a 200 fs lifetime, broad absorption and a hot ground state formed by vibrational relaxation are assigned to water molecules weakly interacting

with DNA.

MO 7.4 Di 11:15 VMP 6 HS-F

**Ultrafast vibrational wavepacket motions in 2-pyridone dimers** — ●MING YANG, ŁUKASZ SZYC, JENS DREYER, ERIK T. J. NIBBERING, and THOMAS ELSAESSER — Max-Born-Institute, D-12489 Berlin, Germany

Hydrogen-bonded N-H groups are ubiquitous in nature, playing a key role in the nucleic acid base pairing in DNA and RNA, and in the secondary structure of proteins. Here, a nitrogen atom donates a hydrogen to an accepting electronegative oxygen or nitrogen. The infrared-active N-H stretching band displays key signatures such as frequency downshifts, line broadening and distinct band substructures providing direct access to the the hydrogen bond strength and anharmonic vibrational mode couplings. Here we present recent results obtained on the hydrogen-bonded 2-pyridone dimer in nonpolar solution, a model system for DNA nucleic base pairing. In femtosecond infrared pump-probe experiments on the N-H stretching band we determine the population decay of the N-H stretching vibration to occur with a 200 fs time constant. Superimposed on the population dynamics of the N-H stretching vibration we observe coherent oscillations indicative of coherent wavepacket motions of the dimer in-plane bending and dimer stretching modes, with respective eigenfrequencies of 100 and  $160\text{ cm}^{-1}$ . These low-frequency vibrational modes, strongly affecting the hydrogen bond distance, are anharmonically coupled to the N-H stretching vibration, and as such are coherently driven and read out by the ultrashort infrared pulses tuned at the N-H stretching band.

MO 7.5 Di 11:30 VMP 6 HS-F

**Vibrational relaxation after spectrally selective excitation in the structured N-H stretching band of 7-azaindole dimer** — ●KOZICH VALERI, DREYER JENS, and WERNCKE WOLFGANG — Max-Born-Institut, Max-Born-Strasse 2A, D-12489 Berlin, Germany

The dimer of 7-azaindole may be regarded as a model system for the base pairs of DNA. Dimerization leads to formation of a highly structured N-H stretching band and an extreme shortening of the lifetime of this vibration. Here we report on investigations of mode-selectivity of vibrational redistribution after spectrally selective excitation within the N-H stretching band by sub-picosecond infrared-pump/anti-Stokes resonance Raman-probe spectroscopy. Generally our measurements indicate ultrafast initial population transfer to fingerprint vibrations with N-H bending character. Subsequently the energy is transferred to modes with lower frequencies. The infrared excitation at different substructures of the N-H stretching band clearly influences the distribution of populations between the different fingerprint modes. Their relative populations correlate with the contribution of the modes to various combination tones coupled to the N-H stretching vibration. Our results provide experimental support to a Fermi resonance model used for modeling the IR spectrum of the N-H stretching band and give insight into relaxation processes and energy redistribution. Relaxation to distinct vibrational fundamentals contributing to the combination bands forming the initially excited sub-band is strongly favoured.

MO 7.6 Di 11:45 VMP 6 HS-F

**Ultrafast Exciton Dynamics in Organic Thin Films** — ●HENNING MARCINIAK<sup>1</sup>, BERT NICKEL<sup>2</sup>, and STEFAN LOCHBRUNNER<sup>1</sup> — <sup>1</sup>Institut für Physik, Universität Rostock — <sup>2</sup>Fakultät für Physik und CeNS, LMU München

Thin films of microcrystalline pentacene frequently serve as active layers in prototypical organic electronic devices. The nature and dynamics of their electronic excitations determine to a large extent the device behavior. We investigate pentacene films with a thickness of about 30 monolayers by femtosecond absorption spectroscopy. The measurements show a decay of the stimulated emission with a sub-100-fs time constant [1]. A possible path is fission into triplet excitons. By tilting the pentacene layers relative to the incident laser beams one can distinguish between singlet and triplet absorption since the corresponding transition dipoles are orientated perpendicular to each other. We find that the triplet absorption rises significantly slower than the emission decays and adopts relatively weak signal strength, indicating that only a small fraction of triplet excitons is formed. We suggest that the dominant relaxation path leads to excimer-like excitons with a

strongly reduced transition dipole moment to the ground state. These singlet excitons determine the subsequent dynamics on the picoseconds timescale, which is found to be excitation intensity dependent. Modeling the kinetic traces shows that the dynamics is governed by diffusion controlled processes, in particular by exciton-exciton-annihilation.

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

MO 7.7 Di 12:00 VMP 6 HS-F

**Efficient Energy Transport by Perylene Bisimides in Organic Films** — FRANZISKA HELLMUTH and •STEFAN LOCHBRUNNER — Institut für Physik, Uniplatz 3, 18055 Rostock

Thin organic films are central components of organic light emitting diodes, solar cells and plastic electronics. We investigate the energy transport via exciton migration in organic films with incorporated dye molecules. The central goal of this research is the optimization of the exciton diffusion length, which is important for many applications. In a first attempt we used perylenedicarboximide molecules (Perylene Orange) as active sites and achieved high exciton mobility with a Förster transfer time of 1.5 ps for a dye concentration of 0.14 M [1]. However, some aggregates are already formed at these concentrations which act as traps and limit the migration distance to about 7 nm. To circumvent this problem we switched to a perylenedicarboximide dye substituted with phenoxy groups at the bay positions (Perylene Red). The

bulky substituents reduce strongly the tendency to aggregate. Transient absorption measurements reveal for a dye concentration of 0.17M a Förster transfer time of 1.5 ps in good agreement with calculations. The reduced aggregate concentration results in a longer excited state lifetime and therefore an increased exciton diffusion length of about 18 nm. The energy transport can also be monitored by cw experiments which evaluate the fluorescence yield from an acceptor dye incorporated in the film.

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

MO 7.8 Di 12:15 VMP 6 HS-F

**Femtosecond dynamic of benzyl radical** — •MARKUS MARGRAF<sup>1</sup>, BASTIAN NOLLER<sup>1</sup>, THOMAS SCHULTZ<sup>2</sup>, and INGO FISCHER<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, University of Würzburg, Germany — <sup>2</sup>Max Born Institute Berlin, Germany

The dynamic of benzyl radical was investigated by femtosecond time-resolved pump probe spectroscopy in a free jet. On the one hand we studied the dependence on pump wavelength (298 nm, 301 nm, 305 nm) at constant probe wavelength of 800 nm at all experiments and on the other hand we used different precursors for generating the benzyl radical. Toluene and 2-phenyl ethyl nitrite showed up as appropriate precursors. In all cases we observe a biexponential decay. The life times increased with pump wavelength.