MO 17: Femtosecond Spectroscopy IV

Time: Thursday 10:30–12:45 Location: V38.03

Invited Talk MO 17.1 Thu 10:30 V38.03

Ultrafast Processes in Single Molecules: from Small Chromophores to Photosynthetic Antenna Complexes — •Richard Hildner[1], Daan Brinks[1], Richard J. Cogdell[2], and Niek F. van Hulst[1,3] — [1]ICFO - Institut de Ciencies Fotoniques, 08860 Castelldefels — [2]University of Glasgow, Glasgow G12 8TA — [3]ICREA - Institucio Catalana de Recerca i Estudis Avancats, 08015 Barcelona

Ultrafast excitation-energy transfer is at the heart of both natural and artificial light-harvesting, and plays a key role in the initial steps of photosynthesis as well as in photovoltaic applications of organic functional materials. However, a detailed nanoscale understanding of energy-transfer processes is hampered to date, because molecular systems are often highly heterogeneous with disordered environments and current ultrafast techniques intrinsically average over large ensembles.

Here, we present our recent advances in combining femtosecond pulse-shaping techniques with single-molecule detection schemes at room temperature. Employing phase-controlled double-pulse excitation, we resolved ultrafast electronic coherences and their femtosecond decay in a model system, individual terrylene molecules embedded in a polymer matrix. We also observed and manipulated vibrational wave packet interference in single molecules by adapting the time and phase distribution of the laser field to the ultrafast molecular dynamics. Finally, we discuss how these techniques can be extended to multi-chromophoric molecular systems. Preliminary results on the ultrafast dynamics of electronic excitations within individual light-harvesting complexes of purple bacteria are presented.

MO 17.2 Thu 11:00 V38.03

Ultrafast Chromophore Dynamics in Xanthorhodopsin — •Miriam Colindres[1], Melanie Geier[2], Ilka Haferkamp[2], Ekkehard Neuhaus[2], and Rolf Diller[1] — [1]Physics Department, University Kaiserslautern, Germany — [2]Biology Department, University Kaiserslautern, Germany

Xanthorhodopsin from the extreme halophile eubacterium *Salinibacter ruber* is one of the simplest bioenergetic systems for collecting light using excited state energy transfer. This member of the retinal protein family is a light driven transmembrane proton pump (SX) (1). We present the first results of ultrafast vibrational dynamics on a sub-ps time scale of the primary photoreaction in xanthorhodopsin. Our experiments show evidence for the proton-pump cycle initiated by Ret isomerization after excitation of SX. The Ret S_1 surface branches into the hot J-state and the hot all-trans-Ret, followed by vibrational cooling and torsional relaxation of J-state and all-trans-Ret. Our results suggest a prolonged protein response compared to bacteriorhodopsin. The protein relaxes slower than in BR (11 ps) (2) and the perturbation of protein is permanent on the experimental time scale. In this context the excited state dynamics of SX as a sensor for protein dynamics are of particular interest. Therefore we are currently investigating the vibrational modes of SX in the carbonyl region between 1700 and 1800 cm^{-1}.

(1) J. Antón et al., IUMS, 52, 485-491 (2002)
(2) R. Groß et al., J. Am. Chem. Soc., 131, 14868-14878 (2009)

MO 17.3 Thu 11:15 V38.03

Possible involvement of multi-photon pathways in femtosecond transient absorption experiments on retinal-isomerization in Bacteriorhodopsin — •Jan Philip Kraack, Tiago Buckup, and Marcus Motzkus — Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, D-69120 Heidelberg, Germany

The photo-isomerization of all-trans retinal in Bacteriorhodopsin (BR) is an important model-reaction in time-resolved spectroscopy on rhodopsins. Upon photon-absorption, the excited-state population decays within less than a picosecond to form the ground state photoproduct with high quantum yield around 0.6. An important issue in the interpretation of BR's photo-dynamics concerns observable dependences of the signal on intensities of excitation pulses.[1-2] Using hyperspectral transient absorption spectroscopy, we investigated the femtosecond reaction kinetics of BR for a series of experimental parameters. In particular, we find that excited state relaxation dynamics depend on the excitation wavelength over a broad energetic range of excitation (500-600 nm). Screening of excitation-pulse intensities influences the ratio between ground state bleaching- and photo-product signal. The results are discussed in the context of existing two-photon pathways for the generation of photo-products not participating in the active photo-cycle of BR.[3]

[1]Florean et al., PNAS 2009, 106, 10896. [2]Prokhorenko et al., J.Chem. Phys. 2011, 134, 085105. [3]Fischer et al. Biophys., J. 2005, 89, 1175.

MO 17.4 Thu 11:30 V38.03

Energy Transfer in Light-Harvesting Systems: Influence of Non-Markovian Environment — •Gerhard Ritschel[1], Jan Roden[2], Walter T. Strunz[3], and Alexander Eisfeld[4] — [1]Max-Planck-Institut für Physik komplexer Systeme, Dresden, Germany — [2]University of California, Berkeley, USA — [3]Technische Universität Dresden, Germany — [4]Harvard University, Cambridge, USA

The transfer of electronic excitation energy as well as optical properties of complexes of interacting chromophores, e.g. the FMO complex or the LH2 antennae in biological photosynthetic systems, are strongly influenced by an environment. For a proper theoretical description it is essential to include non-Markovian effects resulting from an electron-environment coupling that is a rather structured function of energy leading to a complicated retroaction on the excitation dynamics.

We developed a new approach based on non-Markovian quantum state diffusion [1] where it is possible to efficiently calculate energy transfer and optical spectra in a non-perturbative way. Within this method, it is possible to capture the whole range from coherent dynamics to incoherent diffusion and to investigate situations where environment-assisted transfer occurs.

Using that approach we described the energy transfer dynamics in one FMO subunit as well as in the full FMO trimer [2, 3] and calculated linear spectra at various temperatures.

[1] Roden et al. PRL 103, 058301 (2009)
[2] Ritschel et al. NJP 13, 113034 (2011)
[3] Ritschel et al. JPCL 2, 2912 (2011)

MO 17.5 Thu 11:45 V38.03

Ultrafast Electronic Deactivation Dynamics of the Rare Natural Nucleobases Xanthine and Hypoxanthine — •Katharina Röttger and Friedrich Temps — Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Olshausenstr. 40, D 24098 Kiel, Germany

Investigations of the photophysical behaviour of rare DNA and RNA bases provide insight into the correlation between structural properties of the nucleobases and their radiationless decay pathways after UV excitation. Here, we report on the first femtosecond time-resolved transient absorption measurements of the rare RNA nucleotide xanthosine monophosphate in buffered aqueous solution at different pH values and on the rare natural RNA base hypoxanthine. Measurements were performed with a transient absorption setup which allows for a highly sensitive, simultaneous detection of broadband absorption spectra (300-700 nm) and single-colour absorption in the deep UV range. The excited-state dynamics of xanthosine monophosphate (XMP) have been found to depend strongly on the excitation wavelength. It was possible to *distinguish* the dynamics of two close lying $\pi\pi^*$ states which are most likely connected via a conical intersection. The direct observation of the consecutive population of these states is quite rare in the case of the nucleobases. The dynamics of hypoxanthine were found to be similar to those of guanine. The results are discussed in comparison with recently published computational studies on possible relaxation channels.

MO 17.6 Thu 12:00 V38.03

Ultrafast dynamics of NH stretch vibrations in adenosine-thymidine base pairs in chloroform solution — •Christian Greve[1], Benjamin Koeppe[1], Henk Fidder[1], Nicholas Preketes[3], Erik T. J. Nibbering[1], Shaul Mukamel[3], Friedrich Temps[2], and Thomas Elsaesser[1] — [1]Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Max Born Strasse 2A, 12489 Berlin, Germany — [2]Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, 24098 Kiel, Germany — [3]Department of Chemistry, University of California, Irvine, USA

The nucleobases adenine (A) and thymine (T), building blocks in na-

tive DNA and RNA, readily form hydrogen bonded complexes both in the gas phase and in solution. To gather key insight into these hydrogen bonding interactions, we perform femtosecond IR-pump-IR-probe and polarization-resolved 2D-IR photon echo spectroscopy of the N-H stretching bands of AT base pairs in chloroform solution which are located between 3100 and 3500 cm^{-1}. Vibrational population dynamics of hydrogen bonded stretch transitions occur on a subpicosecond time scale. Cross peaks in the 2D-IR spectra, monitored as a function of waiting time, show the connectivities in the N-H stretching manifold. The polarization dependence of the cross peaks indicate that the hydrogen-bonded and the free N-H stretching dipole moments in these AT base pairs have a well-defined relative orientation. Our experimental results are combined with quantum chemical calculations to allow for N-H stretching mode assignments of the Watson-Crick and Hoogsteen base pair structural motifs present in solution.

MO 17.7 Thu 12:15 V38.03

Time-resolved spectroscopy of triplet states of thymidylic acids — •Bert Manuel Pilles — LMU Munich

Solar UV radiation is known to induce harmful mutagenic products in DNA. The major photoproduct is the cyclobutane pyrimidine dimer (CPD) between neighboring thymine residues. In recent studies it was shown that the photodimerization reaction induced via 266 nm excitation occurs predominantly on a 1 ps time scale . This finding suggests that the reaction occurs via a singlet pathway [1,2]. Nevertheless triplet states are discussed to be possible precursors of thymine dimer formation.

We used time resolved UV pump, IR probe spectroscopy - covering picoseconds to microseconds - to investigate different single stranded thymidylic acids (TpT, (dT)18) and the corresponding mononucleotide (thymidine monophosphate, TMP). We show that femtosecond infrared spectroscopy can address triplet specific bands and that the excitation of the samples leads to the formation of triplet states that decay on the ns time scale. Different quenching mechanisms (CPD formation, self quenching, oxygen quenching) will be discussed.

[1]: Schreier, W. J., J. Kubon, et al. (2009). "Thymine Dimerization in DNA Model Systems: Cyclobutane Photolesion Is Predominantly Formed via the Singlet Channel." Journal of the American Chemical Society 131(14): 5038-5039.

[2]: Schreier, W. J., T. E. Schrader, et al. (2007). "Thymine dimerization in DNA is an ultrafast photoreaction." Science 315(5812): 625-629.

MO 17.8 Thu 12:30 V38.03

Excited state dynamics and binding energies of DNA bases in aqueous solution — •Franziska Buchner and Andrea Lübcke — Max-Born-Institut, Max-Born-Strasse 2A, 12489 Berlin, Germany

Interaction of UV light with DNA may lead to photodamage. Photodamage of DNA can occur either by direct absorption of uv photons or by attachment of solvated electrons formed by a photodetachment process in the vicinity.

We report on the excited state dynamics of DNA bases in aqueous solution observed by time-resolved photoelectron spectroscopy, exploiting the liquid jet technique. Sub-100 fs pulses of 200 nm or in the range of 240-266 nm are used to excite a 1 mmolar solution of the DNA base or its sugar conjugate. Excited state dynamics is probed by photoionization with a delayed UV pulse (also sub-100 fs).

Depending on the photon energy of the pump pulse we either see formation and recombination of solvated electrons or excited state dynamics of the base itself. Both population dynamics and binding energies of the excited states will be discussed.