MO 45 Biomolecules II

Zeit: Mittwoch 16:30–18:30 Raum: H10

MO 45.1 Mi 16:30 H10

Femtosecond Two-Photon Spectroscopy determines hidden carotenoid dark state dynamics — •Peter Jomo Walla[1,2], Wehling Axel[2], and Michael Hilbert[1] — [1]Max-Planck-Institut für Biophysikalische Chemie, Am Faßberg 11, D-37077 Göttingen — [2]Institut für Physikalische und Theoretische Chemie, Abt. Biophysikalische Chemie, Hans-Sommerstr. 10, D-38106 Braunschweig

Carotenoids play an important role as light-harvesting pigments and in the regulation of the energy flows in the photosynthetical apparatus under changing environmental light conditions. However, a detailed insight in the underlying mechanisms was very often impossible due the optical forbidden character of the first excited state of carotenoids, Car S1. This is because it has the same Ag symmetry as the ground state, Car S0. An elegant approach is the investigation via two-photon excitation because Ag->Ag-transitions are generally two-photon allowed. Using this approach we access directly and selectively the forbidden state and gain important information about the light harvesting mechanisms and the regulation of excessive excitation energy under high-light conditions in the photosynthetic apparatus. We will present latest femtosecond two-photon results from several photosynthetic protein complexes and real plants. With these data it is possible to gain a detailed understanding of the energy transfer mechanisms and the regulation of the photosynthetic apparatus in living plants.

MO 45.2 Mi 16:45 H10

Spektroskopie optisch dunkler Carotenoid-Anregungszustände mittels simultaner Zweiphotonen-Fluoreszenz-Anregung durch fs-Laserpulse — •Alexander Betke[1], Bernd Voigt[1], Maria Krikunova[2], Dieter Leupold[1], Heiko Lokstein[1] und Ralf Menzel[1] — [1]Universität Potsdam, Am Neuen Palais 10, 14469 Potsdam — [2]Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg

Carotenoide haben in photosynthetisierenden Organismen wichtige Funktionen: als Strukturkomponenten der Pigment-Protein-Komplexe, als accessorische lichtsammelnde Pigmente, und in der Photoprotektion. An den beiden letztgenannten Funktionen sind optisch "dunkle", d.h. durch Einphotonenabsorption nicht zugängliche Zustände beteiligt, die in enger energetischer Nachbarschaft von (Bacterio-)Chlorophyll-Anregungszuständen liegen. Ein methodischer Ansatz, die Rolle der "dunklen" Zustände beim Anregungsenergie-Transfer und der Dissipation überschüssiger Anregungsenergie in Lichtsammel-Komplexen (LHCs) zu studieren, ist die mittels (Bacterio-)Chlorophyllfluoreszenz detektierte simultane Zweiphotonenabsorption von durchstimmbaren fs-NIR-Impulsen. Im Vortrag werden Vor- und Nachteile dieses Ansatzes und experimentelle Details vorgestellt, sowie neuere Ergebnisse diskutiert. Dieser Beitrag wird von der DFG im Rahmen des SFB 429 gefördert.

MO 45.3 Mi 17:00 H10

Energy flow in β-carotene after multiphoton excitation using tunable sub-30 fs pulses in the near-IR — •Tiago Buckup, Alexander Weigel, and Marcus Motzkus — Physikalische Chemie, Phillips Universität Marburg, 35043 Marburg, Germany

Carotenoids perform a variety of critical functions in nature, which are strongly dependent on their energy deactivation network. The classical three-level-scheme of carotenoids describes the deactivation of the photoexcited S_2 state by ultrafast internal conversion to the dark S_1 state which in turn decays to the ground state S_0 on the picosecond time scale. As it has been shown in previous contributions, the S_1 state can be excited via a two-photon transition directly from S_0. Here we extend the concept of multiphoton Pump-Probe spectroscopy to beta-carotene in a new excitation range (900-1100 nm) using tunable sub-30 fs pulses. Besides the well-known S_1 deactivation, long-lived contributions can also be observed in the blue region of the visible spectra and in the near-IR. These two contributions are associated with the absorption of a triplet and a cation state, respectively. The presence of additional dark states is also considered and a model taking into account all observations is presented.

MO 45.4 Mi 17:15 H10

Thymine dimer formation probed by femtosecond infrared spectroscopy — •Wolfgang Schreier[1], Tobias Schrader[1], Florian Koller[1], Peter Gilch[1], Wolfgang Zinth[1], and Bern Kohler[2] — [1]Ludwig-Maximilians-Universität, Department of Physics, Chair for BioMolecular Optics, Oettingenstr. 67, 80538 München — [2]The Ohio State University, Department of Chemistry, 100 West 18th Avenue, Columbus, Ohio 43210

Absorption of UV radiation by DNA bases is known to induce harmful mutagenic products. One major photoproduct at bipyrimidine sites is the photodimerization of neighboring thymine residues. Despite the intense work in this field there is still a lack of information regarding the time scale at which these dimers are formed [1], [2].

We used time resolved UV pump, IR probe spectroscopy to investigate the 18-mer of single-stranded thymidylic acid [(dT)18] and the corresponding mononucleotide (thymidine monophosphate, TMP). We show that femtosecond infrared spectroscopy can address dimer specific marker bands between 1300 and 1500 cm^{-1} and that the excitation of the oligonucleotide leads to the formation of cyclobutane dimers in less than 20 ps. Additionally we find no slow growth in these marker bands as expected for a triplet intermediate. This points to a singlet precursor for these photoproducts.

[1] Crespo-Hernandez CE, Cohen B, Kohler B, NATURE 436 (7054): 1141-1144 (2005)
[2] Marguet S, Markovitsi D, JACS 127 (16): 5780-5781 (2005)

MO 45.5 Mi 17:30 H10

Photoinduced conformational dynamics of a photoswitchable peptide: A nonequilibrium molecular dynamics simulation study — •Phuong Hoang Nguyen, Roman Gorbunov, and Gerhard Stock — Institute of Physical and Theoretical Chemistry, J. W. Goethe University, Marie-Curie-Str. 11, D-60439 Frankfurt, Germany

Recent advances in femtosecond laser experiments allow for real-time observations and true-multidimentional views of the dynamics of chemical reactions. A beautiful example is the femtosecond infrared spectroscopy experiments on photoswitchable peptides which provide a new and promising way to study the peptide folding and unfolding in unprecedented detail[1,2]. To obtain an appropriate theoretical description of these experiments, we suggest to extend well-established all-atom molecular dynamics simulation techniques to the description of nonequilibrium photoinduced conformational dynamics in peptides[3]. We then performed the true nonequilibrium molecular dynamics simulations on the octapeptide which is covalently bound to both ends of an azobenzene conformational switch. This study allows us to monitor the progress of photoinduced peptide folding, including cooling phase, global and local conformational rearrangements, and photoinduced spectral response. The results are discussed in the light of experiments[1,2].

References
[1] J. Bredenbeck et al., Proc. Natl. Acad. Sci. USA 100, 6452 (2003).
[2] J. Bredenbeck et al., J. Phys. Chem. B 107, 8654 (2003).
[3] P. H. Nguyen and G. Stock, Chem. Phys. (in press).

MO 45.6 Mi 17:45 H10

First Steps of Retinal Photoisomerization in Proteorhodopsin — •Martin O. Lenz[1], Robert Huber[1], Bernhard Schmidt[2], Peter Gilch[2], Rolf Kalmbach[3], Martin Engelhard[3], and Josef Wachtveitl[1] — [1]Institut für Physikalische und Theoretische Chemie, Marie-Curie-Str. 11, Johann-Wolfgang-Goethe-Universität Frankfurt, 60439 Frankfurt am Main — [2]Universität München, Department für Physik, Lehrstuhl für BioMolekulare Optik, Oettingenstraße 67, 80538 München — [3]Max-Planck-Institute of Molecular Physiology, Department of Physical Biochemistry, Otto-Hahn-Str. 11, 44227 Dortmund

The early steps (< 1 ns) in the photocycle of the proton pump proteorhodopsin (PR) are analyzed by ultrafast spectroscopic techniques. A comparison to the first primary events of well known retinal proteins like the archaeal proton pump bacteriorhodopsin (BR) is given. A dynamic Stokes shift observed in fs-time resolved fluorescence experiments allows a direct observation of early motions on the excited state potential energy surface. The initial dynamics is dominated by sequentially emerg-

ing stretching (<150 fs) and torsional (˜300 fs) modes of the retinal. The different protonation states of the primary proton acceptor Asp97 drastically affect the reaction rate and the overall quantum efficiencies of the isomerization reactions mainly evidenced for time scales above 1 ps. However, no major influence on the fast time scales could be seen, indicating that the movement out of the Franck-Condon region is fairly robust to electrostatic changes in the retinal binding pocket. Taking into account investigations on the primary events of BR a reaction scheme is presented.

MO 45.7 Mi 18:00 H10

Primäre Dynamik der Mutante D85T des Transmembranproteins Bakteriorhodopsin — •Constanze Sobotta[1], Markus Braun[1], Jörg Tittor[2] und Wolfgang Zinth[1] — [1]Lehrstuhl für BioMolekulare Optik, Oettingenstr. 67, Ludwig-Maximilians-Universität München, 80538 München — [2]Max-Planck-Institut für Biochemie, Am Klopferspitz 18, 82152 Martinsried

Das Archaeon Halobakterium salinarum lebt unter nativen Bedingungen in Umgebungen mit sehr hohen Salzkonzentrationen. In der Membran des Bakteriums befinden sich die Transmembranproteine Bakteriorhodopsin (BR) und Halorhodopsin (HR). Obwohl die Proteine strukturell sehr ähnlich sind, unterscheiden sie sich zum einen in ihrer Primärreaktion und zum anderen auch in ihrer Funktion als lichtgetriebene Protonen- bzw. Chlorid-Pumpe. Als wichtigster Unterschied der BR- und HR-Struktur wurde die Ladung der Aminosäure an der Position 85 (BR: Aspartat; HR: Threonin) in der Nähe der Schiffschen Base (Retinal-Chromophor) identifiziert, welche das optische Spektrum und die Dynamik der Isomerisierungsreaktion des Retinal-Chromophors verändert.

Daher wurden femtosekunden-zeitaufgelöste transiente Absorptionsmessungen an punktmutierten BR-Proteinen D85T (Aspartat wird ersetzt durch Threonin) durchgeführt. Durch Änderung von pH-Wert und Salzkonzentration soll so die Ladung an der Stelle 85 gezielt variiert werden. Es zeigt sich, dass die Isomerisierung beeinflusst wird und je nach Wahl der eingestellten Bedingungen eher der Dynamik von BR bzw. HR ähnelt.

MO 45.8 Mi 18:15 H10

Photoinduced processes in microhydrated adenine clusters — •Elena Samoylova, V. R. Smith, T. Schultz, H.-H. Ritze, W. Radloff, and I.V. Hertel — Max-Born-Institut Berlin, Max-Born Strasse 2a, 12489 Berlin, Germany

Photochemical reactions can be efficiently quenched by fast radiationless decay to the electronic ground state. We investigate such mechanisms in DNA, first, in isolated bases followed by bigger and microhydrated clusters using time-resolved ion and electron spectroscopy. For adenine-monomer the excited state dynamics could be characterized by an exponential decay containing two components with 100 fs and 1 ps life time. The 100 fs component is due to a very short living electronic state of $\pi\pi^*$ character and the 1 ps component is due to an optically dark $n\pi^*$ state. In the microhydrated adenine we did not observed the 1 ps contribution. That indicated a different very fast relaxation pathway due to a $\pi\sigma^*$ electronic state. In adenine-dimer we found a similar mechanism of excited state deactivation as for $A(H_2O)$, with a minor contribution of the $n\pi^*$ state. Very different behaviour was observed in adenine-dimer cluster with three or more water molecules when the cluster changed from a planar, H-bound to a π-stacked structure. With photoelectron-photoion coincidence spectroscopy an additional relaxation pathway with ns life time was identified which we assigned to the formation of an eximer state. Our observations in the gas phase reproduce similar experiments in water solution and are discussed in the context of high-level theoretical calculation.