MO 12 Biomolecules I

Zeit: Freitag 14:00–16:00 Raum: HU 2091

Hauptvortrag

MO 12.1 Fr 14:00 HU 2091

Initial electron donor and acceptor in isolated Photosystem II reaction centers identified with femtosecond midinfrared spectroscopy — •M. L. Groot[1], N. Pawlowicz-Wereszczynska[1], L. J.G.W. van Wilderen[1], J. Breton[2], I. H.M. van Stokkum[1], and R. van Grondelle[1] — [1]Faculty of Sciences, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands — [2]Service de Bioénergétique, Bât. 532, CEA-Saclay, 91191 Gif-sur-Yvette, France

The primary steps in photosynthesis of energy- and electron transfer occur in green plants in two large chlorophyll-containing protein complexes called Photosystem I and Photosystem II. We measured the time-dependent absorption changes of isolated reaction centers of Photosystem II upon excitation at 670 and 681 nm in the mid-infrared, in the region of the ester and keto modes, between 1775 and 1585 cm^{-1}, with 150 fs time resolution. A detailed comparison with steady state P^+/P and H^-/H spectra reveals that the primary electron donor is not P^+, but the accessory chlorophyll on the D1 polypeptide, Chl_{D1}. The charge separated pair $Chl_{D1}{}^+H^-$ is formed with a time constant of 0.6-0.8 ps, upon excitation at 681 nm. The hole is transferred from $Chl_{D1}{}^+$ to P with an intrinsic rate of $(4\ ps)^{-1}$. Slow energy transfer leads to a part of the P^+H^- state to appear with a time constant of 36 ps. Relaxation of the radical pair, with a drop in free energy of ~ 60 meV, occurs in ~ 200 ps.

MO 12.2 Fr 14:30 HU 2091

Ultrashort Time Resolved VIS-NIR Spectroscopy of the Photosynthetic Unit of Rhodospirillum Rubrum: Importance of RC-H Subunit — •Sergiu Amarie[1], Martin O. Lenz[1], Domenico Lupo[2], Robin Ghosh[2] und Josef Wachtveitl[1] — [1]Institut für Physikalische und Theoretische Chemie, Goethe Universität Frankfurt, Marie-Curie-Str. 11, 60439 Frankfurt am Main — [2]Department of Bioenergetics, Institute of Biology, University of Stuttgart, Stuttgart

In the photosynthetic light reaction the primary reactions occur on the subpicosecond and picosecond time scale. The first step is the absorption of a photon by the light harvesting antenna systems (LH), followed by a rapid and efficient transfer of the excitation energy to the reaction center (RC). A series of fast electron transfer (ET) reactions along a chain of chromophores within the RC stabilizes the electrochemical energy via charge separation. The SPUHK1 mutant of R. rubrum was created by deleting the reaction center H subunit during site-directed interposon mutagenesis. The H subunit of the RC is necessary neither for maximal formation of LH1 nor for photosynthetic membrane formation but is essential for functional RC assembly. The spectroscopic properties of the wild-type Rhodospirillum rubrum S1 and the SPUHK1 mutant were studied using femtosecond time-resolved transient absorption spectroscopy from 400 to 1000 nm. Differences in the VIS and NIR region can be identified and attributed to the different temporal behaviour of the energy transfer steps after photoexcitation of the antenna carotenoids around 500 nm. The stabilizing role of the carotenoids for LH1 formation in the absence of the H subunit will be discussed.

MO 12.3 Fr 14:45 HU 2091

Femtosecond Fluorescence Spectroscopy of Bacteriorhodopsin Features a Dynamic Stokes Shift — •Bernhard Schmidt, Constanze Sobotta, Björn Heinz, Stefan Laimgruber, Markus Braun, and Peter Gilch — Department für Physik, Ludwig-Maximilians-Universität München, Oettingenstr. 67, D-80538 München, Germany

Bacteriorhodopsin (BR) acts as a light driven proton pump which allows archea to benefit from solar energy. A crucial step in the photocycle of BR is the isomerisation of its retinal chromophore. By virtue of numerous femtosecond experiments there is now consensus on time scales involved, but the underlying molecular processes are still under debate. As time resolved fluorescence spectroscopy is particularly suitable to probe the primary dynamics in the excited state, we report such experiments relying on the Kerr technique. The resulting spectra feature a dynamic Stokes Shift occurring on a timescale of 0.2 ps, which is indicative for a fast re-arrangement on the reactive potential energy surface. In agreement with other experiments time constants of ≤ 0.15 ps and 0.45 ps for the decay of the fluorescence have been determined.

MO 12.4 Fr 15:00 HU 2091

Bedeutung des Lösungsmittels für die ultraschnellen Faltungsvorgänge in Peptid-Chromophor-Systemen — •Christopher Root[1], Helmut Satzger[1], Markus Löweneck[2], Christian Renner[2], Luis Moroder[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 18a, 82152 Martinsried

In Peptid-Chromophorverbindungen kann durch die photochemisch ausgelöste Isomerisation des Farbstoffs gezielt die Faltung und Entfaltung eines kurzen Peptidstranges getriggert und durch zeitaufgelöste transiente Absorptions-Spektroskopie beobachtet werden. Die Bewegung des Peptid-Rückgrates wird dabei indirekt durch seinen Einfluss auf den Chromphor sichtbar.

Das jüngst synthetisierte System PDI bietet die Möglichkeit in verschiedenen Lösungsmitteln untersucht zu werden. Dadurch kann im direkten Vergleich der Ergebnisse der reine Einfluss des Lösungsmittels auf die ersten Schritte der Peptidfaltung sichtbar gemacht werden. Wie frühere Untersuchungen bereits nahelegten, wirkt sich die Lösungsmittelviskosität direkt auf die Geschwindigkeit der Faltungsvorgänge aus.

MO 12.5 Fr 15:15 HU 2091

Untersuchung des Konformerenraums von Tryptamin mit rotationsauflösender elektronischer Spektroskopie — •Michael Schmitt[1], Leo Meerts[2] und Marcel Böhm[1] — [1]Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie — [2]Radboud University Nijmegen, Department of Molecular and Laser Physics,The Netherlands

Der Neurotransmitter Tryptamin kommt in der Gasphase in sieben verschiednen Konformeren vor, die bisher mit IR-UV Doppelresonanzspektroskopie untersucht wurden. Wir haben die elektronischen Ursprünge aller Konformere und einiger ihrer deuterierten Isotopomere mit Rotationsauflösung gemessen. Die stark überlappenden roibronischen Banden wurden mit Hilfe eines automatisierten Fits, der auf der Anwendung genetischer Algorithmen beruht zugeordnet und interpretiert. Aus den so bestimmten Trägheitsparametern konnte zum ersten Mal eindeutig und direkt die vorliegende Konformation für jedes der Konformere bestimmt werden. Clusterbildung des Tryptamins mit einem Argonatom (van der Waalscluster) oder mit einem Wassermolekül (H-Brückenbindung) läßt den Konformerenraum in ein einziges Konformer kollabieren, dessen Struktur ebenfalls aus den Trägheitsparametern bestimmt werden konnte.

MO 12.6 Fr 15:30 HU 2091

Analysis of isolated extended beta-sheet model systems in the gas phase — •M. Gerhards, H. Fricke, and A. Gerlach — Institut für Physikalische Chemie I, H.-Heine Universität Düsseldorf, Universitätsstraße 1, 40225 Düsseldorf

Proteins have a well defined three dimensional structure which is essential for their function. An important secondary structure element is the β-sheet. We investigate isolated peptides and peptide clusters with β-sheet binding motifs in molecular beam experiments. The chosen combined IR and UV spectroscopic methods are mass-, isomer-, and state-selective yielding an IR spectrum for each individual isomer. With our new developed nanosecond narrow band-width and high power IR laser we are able to obtain spectra in the complete region from 1000 to 4000 cm-1. By investigating isolated clusters we would like to answer the questions (a) what are the driving forces of peptides to form either inter- or intramolecular hydrogen-bonds and (b) how strong are the individual hydrogen bonds of a β-sheet structure. Our group has started with the investigations of smaller β-sheet models containing clusters of protected amino acids (phe, trp, tyr). We now present results both on the larger isolated tri- and tetrapeptides and on the extended β-sheet models formed by the clusters of the tri- and tetrapeptides. These are the largest peptide aggregates investigated up to now with the chosen highly selective spectroscopic methods.

MO 12.7 Fr 15:45 HU 2091

THz-Biology: Studying protein dynamics in solution — •Udo Heugen[1], Erik Bründermann[1], Matthias Krüger[1], David Leitner[2], Seung Joon Kim[3], Martin Grübele[3] und Martina Havenith[1] — [1]Dept. of Physical Chemistry II, Ruhr-Universität, Bochum, Germany — [2]Dept. of Chemistry, University of Nevada, Reno, USA — [3]Dept. of Chemistry and Physics, University of Illinois, Urbana, USA

We have developed a THz spectrometer to measure absorption spectra of solvated proteins. The radiation source is a p-type germanium laser which delivers output powers of several watts in the THz regime (from 1-4 THz). This allows us to penetrate relatively thick water layers (up to 0.3 mm) yielding reliable absorption in this experimentally difficult to access region. Using this setup we have investigated the changes in the water network by adding a solute in water and have started to systematically investigate the relation of tertiary and secondary structural changes to its spectrum. We will present the results for different mutants of ubiquitin and Lambda-repressor which serve as prototype systems and compare them with theoretical studies using molecular dynamics simulation. Our goal is to explore the large amplitude motions of proteins, which are assumed to be important for signal transfer and will foster folding. THz spectroscopy might open a new experimental window of fast protein dynamics in the future. We want to discuss the experimental setup and show first results that these methods allow direct experimental access to the change in the water network around the solute.