BP 26: Photobiophysics

Time: Friday 11:00–13:00 Location: ZEU 260

BP 26.1 Fri 11:00 ZEU 260

Photon statistics in the fluorescence from single light-harvesting complexes — •Gregor Hehl, Sandeep Pallikkuth, and Andreas Volkmer — 3rd Insitute of Physics, University of Stuttgart

The photosynthetic apparatus of purple bacteria contains pigment-protein complexes that are optimized for efficient energy transfer, such as the light-harvesting complex (LH2) with bacteriochlorophyll a (BChla) pigments arranged in ring-like structures. Strong electronic interaction among the BChla governs their excited state properties, which are theoretically described in terms of excitonic wave functions. In contrast to prior fluorescence excitation/emission single-molecule spectroscopy, here we report on the photon statistics in the fluorescence of individual LH2 complexes at room-temperature that provides information about photo-physical processes ranging from picoseconds to milliseconds. The fluorescence of individual LH2 complexes is investigated by means of their photon arrival times, and analyzed in terms of interphoton time distributions and second-order correlation functions. These measurements revealed photon antibunching at short times, indicating sub-Poissonian photon statistics and singlet-singlet annihilation, and an excitation power-dependent photon bunching effect at longer times.

BP 26.2 Fri 11:15 ZEU 260

Absorption and Fluorescence Spectroscopic Characterisation of the Circadian Blue-Light Photoreceptor Cryptochrome from Drosophila melanogaster (dCry) — •Javid Shirdel[1,3], Peyman Zirak[1], Alfons Penzkofer[1], Helena Breitkreuz[2], and Eva Wolf[2] — [1]Institut II-Physik, Universität Regensburg, D-93053 Regensburg, Germany — [2]Max-Planck-Institute of Molecular Physiology, D-44227 Dortmund, Germany — [3]Institut für Physik, Carl Von Ossietzky Universität Oldenburg, D-26129 Oldenburg, Germany

Cryptochromes are blue-light sensitive flavoproteins that are related to photolyases, but do not have the DNA repair mechanism of photolyases. They regulate growth and development in plants, regulate circadian rhythms in plants and animals, act as chemical magneto receptors in migratory birds, and are functioning in bacteria and algae. Here we report the absorption and fluorescence behaviour of the circadian blue-light photoreceptor cryptochrome from Drosophila melanogaster (dCry) in a pH 8 aqueous buffer solution. The flavin adenine dinucleotide (FAD) cofactor of dCry is identified to be present in its oxidized form, and the 5,10-methenyltetrahydrofolate (MTHF) cofactor is found to be hydrolyzed and oxidized to 10-formyldihydrofolate (10-FDHF). Photo-excitation of oxidized FAD in dCry causes a reductive electron transfer to the formation of anionic FAD semiquinone, and photo-excitation of the generated anionic FAD semiquinone causes an oxidative electron transfer to the back formation of oxidized FAD.

BP 26.3 Fri 11:30 ZEU 260

Analysis of pigment-protein-complexes by hole burning- and time resolved fluorescence spectroscopy — •Elmar Hassan Hubrich[1], Franz-Josef Schmitt[1], Jörg Pieper[2], Hans Joachim Eichler[1], and Gernot Renger[2] — [1]Institut für Optik und Atomare Physik — [2]Max-Volmer-Laboratorium, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin

The water-soluble chlorophyll-binding protein (WSCP) found in plants is primarily expressed under stress conditions (drought, heat). The precise function is still not clearified. In contrast to other photosynthetic pigment-protein complexes WSCP binds a maximum number of one molecule chlorophyll (Chl *a* or *b*) per subunit and does not contain carotenoids. WSCP forms tetrameric complexes, with two strongly excitonically coupled chlorophylls in an "open sandwich" geometry. Chl bound to WSCP shows a drastically reduced formation of reactive singlet oxygen in comparison to Chl in solution. WSCP is an excellent minimal model system to investigate pigment-pigment and pigment-protein interactions. We applied the complementary techniques of picosecond fluorescence spectroscopy (time- and wavelength-correlated single photon counting) and hole-burning spectroscopy. A fluorescence rise kinetics was found with a characteristic lifetime of 80 ps at 10 K, noticeably shorter lifetime and markedly reduced amplitude at 160 K and a time constant below the detection limit at higher temperatures. Hole burning and temperature dependent absorption spectroscopy were used to determine the spectral positions of the exciton states and to characterize their coupling to protein vibrations.

BP 26.4 Fri 11:45 ZEU 260

Polarisation-dependent Raman measurements of crystallized photosystem II — •Katharina Brose[1], Athina Zouni[2], Peter Hildebrandt[2], Christian Thomsen[1], and Janina Maultzsch[1] — [1]Institut für Festkoerperphysik, Technische Universität Berlin, Hardenbergstrasse 36, 10623 Berlin — [2]Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin

Raman spectroscopy is one of the standard methods to analyse the structural and vibrational properties of molecules and solids. In photosynthesis, the energy of light is converted into a separation of charge in the photosystem II reaction center. Using the newest photosystem II (PSII) dimer crystal structure (3.0 Å resolution), in which 11 β-carotene molecules (Car) and 14 lipids are visible in the PSII per monomer [1]. In the reaction center two Car molecules Car_{D1} and Car_{D2} are assigned, which are oriented perpendicular to each other. The function of these two carotene molecules in the photosynthesis process is still under debate. Polarisation-dependent Raman measurements are expected to give deeper insights in the structure-function relationship of these two Car molecules in the reaction centre of PSII. In this talk, we will present polarisation dependent Raman measurements on single PSII crystals of PSII.

[1] Loll, B., Kern, J., Saenger, W. Zouni, A., Biesiadka, J. (2005). Towards complete cofactor arrangement in the 3.0 Å resolution structure of photosystem II. Nature 438, 1040-1044.

BP 26.5 Fri 12:00 ZEU 260

Dynamics of light induced charge separation in PS II Core Complexes from thermophilic cyanobacteria (Thermosynechococcus elongatus) and higher plants (spinach) — •Rachel Olliges[1], Franz-Josef Schmitt[1], Athina Zouni[2], and Gernot Renger[2] — [1]Institut für Optik und Atomare Physik — [2]Max Volmer Laboratorium TU Berlin, Straße des 17.Juni 135, 10623 Berlin

The key steps of solar energy exploitation through photosynthetic water splitting take place in Photosystem II (PS II) of cyanobacteria, alga and higher plants. The light absorbed by antenna systems generates excited singlet-states that are efficiently funnelled to the photoactive pigment P680 of the reaction-center (RC) where the transformation takes place leading to the radical ion pair $P680^{+\bullet}$ $Q_A^{-\bullet}$. The rate of these processes can be gathered from measurements of the time resolved fluorescence decay and model based data evaluation. At present two basically different types of models are discussed: a) radicalpair/exciton equilibrium (REE) model and b) transfer to the trap limited (TTL) model (diffusion limited model).

Time resolved fluorescence-spectroscopy was performed on PS II core complexes (PS IICC) from thermophilic cyanobacteria (Thermosynechococcus elongatus) and higher plants (spinach) by using single photon counting techniques providing a time resolution of about 10 ps. The data shows that the widely used REE model is not able to describe the dynamics completely.

BP 26.6 Fri 12:15 ZEU 260

Multidimensional Optical Probes of Electronic Correlations and Exciton Dynamics in Photosynthetic Complexes — •Dmitri V. Voronine[1], Darius Abramavicius[2], and Shaul Mukamel[2] — [1]Institut für Physikalische Chemie, Am Hubland, Universität Würzburg, Würzburg, Germany — [2]Department of Chemistry, University of California, Irvine, USA

We simulate the multidimensional electronic chirality-induced (2D ECI) signals of excitons in the photosynthetic Fenna-Matthews-Olson (FMO) complexes from two species of green sulfur bacteria Chlorobium tepidum (C.t.) and Prosthecochloris aestuarii (P.a.). The spectra provide sensitive probes of local protein environment of the constituent bacteriochlorophyll a chromophores and reflect electronic structure variations (site energies and couplings) of the two complexes. Pulse polarization configurations are designed which can separate the coherent and incoherent exciton dynamics. Two main energy transfer pathways are revealed by varying the middle time delay in t2-dependent electronic 2D ECI spectra of FMO. Using coherent control we demonstrate optimal laser polarization configurations which

enhance chirality-sensitive spectral features, revealing a slow energy transfer pathway which was not resolved in the non-chiral spectra. We show that coherent control can be used to optimize the resolution of cross-peaks and corresponding energy transfer pathways in 2D optical spectroscopy.

BP 26.7 Fri 12:30 ZEU 260

Resolution limits in nanobiophotonics — •Franz-Josef Schmitt — Institut für Optik und Atomare Physik, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin

According to recent progress in high resolved fluorescence microscopy literature presents new relations for the spatial resolution limit suggesting a principally infinite resolution of fluorescing pigments. We show that similar relations would also be found for the time resolution and present examples where time- and space-correlated single photon (TSCSPC) counting is used to determine sub-nm distances and sub-ps energy transfer and exciton relaxation processes in biophysical pigment-protein complexes (e.g. plant proteins containing chlorophyll). Up today TSCSPC still did not reach an unbreakable limitation of the resolution. We show results of 24 h measurements which are limited by the long time stability of the sample and the long time stability of the measurement setup. The possible refinements of these both stability problems are shortly discussed (e.g. by correction of thermal drift, deep temperature measurements to reduce photobleaching). Even in a principal approach without respect to sample and setup stability one will find that an infinite resolution is not possible although fluorescence spectroscopy might be still far away from the principal lower bound of resolution for arbitrary big and arbitrary stable systems.

BP 26.8 Fri 12:45 ZEU 260

Evolutionäre Bestimmung kinetischer Parameter für Simulationen metabolischer Systeme — •Tihamér Geyer, Xavier Mol und Volkhard Helms — Zentrum für Bioinformatik, Universität des Saarlandes, Saarbrücken

Sollen für ein metabolisches System die Raten für die individuellen Reaktionen bestimmt werden, so stellt sich oft das Problem, daß die Antwort des Systems von einer Reihe von Raten bestimmt wird, die experimentell nicht unabhängig gemessen werden können. Wir zeigen am Beispiel des photosynthetischen Apparats des Purpurbakteriums *Rhodobacter sphaeriodes*, wie mit einem evolutionären Algorithmus die Parameter für eine stochastische Simulation so angepasst werden können, daß ein Satz zeitabhängiger Experimente möglichst gut reproduziert wird. Für die Photosynthese wurden etwa zwei Drittel der Parameter in die Optimierung, die mit publizierten Experimenten durchgeführt wurde, einbezogen. Werden die Experimente auf die Optimierung abgestimmt, sollten auf diese Weise auch für andere Systeme fast alle Parameter durch den Fit bestimmbar sein.