

BP 5: Photobiophysics

Time: Monday 16:15–17:15

Location: PC 203

BP 5.1 Mon 16:15 PC 203
Optically "Dark" States of Carotenoids in the Major Plant Light-Harvesting Complex Investigated by Femtosecond Two-Photon Fluorescence Excitation Spectroscopy —

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Carotenoids play several important roles in photosynthetic organisms: as structural components of pigment-protein-complexes, as accessory light-harvesting pigments, and in photoprotection. To understand the latter two functions and the underlying mechanism(s) it is vital to know the energetic positions of the first excited singlet state S_1 (2^1Ag^-) of relevant xanthophylls (carotenoids). Because single photon absorption is symmetry-forbidden for the S_0 (1^1Ag^-) \rightarrow S_1 (2^1Ag^-) transition, the carotenoid 2^1Ag^- state cannot be readily investigated by conventional spectroscopy. This transition, however, is two-photon allowed. Moreover, the carotenoid S_1 state is assumed to lie close to the lowest excited chlorophyll singlet state. Thus, simultaneous two-photon absorption of tuneable fs-NIR-pulses being monitored by chlorophyll fluorescence is a useful approach to study the role of the "dark" states in excitation energy transfer and dissipation in light-harvesting complexes. Two-photon excitation spectra of the plant major light-harvesting complex (LHC II) with different xanthophyll-cycle pigment complements (violaxanthin, zeaxanthin) will be presented and implications for the photoprotective mechanism will be discussed. This research is supported by the DFG (SFB 429, TP A2).

BP 5.2 Mon 16:30 PC 203

Metal - enhanced fluorescence of chlorophylls in single light - harvesting complexes — •SEBASTIAN MACKOWSKI^{1,2}, STEPHAN WÖRMKE¹, ANDREAS MAIER¹, TATAS BROTSUDARMO³, HAYK HARUTYUNYAN¹, ACHIM HARTSCHUH¹, ALEXANDER GOVOROV⁴, HUGO SCHEER³, and CHRISTOPH BRÄUCHLE¹ — ¹Department of Chemistry and Biochemistry, Ludwig-Maximilian-University, Munich, GERMANY — ²Institute of Physics, Nicolaus Copernicus University, Torun, POLAND — ³Department of Biology, Ludwig-Maximilian-University, Munich, GERMANY — ⁴Department of Physics and Astronomy, Ohio University, Athens OH, USA

Ensemble and single-molecule spectroscopy demonstrates that both emission and absorption of peridinin-chlorophyll-protein photosynthetic antennae can be largely enhanced through plasmonic interactions. We find up to 18-fold increase of the chlorophyll fluorescence for complexes placed near a silver metal layer. This enhancement, which leaves no measurable effects on the protein structure, is observed when exciting either chlorophyll or carotenoid and is attributed predominantly to an increase of the excitation rate in the antenna. The enhancement mechanism comes from plasmon-induced amplification of electromagnetic fields inside the complex. This result is an important step toward applying plasmonic nanostructures for controlling the optical response of complex biomolecules and improving the design and functioning of artificial light-harvesting systems.

BP 5.3 Mon 16:45 PC 203

Chlorophyll binding protein complexes: Nanostructure and optical properties — •FRANZ-JOSEF SCHMITT¹, CHRISTOPH THEISS¹, GERNOT RENGER², and HANS JOACHIM EICHLER¹ — ¹Institut für Optik und Atomare Physik — ²Max Volmer Laboratorium TU Berlin, Strasse des 17. Juni 135, 10623 Berlin

The photophysical and biochemical properties of pigments change due to surrounding protein environments. This principle has been perfectly in the biosphere. Photosynthetic organisms developed pigment-protein complexes for efficient light collection, transfer of electronically excited states and transformation into electrochemical free energy. In addition to the photosynthetic apparatus plants contain also water soluble chlorophyll (Chl) binding proteins (WSCP) which most likely exert not yet clarified regulatory functions. A striking feature -among several interesting properties-is the retardation of the formation of highly reactive singlet oxygen in WSCP. Although the origin of this effect is not yet clarified, it seems likely that the protein matrix is able to diminish the sensitized reaction of bound chlorophyll with the surrounding oxygen.

A wide range of linear and non-linear optical techniques have been used to determine successfully the properties of these pigment protein complexes providing a deeper understanding of the influence of protein interactions on the electronic structure of the pigments. Time resolved fluorescence spectroscopy combined with two photon excitation will help to investigate the pigment interactions directly in biological tissues.

BP 5.4 Mon 17:00 PC 203

Resonanz-Ramanspektroskopie an β -Karotin und polarisationsabhängige Messungen an Photosystem II - Kristallen — •KATHARINA BROSE¹, NORMAN TSCHIRNER¹, CHRISTIAN THOMSEN¹, MATTHIAS SCHENDERLEIN², PETER HILDEBRANDT² and ATHINA ZOUNI² — ¹Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstrasse 36, 10623 Berlin — ²Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin

Pflanzen wandeln Photonenenergie mit Hilfe der Photosysteme I und II (PS I und PS II) in chemische Energie um. An diesem Prozess ist unter anderem das Pigment β -Karotin beteiligt, von dem sich im Reaktionszentrum des PS II zwei befinden, die zueinander senkrecht angeordnet sind.

Telfer et al. beobachteten wellenlängenabhängige Unterschiede in Resonanz-Ramanspektren des PS II, welche den unterschiedlich angeordneten Karotinen zugeordnet wurden [1]. Messungen an dem reinen Pigment β -Karotin zeigen jedoch dasselbe Verhalten. Unsere Messergebnisse deuten auf zwei nahe beieinander liegende, nicht auflösbare Peaks hin, deren Resonanzverhalten für verschiedene Anregungswellenlängen variiert. Um die β -Karotine im PS II dennoch unterscheiden zu können, wurden polarisationsabhängige Messungen an Photosystemkristallen [2] durchgeführt.

[1] A. Telfer, D. Frolov, J. Barber, B. Robert und A. Pascal, *Biochemistry* 2003, 42, 1008-1015

[2] A. Zouni, H.-T. Witt, J. Kern, P. Fromme, N. Krauß, W. Saenger und P. Orth, *NATURE*, Vol. 409, 739 (2001)