Steps toward time-resolved single-frequency IR absorption spectroscopy on photosystems for investigation of electron-coupled proton transfer

*P. Simon, M. Schönborn, Y. Zilliges, P. Chernev, H. Dau

FU Berlin, Physik, Berlin, Germany

Photosystem II (PSII) is a transmembrane protein performing photosynthetic water oxidation. It is activated by the absorption of photons by its pigments. The excitation energy is transferred to the special chlorophyll pair and a charge separation takes place. The electron is transferred over a firmly bound quinone, QA, to a transiently bound quinone, QB. The positive charge is transferred by coupled electron-proton transfer to the catalytic center, a Mn4Ca-oxo cluster, where oxidation of a Mn atom takes place (Dau et al, 2012, Curr. Opin. Chem. Biol. 16, 3-10). After accumulation of four of these oxidizing equivalents, the O-O bond is formed and O2 is released. The released protons, electrons and oxygen molecules and the substrate water are transported over large distances of up to 30 Å involving an alternating sequence of electron and proton removal from the catalytic site (Klaus et al. 2012, PNAS 109, 16035-16040).

Understanding of these processes at an atomic level does not only answer fundamental questions of protein functions but can also provide hints on the development of catalysts for artificial photosynthesis, a clean way of producing storable energy.

We want to analyse the dynamics of these processes by time resolved experiments in time domains from 100 ns to 100 ms. The spatiotemporal coupling of electron and proton transfer as well as different transport pathways will be investigated.

To do so a new infra-red absorption experiment is being designed complementing an FTIR step-scan experiment. The central part of the new setup is a continuous-wave quantum-cascade laser emitting in the spectral region from 1300 to 1650 cm-1 and thus covering the amide II region, partly the amide I and COO- stretching region as well as bands of special interest like the ones of the quinones or the redox active tyrosine denoted as YZ. The time resolution is in the microsecond range, which enables us to observe structural changes and proton transfer dynamics. In the future also measurement on site directed point mutations of cyanobacterial PSII will be done.

Here the setup and first measurements on the dynamics of selected vibrational bands, specidically the band assignable to QA, will be presented.