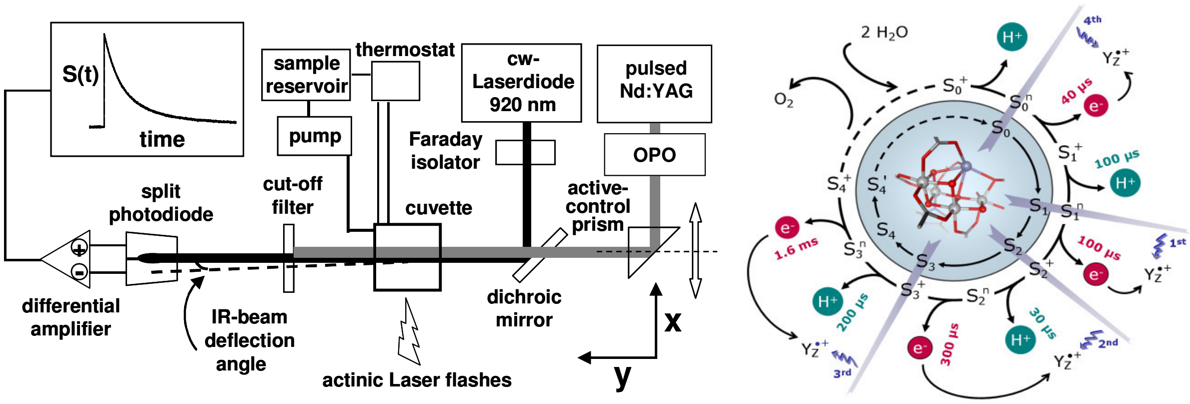
Electron transfer in water oxidation by photosystem II: thermodynamics, kinetics, and protein dynamics studied by time-resolved photothermal beam deflection (PBD) spectroscopy



Setup for time-resolved PBD measurements (left) and reaction cycle of photosynthetic water oxidation with time constants partly based on PBD results (right).

Summary:

Photosynthetic water oxidation at the manganese complex of photosystem II (PSII) is the sole source of the dioxygen (O_2) of the atmosphere. Understanding the nature of the electron transfer (ET) reactions in the four-stepped catalytic cycle of the Mn complex of PSII is essential to unravel the mechanism of water oxidation. The goal is to determine the restraints that govern the ET reactions at the atomic and molecular levels, namely the thermodynamic parameters (enthalpy and entropy changes), dynamics of the cofactors and of the protein matrix, and proton transfer reactions. This information is crucial, on the one hand, to understand the unique water oxidation reaction of the native PSII. It is also important for the future use of the water oxidation reaction in biomimetic and biotechnological systems, aiming at the replacement of fossil fuels by sunlight-powered hydrogen production.

In this project we developed, implemented, and applied a high-sensitivity time-resolved technique, photothermal beam deflection spectroscopy (PBD), to study the ET reactions at the Mn complex of PSII. By the PBD technique, the enthalpy changes (ΔH) that accompany the ET reactions in the micro- to milliseconds time range directly are determined (time-resolved calorimetry). In addition, e.g. information on volume changes of the protein matrix and on proton release, occurring concomitantly or sequential to the ET, is obtained.

A new PBD spectrometer has been build in our laboratory. It comprises (i) collinear alignment of a nanosecond-pulse pump laser beam and a continuous-wave probe laser in the near infrared, (ii) tuneable wavelength of the pump laser as achieved by an optical parametric oscillator (OPO), (iii) a thermostated flow-through cuvette and pump system for rapid sample exchange (high-throughput measurements), and (iv) specialized data acquisition and evaluation software. The whole setup is computer-controlled, allowing for automated measurements on large amount of PSII samples.

In conclusion, we consider the project as successful. The main goals mostly have been reached, The PBD experiments are ongoing in our laboratory and expected to yield a more complete picture of the energetics of the ET reactions of photosynthetic water oxidation.