

## **Time-resolved recording of protonation dynamics in the water splitting Photosystem II using step-scan Fourier transform infrared spectroscopy**

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

*Freie Universität Berlin, Fachbereich Physik, Berlin, Germany*

In photosynthesis, Photosystem II plays the role of water splitting. Upon absorption of photons, H<sub>2</sub>O is split in oxygen and hydrogen at the site of the oxygen evolving complex (OEC). The oxygen evolving complex undergoes a cycle of different states, with the states being advanced by the absorption of one photon, and four photons are needed to split one water molecule. Understanding how this water splitting takes place at the atomic level plays a major role in the development of artificial catalysts, which are needed for sustainable production of hydrogen, an anticipated clean, sustainable and renewable fuel source.

Several possible proton paths from the oxygen evolving complex to the lumen have been proposed based on a crystal structure with 1.9 Å resolution [1]. In these paths, amino acid residues like carboxylic acids play a role in passing on the protons. Fourier transform infrared spectroscopy is a powerful tool to track protonation dynamics of amino acid residues [2]. In steady-state difference spectra, the states of the OEC are investigated by comparing the spectra before and after applying a laser flash. Time-resolved spectra can be obtained using the step-scan technique.

One of the obstacles of step-scan measurements to overcome are laser artifacts [3]. These are artifacts in the detector signal domain which stem from the laser flash which advances the OEC to the next state. The decay of these artifact signals is in the time domain of the signals to be examined, so careful examination and extensive averaging of several spectra are needed. What is more, many samples are needed to record only one spectrum, because the water splitting cycle can be repeated only a few times.

To solve these problems, a setup has been designed to automatically record many measurements in a row [4]. The next step in researching photosynthetic water oxidation will be to record a time-resolved spectrum using the step-scan method.

### **References:**

- [1] Yasufumi Umena et al. "Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å." In: *Nature* 473.7345 (2011), pp. 55-60.
- [2] Takumi Noguchi. "Fourier transform infrared analysis of the photosynthetic oxygen-evolving center". In: *Coordination Chemistry Reviews* 252.3-4 (2008). The Role of Manganese in Photosystem II, pp. 336-346.
- [3] C. Rödiger and F. Siebert. "Errors and Artifacts in Time-Resolved Step-Scan FT-IR Spectroscopy". In: *Appl. Spectrosc.* 53.8 (Aug. 1999), pp. 893-901.
- [4] Björn Süss. "Entwicklung eines Step-Scan FTIR-Experiments zur Untersuchung der lichtinduzierten Wasserspaltung der oxygenen Photosynthese". FU Berlin, 2011.