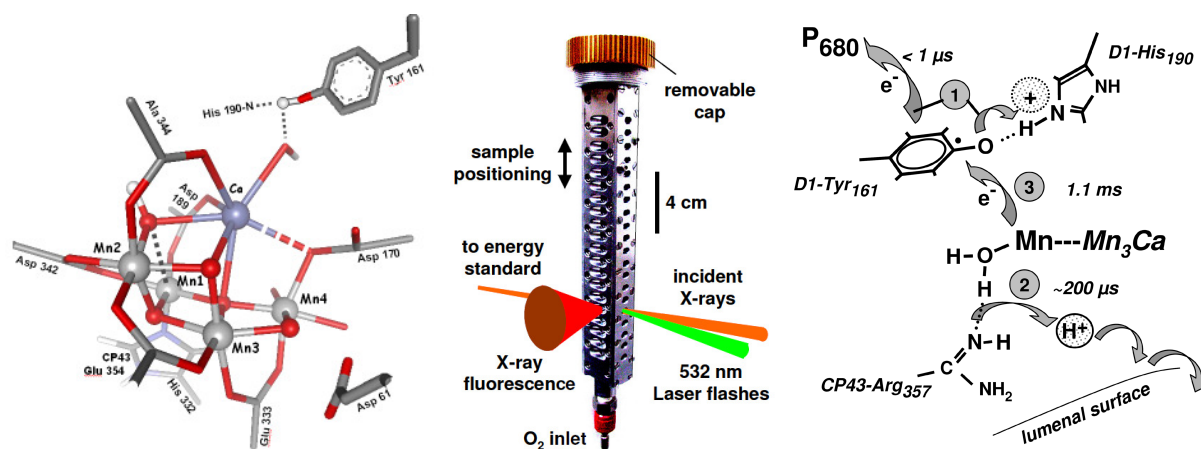


## Structural changes at the manganese complex of photosystem II followed by XAS



Structural model of the Mn<sub>4</sub>Ca complex of PSII (left), pressure cell for time-resolved XAS under 20 bar O<sub>2</sub> (middle), and ET/PT sequence during the O<sub>2</sub>-evolving transition (right).

### Summary:

Structure-function relations were investigated for the manganese complex of oxygenic photosynthesis, a pentanuclear Mn<sub>4</sub>Ca complex bound to the protein subunits D1 and CP43 of photosystem II (PSII). At this manganese complex water is oxidized and the atmospheric O<sub>2</sub> is formed. Central objective was the analysis of the structural changes that occur upon transitions between intermediate states of the water-oxidation/O<sub>2</sub>-production cycle using X-ray absorption spectroscopy and complementary methods. Changes in the nuclear coordinates of atoms in the core of the metal complex were followed by analysis of the EXAFS (extended X-ray absorption fine-structure) using also unidirectionally oriented samples. The X-ray absorption near-edge structure (XANES) in combination with *ab-initio* scattering calculations and supplemented by molecular orbital considerations provided insights into the details of the coordination geometry and relevant aspects of the electronic structure (oxidation states, orbital occupancies).

By time-resolved XAS measurements after laser-flash excitation (time resolution of 10 μs has been achieved), we recently discovered the existence of a kinetically resolvable intermediate in the crucial S<sub>3</sub>→S<sub>0</sub> transition during which water is finally oxidized and the O-O bond formation proceeds. This intermediate could be the missing links in the efforts to unravel the mechanism of light-driven water splitting in PSII. Their identification and characterization by freeze-quench XAS and time-resolved XAS supplemented by visual optical and EPR spectroscopy was the central point on the agenda 2006–2009. Furthermore, the electronic and magnetic structure of the PSII manganese complex in relation to the inter-atomic distances was addressed by a combination of advanced XAS techniques.

The XAS-based models for the structural changes of the PSII manganese complex in its catalytic cycle were refined on the basis of the novel crystallographic information that has become available.