Time-resolved XES studies on photosystem II and manganese model compounds

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X-ray Free Electron Lasers (XFELs) have opened a new chapter in the study of the dynamics of biomolecules, as time-resolved structural snapshots of biomolecular reactions can be captured from crystals at room temperature in native aqueous environment using ultra-bright femtosecond X-ray pulses. The aim is for diffraction snapshots to be recorded before molecules are destroyed by the process of photoionization leading to a coulomb explosion in the time range of femtoseconds. However, the reports on the pulse length where damage-free data can be collected vary from the sub fs range to 50fs [1-3]. It is also clear that alteration of the electronic structure of molecules precedes photoionization and the final destruction of the molecules and the crystals in the process of coulomb explosion. The time required for photoionization and Auger decay also depends on the chemical element, with metals being most easily photoionized.

The main focus of this work was an XES study of the changes in Mn oxidation states during the water splitting cycle and the damage threshold of the Mn cluster in its different oxidation states. As a first step we aimed to systematically study the X-ray radiation damage of the Mn model compounds as a function of the X-ray energy above the Mn absorption edge, the photon flux and the pulse duration.

The results provided clear evidence that there is a very strong correlation between the X-ray induced photoreduction of the Mn compounds and the pulse duration as well as the beam energy. Data collected at two energies (9.5 and 7.25 keV) showed significant differences, with significant more changes in the electronic states observed at the lower energy, even below 10fs pulse duration, while the data at higher energy indicated that the OEC electronic structure might be intact at pulse durations below 15fs.

References

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