

X-ray emission spectroscopy for study of photosystem II electronic structure evolution

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Photosynthetic water oxidation is a fundamental process that sustains the biosphere. A Mn₄Ca cluster embedded in the photosystem II (PSII) protein environment is responsible for the production of atmospheric oxygen. Enzyme reactivity is usually associated with changes in oxidation state, spin state, and metal-ligand covalency of corresponding metallocofactors. The inner-shell X-ray spectroscopy is the direct probe for the local electronic structure of the transition metal that makes spectroscopic methods essential for elucidating mechanisms underlying the dynamic processes involving metal ions. I am going to present an overview of x-ray spectroscopy techniques used in our laboratory for studying the processes in biological species and the results of our recent study conducted on PS II protein samples. We used time-resolved x-ray emission spectroscopy (XES) to observe the process of oxygen evolution initiated by sequential laser flashes, that is accompanied by rapid (within 50 μs) changes to the Mn Kα XES spectrum.