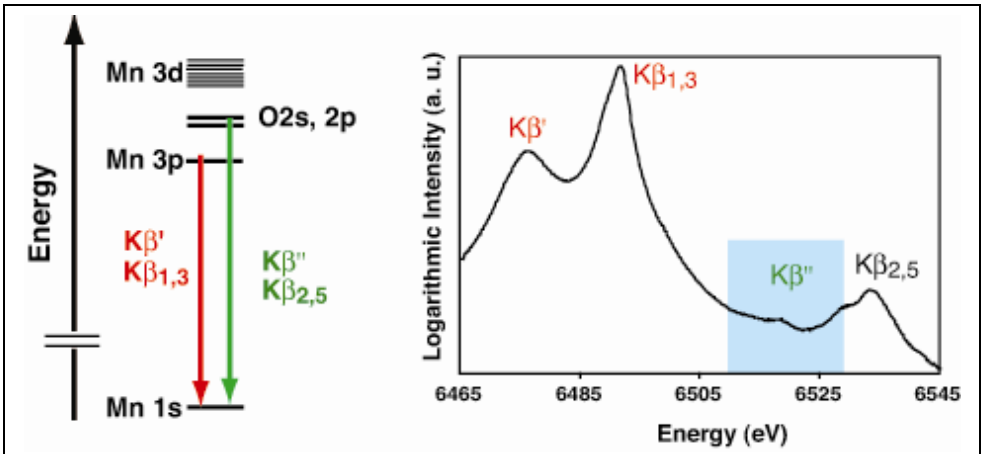
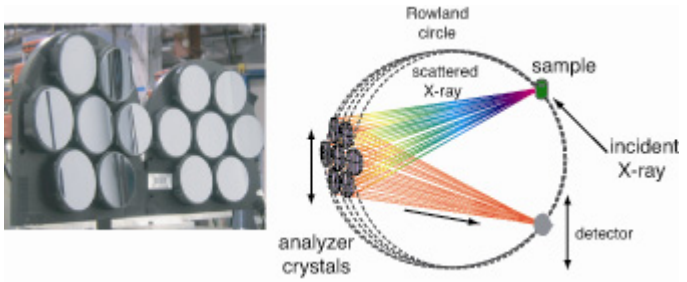
Researchers Directly Observe Oxygen Signature in the Oxygen-evolving Complex of Photosynthesis



Energy Diagram of the Mn Kβ transitions in MnO.

Arguably the most important chemical reaction on earth is the photosynthetic splitting of water to molecular oxygen by the Mn-containing oxygen-evolving complex (Mn-OEC) in the protein known as photosystem II (PSII). It is this reaction which has, over the course of some 3.8 billion years, gradually filled our atmosphere with O_2 and consequently enabled and sustained the evolution of complex aerobic life. Coupled to the reduction of carbon dioxide, biological photosynthesis contributes foodstuffs for nutrition while recycling CO_2 from the atmosphere and replacing it with O_2. By utilizing sunlight to power these energy-requiring reactions, photosynthesis also serves as a model for addressing societal energy needs as we enter an era of diminishing fossil fuel resources and climate change. Understanding, at the molecular level, the dynamics and mechanisms behind photosynthesis is of fundamental importance and will prove critical to the future design of devices aimed at converting sunlight into electrochemical energy and transportable fuel.

A team led by scientists from the SLAC National Accelerator Laboratory and Lawrence Berkeley National Laboratory has reported the first direct observation of oxo-bridges in the Mn-OEC by means of x-ray emission spectroscopy (XES). Using x-rays produced at Beam Line 6-2 at SLAC's Stanford Synchrotron Radiation Lightsource, the scientists excited inner shell Mn electrons from the Mn-OEC in concentrated spinach samples. Usually this very short lived 1s-hole in the electron shell is filled by an inner-shell Mn 2p-electron, resulting predominantly in what is known as Kα x-ray fluorescence. However, about once every 10,000 Kα events, an electron from a ligand oxygen atom fills the hole. By tuning a novel x-ray spectrometer (the most efficient of its kind in the world) to an energy region where these signals occur, the team was able to observe the weak oxygen spectrum for the first time. This enabled the researchers to get a spectroscopic signature of only the few oxygen atoms bound to the Mn-OEC out of the many oxygen atoms in the surrounding water and protein.



Schematic drawing of the setup for x-ray emission spectroscopy (right) and the 14-crystal analyzer (left).

From model compounds also investigated in the study, it was shown how the strength and shape of the oxygen spectrum changes depending on how the oxygen atoms are bound to the Mn. Understanding these changes could help researchers in the future directly follow the splitting of two water molecules and the emission of the O_2 molecule seen from the catalytic center, i.e. the Mn-OEC. Such research is planned at SSRL, where PSII in frozen systems prepared at different states of photo illumination will be studied. Even more exciting is the prospect of following this amazing reaction in real-time using the Linac Coherent Light Source.

Primary Citation

Yulia Pushkar, Xi Long, Pieter Glatzel, Gary W. Brudvig, G. Charles Dismukes, Terrence J. Collins, Vittal K. Yachandra, Junko Yano, and Uwe Bergmann, *Direct Detection of Oxygen Ligation to the Mn_4Ca Cluster of Photosystem II by X-ray Emission Spectroscopy*, Angew. Chem. Int. Ed.

http://www3.interscience.wiley.com/cgi-bin/fulltext/123215603/PDFSTART

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