Evaluation of TR-XRD and DFT based models of the Oxygen-Evolving Complex of Photosystem II versus EXAFS data

Hasan Tunçer[1], Gabriel Bury[1] and Yulia Pushkar[1]

[1]*Department of Physics and Astronomy, Purdue University, IN, USA*
htuncer@purdue.edu

Photosystem II (PSII) is a crucial component of oxygenic photosynthesis, responsible for splitting water molecules to produce molecular oxygen. At the core of this process is the oxygen-evolving complex (OEC), containing a Mn4Ca cluster, which catalyzes the water-splitting reaction. Understanding the precise structure of this Mn4Ca cluster under functional conditions is key to gaining insights into the mechanism of water oxidation in natural photosynthesis.
In this study, we aim to refine the structure of the OEC of PSII via comparison of structural models obtained in recent time-resolved X-ray diffraction experiments [Bhowmick et al. 2023; Li et al. 2024] and via DFT analysis. Several controversies still exist such as proposal of low oxidation state OEC where instead of more widely accepted 2xMnIII2xMnIV OEC composition in the S1 state, a two-electron reduced form of 4xMnIII is hypothesized. We compared EXAFS spectra derived from DFT models of the low oxidation state paradigm [Chen et al. 2018] with high quality room temperature EXAFS of the S1 state. Poor agreement with the experiment indicates that these models are unlikely to represent the actual S1-state.
One more open question is the discrepancy of the O5-O6 distance in the S3 state between XRD results indicating ~2.0 Å and majority of DFT models of this state indicating ~2.5-2.6 Å distance. Researchers conducting XRD consider this discrepancy to be above the uncertainty of the XRD method, thus, explanation is needed. One approach is to propose a dynamic interconversion, or low barrier O-O coordinate in this state. [Corry and O'Malley. 2020] Others implicated X-ray induced damage.[Chrysina et al. 2023] Our modeling of the S3-state EXAFS has shown that this state can be satisfactory modeled with a combination of two states with protonated Mn-O6-H and deprotonated Mn=O6 both featuring the O5-O6 distances of 2.5-2.6 Å.[Bury and Pushkar 2024] Studying the Mn4Ca cluster at room temperature poses significant challenges due to its sensitivity to X-ray radiation which will also be discussed.

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