

# Geometrical, electronic and spin structures of the $\text{CaMn}_4\text{O}_5$ cluster in oxygen evolving complex of photosystem II. Possible intermediates in the $\text{S}_3$ state of the Kok cycle

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Recently serial femtosecond X-ray (SFX) crystallography experiments [1, 2, 3] were performed to elucidate the geometrical structure of the intermediate in the  $\text{S}_3$  state of the Kok cycle for water oxidation in oxygen evolving complex (OEC) of photosystem II (PSII). Kupitz et al. first performed the SFX experiment [1]. Young et al. [2] have concluded no insertion of hydroxide anion for the SFX structure in the  $\text{S}_3$  state. On the other hand, Suga et al. [3] have elucidated insertion of extra oxygen atom in their SFX  $\text{S}_3$  structure. Different conclusions were presented for the  $\text{S}_3$  structures based on the same SFX experiments.

We have performed full geometry optimizations of the possible intermediates in the  $\text{S}_3$  state by hybrid DFT (B3LYP) methods [4, 5], assuming 1) insertion of water molecule and 2) no insertion of water molecule. The left-opened (closed-cubane) structure was found to be more stable than the right-opened (open-cubane) structure under the assumption 1). On the other hand, nine possible intermediates with different mixed-valence and spin states were found in the  $\text{S}_3$  state under the assumption 2). Relative stabilities of these intermediates were variable, depending on the weak, intermediate and strong electron correlation regimes. Implications of the computational results are discussed in relation to the SFX results [1-3] as well as X-ray emission (XES), EPR and EXAFS experimental results.

[1] C. Kupitz, *Nature* **513**, 261(2014)

[2] I. D. Young et al., *Nature*, 540, 453 (2016).

[3] Suga et al. *Nature*, **543**, 131 (2017).

[4] H. Isobe et al., *Inorg. Chem.* 55, 502 (2016).

[5] M. Shoji et al., *Faraday Discussions*, 198, 83 (2017).