Theoretical Studies of Damage-Free XFEL Structures of the $CaMn_4O_5$ cluster in Oxygen Evolving Complex of Photosystem II

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Very recently, Suga, Akita and Shen et al [1] determined damage-free structures of the oxygen evolving complex (OEC) of photosystem II (PSII) by using the X-ray free electron laser (XFEL) at 1.95 Å resolution. However, positions of hydrogen atoms were not determined. We theoretically examined the XFEL structures under the assumption of four protonation cases [2]. Spin densities calculated at the high-spin UB3LYP level revealed that the Mn-O bonds entail a partial internal reduction by the high-valent Mn ions in the $CaMn_4O_4X(H_2O)_3Y$ cluster and the O(5)(=X) site is considered to be protonated at the the S_1 structure [1]. In this paper several key concepts and selection rules for the Mn-Mn, Ca-Mn and Mn-O distances of the $CaMn_4O_5$ cluster elucidated by our QM and QM/MM calculations were examined for lucid understanding of the damage free S_1 structure of OEC of PSII revealed by XFEL. A simple equation for estimation of the Mn_a-Mn_b distance with the Mn_a-$O_{(5)}$ bond length was derived in relation to the Jahn-Teller (JT) effect for the labile Mn_a-X-Mn_d bond (X=$O_{(5)}$=oxygen dianion or hydroxide anion), indicating that the XFEL structure is regarded as a slightly right-elongated quasi-central structure in contradiction to a right-opened structure by the EXAFS.

[1] M. Suga et al, Nature DOI: 10.1038/nature13991 (2014).

[2] M. Shoji et al, chem. phys. lett. in press.