The mechanism for dioxygen formation in PSII studied by quantum chemical methods

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In the area of enzymatic mechanisms, there are two cases of fundamental importance remaining to be solved which stand out from the other ones. The first one is the mechanism for proton pumping in cytochrome oxidase and the second one the formation of dioxygen in photosystem II. In the case of dioxygen formation, a severe difficulty has been the lack of a well defined structure for the oxygen evolving center (OEC). The first step in this direction came with the X-ray structure of Zouni et al [1]. At rather low resolution they were able to suggest positions for the four manganese atoms. A year ago, Ferreira et al [2] took a big step forward with a new X-ray structure where an OEC cluster could be suggested including calcium and with reasonable assignments of the amino acid ligands. However, since both these X-ray structures have a low resolution of only 3.2-3.5 Å, even the general structure of the OEC is still debated. The present contribution reports a theoretical investigation by hybrid density functional theory (DFT) of models of the proposed X-ray structure, and possible S-state transitions based on this structure [3]. After a very large number of model calculations the main features of a mechanism for dioxygen formation start to become visible. To reach a mechanism, positions and protonation states for eight additional water derived ligands, not seen in the X-ray structures, had to be suggested. The main requirement for forming the O-O bond is to have a low-lying precursor state with an oxygen radical ligand. The position of this radical in the OEC is suggested to be at a manganese in the cube which has contacts both to calcium and the loose manganese outside the cube. It is furthermore suggested that to reach this radical state a structural rearrangement is needed in the S_2 to S_3 transition. Comparisons to experimental evidence will be presented.

References

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