

Electronic structures of CaMn_4O_5 cluster in oxygen evolving complex of photosystem II. Theoretical calculations by LPNO-CC methods in the S_2 state of the Kok cycle

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Photosynthesis is one of the most important chemical processes on our planet. Oxygen-evolving complex (OEC) of PSII plays very prominent roles to make carbohydrates and provide molecular oxygen. This catalytic site of the OEC consists of four manganese ions and one calcium ion linked by oxo (or hydroxo) bridges, i.e. CaMn_4O_5 , and is well designed for the most effective water-oxidation in the nature. Main cyclic process to catalyze the water oxidation consists of four successive steps, namely, Kok cycle. During this process, OEC Mn cluster takes five oxidation states (S_0 , S_1 , S_2 , S_3 , and S_4) to catalyze water-splitting reaction. In nature the dark-stable S_1 is the most essential state in this successive chemical reaction. Since our studies were already reported for S_1 state, we present theoretical analyze in the S_2 state.

The CaMn_4O_5 cluster in the catalytic site for water oxidation in OEC of PSII is known to exhibit two types of EPR signals in the S_2 states : multiline signal ($S=1/2$, $g=2$) and broad signal ($S=5/2$, $g=4.1$). Accordings to these stable structures, we employed hybrid-DFT methods in order to execute geometry optimization in fourteen different S_2 intermediates. However, these hybrid-DFT methods contain many numerical parameters in its formalism, though UB3LYP (or UB3LYP*) can reproduce very accurate electronic properties. Thus, in our next research stage, domain-based local pair natural orbital (DLPNO) coupled cluster single and double (CCSD) with triple perturbation (T) correction methods as one of highly electronic correlation correction methods were applied to study relative stability among these structures.

