Molecular details of the first steps in photosynthesis

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Although photosynthesis in plants and bacteria is sustaining all the life on earth since about two and a half billions of years, the details of its mechanisms of working are still elusive. The overall mechanism of energy conversion in photosynthesis include the capture of light by antenna systems, the primary charge separation that convert the photon energy into chemical energy, and the subsequent cascade of biochemical processes leading to the formation of stable high-energy organic products that can be stored in the living organisms (ATP and sugar). One fundamental step of such mechanisms is the conversion of the electronic excitations into chemical energy used to perform the light-driven transformation of water molecules into molecular oxygen and hydrogen equivalents, i.e. water splitting. This water oxidation in photosynthetic organisms occurs through a series of intermediate steps S0-S4 of the so-called Kok-Joliot's cyle in the Oxygen Evolving Center of Photosystem II (PSII). The four electrons necessary for the water splitting reaction are subsequently removed by a radical tyrosine (Tyr_Z) from the Mn_4CaO_5 core, where they are accumulated to perform the more difficult catalytic step: the formation of molecular oxygen. The Photosystem II protein complex has been in the last 5 years the target of several cutting-edge experiments of X-ray crystallography also using the Free Electron Laser. [1-3] The molecular details of the single steps occurring in water oxidation catalysis are starting to be revealed also thanks to the supporting use of electronic structure calculations.
Beyond their interests in biophysics, the comprehension of photosynthetic water splitting mechanisms is also important to inspire artificial catalysts and possible biomimetic catalysts for water oxidation [4-6].
Using QM/MM dynamics and gas phase models we have built a comprehensive pathways of intermediate steps which involves interconversions between open and closed cubane isomers and the binding of a water molecule to Mn4, upon its oxidation. [7-9] Along this pathway, we have also calculated vibrational properties through dipole-dipole autocorrelation function and vibrational density of states from QM/MM dynamics. Our results allowed us to assign specific vibrational bands to molecular motions in different regions of the catalytic pocket and in different parts of the vibrational spectra. [10] In particular to help the interpretation of the computational and experimental data in the low frequency region (400-700 cm-1), we propose a decomposition of the Mn4CaO5 moiety into five separate parts, composed by "diamond" motifs, each one involving four atoms. The spectral signatures arising by this analysis can be easier interpreted to assign experimentally known bands to specific molecular motions. A similar analysis is also extended to all the Mn-ligands in the S1, S2 and S3 state. Starting from the S3 state we have also investigated several possible pathways and spin surfaces that may lead to the formation of the O-O bond.

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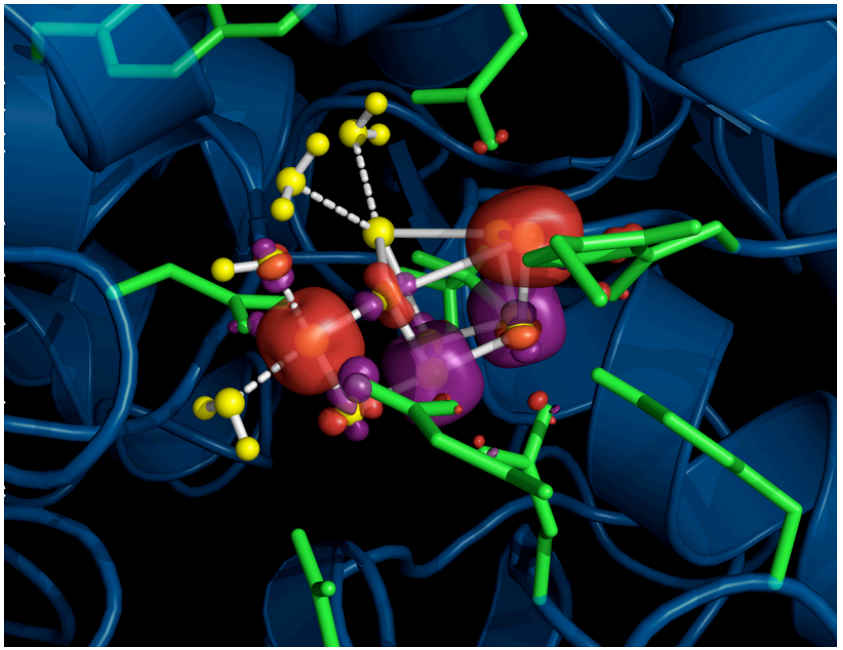

Figure
Quantum Mechanics / Molecular Dynamics simulation of catalytic site of the Photosystem II complex. The up and down spin density is highlighted in red and violet.