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AB INITIO MOLECULAR DYNAMICS IN NATURAL AND ARTIFICIAL PHOTOSYNTHESIS*

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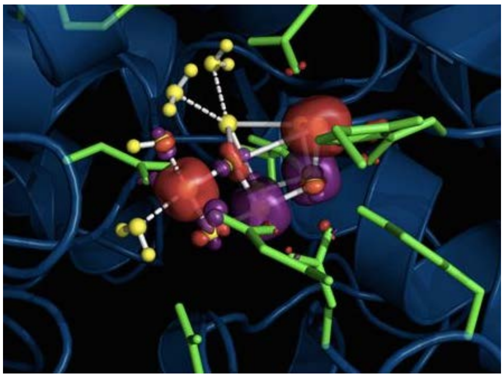

A Holy Graal in Chemistry research is represented by the understanding of the fundamental mechanisms underlying the water splitting reaction, which allows plants and bacteria to store the solar energy into highly energetic organic molecules. Ab initio molecular dynamics simulations can help in the study of the reaction mechanisms of the enzymes involved in natural photosynthesis as well as of their inorganic analogues, that can be used in the future as "artificial leaves" to produce clean energy from the sun.

The most difficult step in photosynthetic solar energy conversion performed by plants, algae and cyanobacteria is the splitting of water into molecular oxygen and hydrogen equivalents. To achieve this challenging catalytic step photosynthetic organisms use a special protein complex: the Photosystem II (PSII). The light-induced oxidation of the water in PSII is catalysed by its Mn_4Ca catalytic core proceeding by the accumulation of four oxidizing equivalents through five (S_0-S_4) states known as Kok's cycle. Recently, a new crystallographic structure of the PSII[1] has revealed for the first time the three-dimensional molecular arrangement of the complex with high-precision atomistic details, opening the way to first-principles computational studies of its catalytic mechanism. The deep understanding of the way Nature has chosen to perform efficiently this difficult task has a great relevance not only for biology but also for inspiring the development of biomimetic artificial systems that can be used to store solar energy in an environmentally friendly way. In recent years different new materials were proposed in this direction. In particular, an inorganic cobalt-based catalyst film (CoCat)[2] has attracted much interest because it is efficient at neutral pH and very stable (self-repairing) under working conditions. Moreover, the CoCat catalyst operates close to the Nernstian potentials for the H_2O/O_2 half-cell reaction, and it is self-assembled from low-cost materials. Prototypes of so-called "artificial leaves" were proposed by

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the group of Daniel Nocera at Harvard University, USA[3]. Nevertheless, the possibility to use less toxic transition metals, such as Mn, which is the one used in natural photosynthesis to achieve water splitting, is further stimulating the deep understanding of the biological device, i.e. the integral membrane protein Photosystem II.

To achieve this goal we have employed quantum chemistry calculations, in particular *ab initio* molecular dynamics, studying the properties of intermediate states of the Kok's cycle, describing the water splitting reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$). Such calculations allow a full account of the electronic structure of the molecules, such as, for instance, the forming and breaking of chemical bonds in a chemical reaction, and, at the same time, they can describe the molecular dynamics of the system and the effect of the temperature. To study the details of this biological process is important to fully take into account the effect of the enzyme environment. To reduce the computational cost we adopted a multiscale method, treating the enzyme environment by classical force-field based Molecular Mechanics (MM) and the reactive species by Quantum Mechanics (QM). Using this QM/MM framework we studied the Photosystem II by reconstructing in a virtual membrane bilayer the recently reported X-ray structure[1] (see Fig. 1).

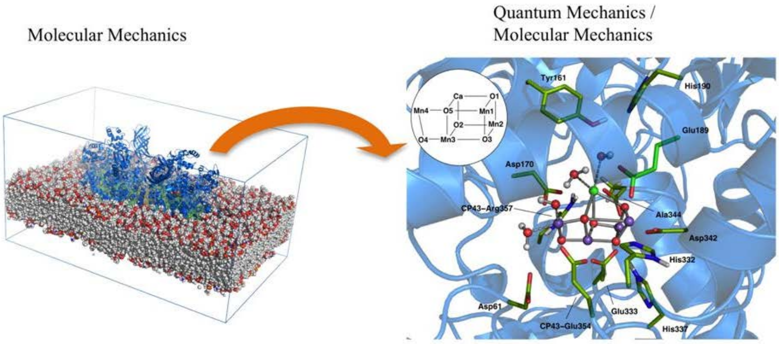

Fig. 1 - The Molecular Mechanics model of the Photosystem II complex in explicit membrane is taken as starting point for the study of the electronic structure of the intermediate states along the water splitting reaction using Quantum Mechanics/Molecular Mechanics ab initio molecular dynamics

The four electrons involved for the water splitting reaction are subsequently removed from the active site (which has a Mn_4CaO_5 core), where they are accumulated to perform the catalytic steps. At each step, the Mn-cluster oxidizing species is the nearby tyrosine Tyr-Z, which is in turn oxidized by the chlorophyll special pair $P680^+$, the photo-induced primary donor in PSII. We have calculated the room temperature free energy landscape associated with the transition between two distinct geometrical structures of the Mn_4CaO_5 catalytic core observed in the S_2 state, namely the S_2^A and S_2^B models introduced by another group[4]. On the basis of our simulations we provided an interpretation of the temperature, illumination, and procedure dependence of historical EPR experimental data, which represented a puzzle for the scientific community since the Eighities[5]. The dynamics also suggested a novel pathway for the substrate water molecules along the transition between S_2 and S_3 states[5]. Our data clarified that the states S_2^A and S_2^B occur sequentially as intermediate states in the Kok's cycle, opening the way to further structural investigations.

In a parallel fashion we investigated the way of working of the cobalt-based catalyst proposed for artificial photosynthesis [2]. On the basis of *ab initio* molecular dynamics of cluster models of such amorphous material in explicit water solution[6], we have provided insights into the pathways for oxygen evolution. In particular we have identified the formation of Co(IV)-oxyl species as the driving ingredient for the activation of the catalytic reaction[7]. The formation of the reactive species is followed by their geminal coupling with oxygen atoms coordinated by the same cobalt ion, as sketched in Fig. 2. Concurrent nucleophilic attack of water molecules coming directly from the bulk is discouraged by high activation barriers.

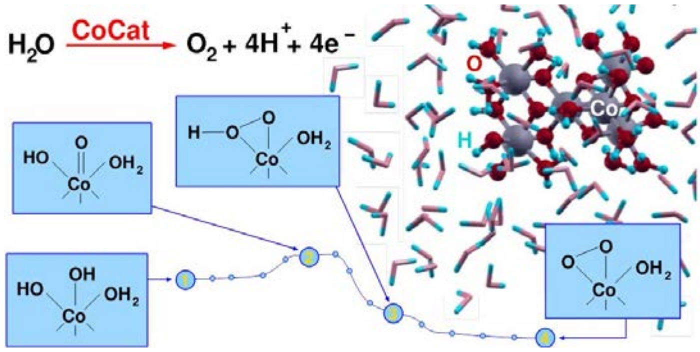

Fig. 2 - Ab initio molecular dynamics simulations reveal intermediate states along the catalytic pathway of a cobalt-based catalyst for water oxidation recently proposed for the so-called "artificial leaf". We identify the Co(IV)-oxyl radical as the active species for the process

The water oxidation mechanism obtained for the CoCat case, additionally offers a starting point for the detailed study of the full catalytic core of PSII. Similarities and differences between the two reaction mechanisms may in the future help to design a new generation of green catalysts for fuel energy production from sunlight.

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