## IS2.1 - The role of the protein in modifying the S- state energies in the oxygen evolving complex

Divya Kaur[1,3], Witold Szejgis[1], Krystle M. Reiss[2], Mikhail Askerka[2], Gary W Brudvig[2], Victor Batista[2], M. R. Gunner[1,3]

[1]Department of Physics, City College of New York, New York 10031, United States
[2]Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States
[3]Department of Chemistry, The Graduate Center, City University of New York, New York 10031

The overall reaction in Photosystem II in higher plants, algae and cyanobacteria releases 4 protons from water into the low pH lumen and binds 4 protons to plastoquinone from the higher pH stromal side of the chloroplast membrane. The products are thus 4 translocated protons, reduced plastoquinone (which is the substrate for the $b_6f$ complex) and the waste product $O_2$. Water oxidation takes place on the lumen side of the protein, requiring 4 electrons to be extracted from the oxygen evolving complex (OEC). OEC oxidation is coupled to proton loss. Likewise, on the stromal side of the protein the secondary quinone ($Q_B$) is sequentially reduced by 2 electrons with associated proton binding..

The oxidation of water to $O_2$ is catalyzed by the OEC, a $CaMn_4O_5$ inorganic complex. The reaction in the OEC progress through 4 S-state transitions, with states from $S_0$ to $S_4$. Each S-state ($S_i$) has one fewer electron than the previous state ($S_{i-1}$). We will describe how simulations based on the crystal structure of the protein with the OEC optimized in different S-states by QM/MM calculations. There are two isomers of $S_2$, one where Mn4 is oxidized ($S_{2,g=2.0}$) the other with Mn1 oxidized ($S_{2,g=4.1}$). The $S_1 \rightarrow S_2$ transition is the only transition where oxidation is not coupled to proton loss. The present work considers the oxidation midpoint potential and changes in protonation states for the $S_1$ to either $S_2$-state isomer under different conditions that have been found to influence OEC activity including pH, Cl binding and several mutations. (Supported by grant DE-SC0001423 from the Department of Energy.)