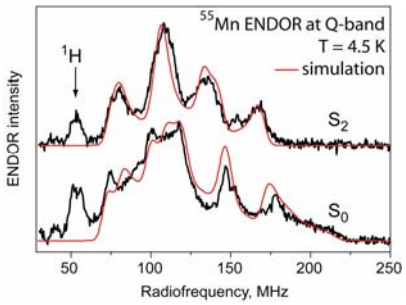
^{55}Mn Pulse ENDOR and X-Ray Absorption Spectroscopy Studies into the Electronic and Geometric Structures of the Oxygen-Evolving Complex in Photosystem II

Leonid Kulik[1], Junko Yano[2], Jan Kern[3], Boris Epel[1], Athina Zouni[3], Vittal K. Yachandra[2], Wolfgang Lubitz[1], Johannes Messinger[1]

[1]Max Planck Institute for Bioinorganic Chemistry, Mülheim an der Ruhr, Germany; [2]Melvin Calvin Laboratory, Physical Biosciences Division, Lawrence Berkeley National Laboratory, USA; [3]Max Volmer Laboratory, TU Berlin, Germany

In photosynthesis the light driven water splitting is performed by a membrane bound pigment-protein complex termed photosystem II (PSII). Its catalytic center, the oxygen evolving complex (OEC), contains a tetra-manganese-calcium complex linked by several μ-oxo bridges (Mn_4O_xCa complex) that is housed in a special protein binding site. During the reaction sequence (Kok cycle) the OEC passes through five oxidation states (S states, $S_0 - S_4$), of which the S_0 and S_2 states have $S = 1/2$ ground states.

We show that under the current conditions it is impossible to derive the correct structure of the Mn_4O_xCa complex on the basis of X-ray crystallography of PSII, because of photo reduction of Mn(III) and Mn(IV) in the S_1 state to Mn(II).[1] Recent progress in determining the structures of the Mn_4O_xCa complex by single crystal EXAFS spectroscopy will also be presented.



In addition we apply ^{55}Mn pulse ENDOR spectroscopy and T_1 measurements of the S_2 and S_0 states at Q-band frequency to investigate the electronic and geometric structures of the Mn_4O_xCa complex.[2] The data strongly favor $Mn_4(III,IV_3)$ and $Mn_4(III_3,IV)$ as oxidation states of the S_2 and S_0 states, respectively. They also show that all four Mn ions are magnetically coupled and that the S_0 state has a low lying excited state. Possible coupling schemes and structures will be presented.

References

(1) Yano, J.; Kern, J.; Irrgang, K.-D.; Latimer, M. J.; Bergmann, U.; Glatzel, P.; Pushkar, Y.; Biesiadka, J.; Loll, B.; Sauer, K.; Messinger, J.; Zouni, A.; Yachandra, V. K. **2005**, submitted.

(2) Kulik, L. V.; Epel, B.; Lubitz, W.; Messinger, J. *J. Am. Chem. Soc.* **2005**, *127*, 2392-2393.