Origin of split EPR signals from the $Tyr_Z^{\bullet}$ and the Ca-Mn_4 cluster in Photosystem II induced by illumination at 5K

Stenbjörn Styring[1,2], Ji-Hu Su[1], Kajsa G.V. Sigfridsson[1], Felix Ho[1], and Fikret Mamedov[1]

[1] *Molecular Biomimetics, Uppsala University, Villavägen 6, 75236 Uppsala, Sweden, and*
[2] *Department of Biochemistry, Center for Chemistry and Chemical Engineering, P.O. Box 124, Lund University, 22100 Lund, Sweden*

In the oxygen evolving complex of PSII, Y_Z (Tyr_Z, D1-Tyr161) is close to the Ca-Mn_4 cluster. Magnetic interaction between $Y_Z^{\bullet}$ and the Ca-Mn_4 cluster can give rise to different split EPR signals depending on the so-called S-states which reflect the oxidation state of the Ca-Mn_4 cluster [1-4]. In the present study, the long-lived neutral $Y_D^{\bullet}$ (D2-Tyr160) radical was pre-reduced to clarify the analysis. Intact PSII samples were given 0-10 short laser flashes at 0℃, and then illuminated at 5 K in the cavity during EPR measurements to induce the split signals.

Three split signals, termed tentatively "Split S_0", "Split S_1" and "Split S_3", were detected in the S_0, S_1 and S_3 states, respectively. We found that these split signals could be well-fitted to a period of four oscillation with respect to the laser flash number. This indicates that the signals involve the Ca-Mn_4 cluster located on the donor side of PSII. This is confirmed by the changes observed in the presence of methanol, a molecule which can bind or penetrate close to the Mn ions [5-7]. Therefore, the magnetic properties of the Ca-Mn_4 cluster, which we interpret in the context of its energy levels, are altered, leading to the observed modifications of the split signals.

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