2D-Hyperfine Sublevel Correlation Investigation of the Tyrosyl Radicals of Photosystem II

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The biological water oxidation is the initial reaction that takes place in Photosystem II (PSII), a multi-subunit protein located in thylakoid membranes of higher plant chloroplasts and cyanobacteria.The light absorption and the subsequent charge separation leads to the generation of the primary oxidant of PSII, $P680^{\bullet+}$, an oxidized multi-chlorophyl pigmentassembly. $P680^{\bullet+}$ is coupled to the chemical catalysis occurring at the Mn_4CaO_5 cofactor that undergoes four oxidation steps, S_0 to S_1, …S_3 to $(S_4)S_0$ and evolves O_2during the last step. Two redox-active tyrosine residues, Tyrosine Z (Y_z) and Tyrosine D (Y_D) exist on the donor side of PSII at symmetrical positions to the P680 (Figure). Y_z is a preferential fast electron donor, mediating the electron transfer from $Mn_4CaO_5$to $P680^{\bullet+}$ [1]. Y_D is a slow auxiliary donor to $P680^{\bullet+}$ and is oxidized ($Y_D^{\bullet}$) at each charge separation step of Mn_4CaO_5. The presence of $Y_D^{\bullet}$ leads to a more efficient photooxidation of the Mn_4CaO_5 cluster, relative to reductive process [2].Although both tyrosine residues play significant role on the proper function of PSII, detailed informationabout their proton environmentis still not available.

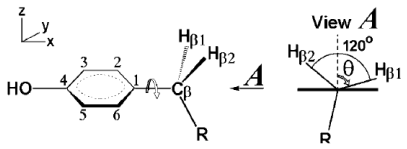

Figure: Schematic representation of a tyrosine

Based on the above, we performed an investigation on the tyrosyl radicals of *spinaciaoleracea* (spinach) PSII at 80 K, with Mn_4CaO_5being either at S_1 or S_2 oxidation states, by using 2D-Hyperfine Sublevel Correlation (HYSCORE) Spectroscopy. The experimental spectra show characteristic peaks originating from the aromatic ring protons and β-methylene ones of $Y_D^{\bullet}$.Our subsequent simulated analysis determine the hyperfine couplings constants of the proton nuclei with the free electron of $Y_D^{\bullet}$ radical.

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