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Proton transfer pathways in Photosystem II

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Using quantum mechanics/molecular mechanics calculations and the 1.9-Å crystal structure of Photosystem II (Umena, Y., Kawakami, K., Shen, J.-R., and Kamiya, N. (2011) *Nature* 473, 55-60), we investigated the H-bonding environment of the redox active tyrosine, TyrD and obtained insights that help explain its slow redox kinetics and the stability of TyrD radical. The water molecule distal to TyrD, 4 Å away from the phenolic O of TyrD (O_{TyrD}), corresponds to the presence of the tyrosyl radical state. The water molecule proximal to TyrD, in H-bonding distance to O_{TyrD} , corresponds to the presence of the unoxidised tyrosine. The H^+ released upon oxidation of TyrD is transferred to the proximal water, which shifts to the distal position, triggering a concerted proton transfer pathway involving D2-Arg180 and a series of waters, through which the proton reaches the aqueous phase at D2-His61. The water movement linked to the ejection of the proton from the hydrophobic environment near TyrD makes oxidation slow and quasi-irreversible, explaining the great stability of the TyrD radical. A symmetry-related proton pathway associated with TyrZ is pointed out and this is associated with one of the Cl^- sites. This may represent a proton pathway functional in the water oxidation cycle.