

Pulsed EPR Studies of Photosystem II and Oxygen Evolution

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We are using pulsed ENDOR and ESEEM methods to study the paramagnetic Mn cluster and tyrosine radicals of the Photosystem II Oxygen Evolving Complex. New instrumentation operating at frequencies of 31 and 130 GHz will be used to complement our previous X-band pulsed EPR work. We are interested in obtaining structural information concerning both the Mn cluster, which consists of four exchange-coupled high valence Mn ions, and the redox active tyrosines Yd and Yz, the latter of which may be directly involved in the water splitting/oxygen evolution chemistry. Of particular interest is the binding of substrate waters, water analogs, and inhibitors at different stages of the 5-intermediate S-state cycle of the enzyme. Comparisons of conclusions from spectral data with those from recent X-ray structures will be discussed.