RECENT ADVANCES TOWARD A STRUCTURAL MODEL FOR THE PHOTOSYNTHETIC OXYGEN-EVOLVING MANGANESE CLUSTER

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INTRODUCTION

Photosynthetic water oxidation occurs in the oxygen evolving complex (OEC) of photosystem II (PS II). One-electron photo-oxidations in the reaction center of PS II are coupled to the four-electron oxidation of water in the OEC. As the PS II reaction center sequentially extracts electrons, the OEC cycles through five intermediate oxidation states (S0-S4) where S0 is the least oxidized and S4 is a transient state which decays to S0 with the release of a dioxygen molecule. A complex of four manganese atoms has been shown to function in charge accumulation and is thought to form the catalytic site for the water oxidation reaction. The structure of this manganese complex and the mechanism of water oxidation have been the subject of vigorous inquiry by a great many research groups (Sauer et al., 1992).

We have proposed a model (Yachandra et al., 1993) for the Mn complex based largely upon extended X-ray absorption fine structure (EXAFS) spectroscopy of Mn in PS II preparations. The core feature of this model is two di-μ-oxo bridged Mn pairs yielding two Mn-Mn interactions of ~2.7 Å. The Mn pairs are connected by a single bridging oxygen which results in another Mn-Mn distance of ~3.3 Å. These distances and structural interpretations arose from a comparison of the Mn-EXAFS fitting results of PS II compared to known structural motifs from a large number of inorganic Mn complexes (DeRose et al., 1994). Experiments on partially oriented preparations indicated that the scattering vectors giving rise to the ~2.7 Å interaction are oriented close to the plane of the membrane (averaging 60°±7° from the membrane normal), while the vectors contributing to the ~3.3 Å interaction are aligned closer to the membrane normal (43°±10°) (Mukerji et al., 1994). This angular information was included in the model to indicate the position of the complex within the membrane. A closely bound Ca was added to the model, based on EXAFS from Sr-substituted preparations, and a directly-ligated chloride was also included, based on a large body of indirect evidence for a chloride binding site in PS II. Finally, a histidine ligand to Mn was included based on electron spin-echo envelope modulation experiments.

In this paper we describe a revised structural model for the manganese cluster in PS II based on the results of recent studies on PS II preparations subjected to various treatments.
(Sr-substitution, ammonia or fluoride inhibition, or low temperature illumination to produce the S2-state exhibiting the g=4.1 EPR signal). The information gained from these studies has helped confirm and extend our structural model. We also present the results of Mn X-ray absorption K-edge spectra from PS II samples advanced through the S-states with saturating flashes of light.

RESULTS AND DISCUSSION

The Mn-Mn Interaction at ~2.7Å

The second Fourier peak in the EXAFS spectrum of PS II is generally agreed to arise from 2-to-3 di-μ-oxo bridged Mn pairs. Although there is certainly more than one Mn-Mn interaction, spectra from unmodified PS II preparations in the S1-state, and in the S2-state where the multiline EPR signal is exhibited, show only a single resolved distance (DeRose et al., 1994). In recent work we have shown that this distance degeneracy is lifted in the S2-state where the g=4.1 EPR signal is exhibited (Liang et al., 1994) and in preparations which have been inhibited with ammonia (Dau et al., 1995) or with fluoride (DeRose et al., 1995). The Fourier transforms of the EXAFS from these preparations are shown in Figure 1. In each of these preparations, the second Fourier peak (peak II) is observed to have a smaller amplitude than in control samples. Also, in each case, curve-fitting results have indicated increased disorder and that the data can be fit with two Mn-Mn interactions, one at approximately 2.69-2.73 Å and a second interaction at ~2.78-2.87 Å.

![Figure 1. Fourier transforms of the EXAFS from ammonia or fluoride treated PS II samples in the S2-state, and from an untreated sample illuminated at 140K to generate the S2-state exhibiting the g=4.1 EPR signal. For comparison each trace is plotted with a control sample in the S2-state exhibiting the multiline EPR signal.](image-url)