Fourier transform infrared difference spectroscopy for studying the molecular mechanism of photosynthetic water oxidation

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INTRODUCTION
Photosynthetic water oxidation is catalyzed by a Mn4Ca cluster and its surrounding protein matrix in photosystem II (PSII; Feast et al., 2004; Loell et al., 2005; Yano et al., 2006; Umema et al., 2011). The oxygen-evolving complex (OEC) accumulates oxidizing equivalents from the photochemical reactions within PSII and cycles through five oxidation states, termed S0 → S1 → S2 → S3 → S4. One of the recent major breakthroughs in PSII research was the report of the crystal structure of oxygen-evolving PSII at 1.9 Å resolution (Umema et al., 2011). The structure of the Mn4Ca3O5 cluster is shown in Figure 1B. Three Mn, one Ca, and four oxygen atoms form a cubane-like structure; the fourth Mn connects to the cubic structure by two μ-oxo-bridges. The Mn4Ca3O5 cluster is connected with four water molecules: two are ligated to Ca and two to Mn (Umema et al., 2011; Figure 1B). These water molecules are candidates for substrates in photosynthetic water oxidation. Another distinct feature in the structure is the apparently longer bond distances between the O5-bridging oxygen atom and neighboring metal ions, which indicates weak bonding of this oxygen atom in the cluster. O5 was proposed as a candidate for one of the substrates in dioxygen formation (Umema et al., 2011). More recent studies have suggested that the structure of the X-ray diffraction (XRD) model of PSII is modified by radiation-induced reduction of the Mn cluster (Luber et al., 2008; Siegbahn, 2009; Grundmeier and Dau, 2012), with differing locations and molecular structures of S-state intermediates (i.e., terminal water molecules or water-derived metal ligands). Several molecular spectroscopic techniques, including advanced electron paramagnetic resonance (EPR) spectroscopy (Brett et al., 2004; McConnell et al., 2011; Rapatskiy et al., 2012) and light-induced Fourier transform infrared (FTIR) difference spectroscopy (see below) have been extensively used to resolve this issue.

Fourier transform infrared difference spectroscopy has been widely used to study the structural changes in the OEC during the S-state catalytic cycle. The S0-minus-S1 mid-frequency (1800–1000 cm⁻¹) FTIR difference spectrum was first reported in 1992 (Noguchi and Sugiura, 1992). The S0-minus-S2 spectrum of the PSII/OEC was reported in 2000 (Chu et al., 2000b), and spectra of flash-induced S-state transitions (S0 → S1 → S2 → S3 → S4) during the complete S-state cycle were reported 1 year later (Hillier and Babcock, 2001; Noguchi and Sugiyama, 2001). Many FTIR studies of the OEC focused on the mid-frequency region (1800–1000 cm⁻¹) of the IR spectrum, which contains information on structural changes of protein backbones and amino acid side-chains associated with S-state transitions of the OEC. One very important development in FTIR studies of the OEC was the report of high-frequency spectra (3700–3500 cm⁻¹) of the OEC, which contain information on structural changes of the weakly H-bonded OH-stretching of active water molecules during S-state transitions of the OEC (Noguchi and Sugiyama, 2000, 2002a,b). The other important developments were reports of low-frequency spectra (<1000 cm⁻¹), which contain information on metal-ligand and manganese-substrate vibration modes.

Several structural models of photosynthetic water oxidation have been proposed (Hoganson and Babcock, 1997; Pecoraro et al., 1998; McElvay and Brudvig, 2006; Kusunoki, 2007; Pushkar et al., 2008; Siegbahn, 2009; Grundmeier and Dau, 2012), with differences in molecular structures of S-state intermediates (i.e., terminal water molecules or water-derived metal ligands). Several molecular spectroscopic techniques, including advanced electron paramagnetic resonance (EPR) spectroscopy, Fourier transform infrared (FTIR) difference spectroscopy, and advanced electron paramagnetic resonance (EPR) spectroscopy (Brett et al., 2004; McConnell et al., 2011; Rapatskiy et al., 2012) and light-induced Fourier transform infrared (FTIR) difference spectroscopy (see below) have been extensively used to resolve this issue.

Abbreviations: EPR, electron paramagnetic resonance; FTIR, Fourier transform infrared; OEC, oxygen-evolving complex; OTG, octyl-β-D-thioglucopyranoside; PSII, photosystem II; Qa, primary quinone electron acceptor in PSII; XRD, X-ray diffraction.

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of the OEC (Chu et al., 1999, 2000a,c; Yamanari et al., 2004; Kimura et al., 2005b).

This mini-review gives an overview of recent important progress in FTIR studies of the OEC, combined with new spectroscopic and XRD structural information, to understand the chemical mechanism of photosynthetic water oxidation. More comprehensive reviews on FTIR studies of the OEC are available (Noguchi, 2007, 2008a,b; Debus, 2008).

OH-STRETCHING VIBRATIONAL MODES OF ACTIVE WATER PARTICIPANT IN THE LOW-FREQUENCY REGION (<1000 cm$^{-1}$) OF THE OEC

The reactions of substrate water during the S-state catalytic cycle of the OEC are of paramount importance to understand the chemical mechanism of photosynthetic water oxidation. In the new XRD structure of the Mn$_4$CaO$_5$ cluster, the four water molecules connected to the OEC are involved in a hydrogen-bonded network linking the Mn$_4$CaO$_5$ cluster and YZ (Umena et al., 2011). The bond distances (2.8–3.3 Å) between oxygen atoms of coordinated water molecules and their neighboring water molecules indicate that most of the O–H groups of the water molecules are weakly hydrogen bonded and will appear in the weakly hydrogen-bonded OH-stretch (3750–3500 cm$^{-1}$) region of the FTIR spectra. Noguchi and colleagues reported flash-induced difference spectra of S-state transitions in the weakly H-bonded OH-stretching region (Noguchi and Sugiura, 2000, 2002a,b). One active water molecule on the OEC, which gave rise to the S$_1$ band at 3585 cm$^{-1}$ and the S$_2$ band at 3618 cm$^{-1}$, was identified at 290 K in light-induced S$_2$–S$_1$ FTIR difference spectrum (Noguchi and Sugiura, 2000) and during the S-state cycle at 10$^\circ$C (Noguchi and Sugiura, 2002a,b) in PSII core complexes from Thermosynechococcus elongatus and Synechocystis sp. These active water molecules detected by FTIR difference spectra on the OEC (e.g., associated with Mn or Ca) in the new XRD structure.

Mn-LIGAND AND Mn-SUBSTRATE VIBRATION MODES IN THE LOW-FREQUENCY REGION (<1000 cm$^{-1}$) OF THE OEC

From studies of Mn model compound, Mn-ligand and Mn-substrate vibration modes of the PSII/OEC are expected to show up in the low-frequency region (<1000 cm$^{-1}$) of the IR spectrum (Chu et al., 2000c). In low-frequency S$_2$/S$_1$ FTIR difference spectra of octyl-β-D-thioglucopyranoside (OTG) PSII core preparations of spinach, a positive mode at 606 cm$^{-1}$ in $^{16}$O water clearly downshifted to 596 cm$^{-1}$ in $^{18}$O water (Chu et al., 2000c; Figure 2A). With double-difference (S$_2$/S$_1$ and $^{16}$O minus $^{18}$O) spectra, the 606 cm$^{-1}$ mode was assigned to an S$_2$ mode, and a corresponding S$_1$ mode at about 625 cm$^{-1}$ was identified (Chu et al., 2000c). In addition, this 606-cm$^{-1}$ mode was up-shifted to about 618 cm$^{-1}$ with Sr$^{2+}$ substitution but not significantly affected by $^{44}$Ca isotope substitution (Chu et al., 2000c; Kimura et al., 2003, Figure 2B). From these results and studies of Mn model compounds, this vibrational mode at 606 cm$^{-1}$ in the S$_2$ state was assigned to a Mn–O–Mn cluster vibration in the OEC (Chu et al., 2000c). The structure of this Mn–O–Mn cluster very likely includes additional oxo and carboxylate bridge(s). IR modes for $v$(Mn=O) and $v_{as}$(Mn–O–Mn) for a singly oxo-bridged Mn cluster usually occur at $>700$ cm$^{-1}$ and typically have a 30–40 cm$^{-1}$ downshift (Chu et al., 2001c). They are unlikely to be the origin of the 606-cm$^{-1}$ mode. Furthermore, this 606-cm$^{-1}$ mode was altered in S$_2$/S$_1$ FTIR difference spectra of Ala344D1Gly, Glu189Gln, and Asp170HisD1 mutants PSII particles (Chu et al., 2001a; Mizuasa et al., 2004; Kimura et al., 2005b). All the above amino acid residues are direct ligands for the Mn$_4$Ca...
Chu FTIR study of oxygen-evolving complex. Therefore, the structure of the Mn–O–Mn cluster is structurally coupled to its surrounding ligand environment.

Low-frequency S3/S2 spectra were reported in OTG PSII core preparations of spinach, in which intense bands at 604(−) and 621 (+) cm\(^{-1}\) were sensitive to 18O water exchange (Chu et al., 2001b). The S2 mode at 621 cm\(^{-1}\) was attributed to the Mn-O-Mn cluster mode of the S2 state. Kimura et al. (2009b) reported on 18O/18O and/or H/D water-sensitive low-frequency vibrations of the OEC during the complete S-state cycle in PSII core particles from T. elongatus. The S2 mode at 606 cm\(^{-1}\) changed their sign and intensity during S-state cycling, which indicates S-state-dependent changes in the core structure of the Mn4CaO5 cluster. In addition, several IR bands sensitive to both 18O/18O and H/D exchanges were attributed to S-state intermediates during the S-state cycling (Kimura et al., 2005b). Furthermore, an intense 577(−) cm\(^{-1}\) band in the S2/S1 spectra was found insensitive to universal 15N- and 13C-isotope labeling and assigned to the skeletal vibration of the Mn cluster or stretching vibrational modes of the Mn ligand (Kimura et al., 2003).

Low-frequency FTIR results demonstrate that one bridged oxygen atom in the Mn–O–Mn cluster of the OEC is accessible to and can be exchanged with bulk-phase water. This exchange occurs within minutes or faster because it is complete within 30 min (Chu et al., 2000b). A recent study involving W-band 17O electron–electron double resonance-detected nuclear magnetic resonance (NMR) spectroscopy reported that one μ-oxo bridge of the OEC can exchange with H217O on a time scale (≤15 s) similar to that of substrate water on the OEC (Rapatskiy et al., 2012). This study also suggested that the exchangeable μ-oxo bridge links the outer Mn to the Mn4CaO5 open-cuboidal unit (O4 and O5 in Figure 1B). The authors of this study favored the Ca-linked O5 oxygen assignment (Rapatskiy et al., 2012). Low-frequency FTIR results showed that the Mn–O–Mn cluster mode at 606 cm\(^{-1}\) is sensitive to Sr2+ substitution but not 44Ca substitution (Chu et al., 2000c; Kimura et al., 2005a). Considering the structure of O5 in the Mn4CaO5 cluster (Umeha et al., 2011; Figure 1B), the 44Ca-induced isotopic shift of the Mn–O–Mn cluster mode may have been too small to be detected by previous FTIR studies. Thus, the O5-bridging oxygen atom is a good candidate for the exchangeable-bridged oxygen atom in the Mn–O–Mn cluster identified by FTIR. A recent continue-wave Q-band electron nuclear double resonance (ENDOR) study reported a much slower 17O exchange rate (on the time scale of hours) with 17O-labeled water into the μ-oxo bridge of the OEC (McConnell et al., 2011). Future study is required to resolve this discrepancy.

EFFECT OF AMMONIA ON THE OEC

Because of the structural similarity between NH3 and H2O and the ability of NH3 to inhibit photosynthetic water oxidation, the NH3 binding site on the OEC might occur at the substrate water-binding site. Previous EPR studies of NH3-treated PSII samples demonstrated that the S2-state multiline EPR signal is altered when samples illuminated at 200 K are subsequently “annealed” above 250 K (Beck et al., 1986; Britt et al., 1989). FTIR studies showed that NH3 induced characteristic spectral changes in the S2/S1 spectra at 250 K (Chu et al., 2004a; Fang et al., 2005). Among them, the S2-state symmetric carboxylate stretching mode at 1365 cm\(^{-1}\) in

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the S2/S1 spectrum of control samples up-shifted to ~1379 cm⁻¹ in NH3-treated samples. This carbonylate mode was also altered by Sr²⁺ substitution (Strickler et al., 2005; Suzuki et al., 2006), which indicates that the action site of NH3 on the OEC is near the Ca²⁺ site. In addition, the conditions that give rise to the NH3-induced up-shift of this S2/S1-state carbonylate stretching mode at 1365 cm⁻¹ are strongly correlated with those producing the modified S2-state multitrace EPR signal (Chu et al., 2004a; Fang et al., 2003). Furthermore, a recent FTIR result showed that NH3 did not replace the active water molecule connected to the OEC during the S1-to-S2 transition at 250 K, whereas the Mn–O–Mn cluster vibrational mode at 686 cm⁻¹ was diminished or underwent a large shift (Hou et al., 2011; Figure 2C). The above results are consistent with the proposal that NH3 may replace one of the bridging oxygen atoms, presumably O1a, in the Mn4CaO4 cluster during the S1-to-S2 transition (Britt et al., 1989).

The other intriguing FTIR finding is that the effect of NH3-induced up-shift of 1365 cm⁻¹ mode in the S2/S1 spectrum was diminished at temperatures above 0°C (Huang et al., 2008). The results indicate that the interaction of NH3 with the OEC is attenuated at temperatures above 0°C (Huang et al., 2008). In addition, a recent FTIR study reported an inhibitory effect of the ammonium cation on the PSII/OEC at 283 K (Tsunoda et al., 2011). The results suggest that the ammonium cation perturbs some carbonylate residues coupled to the Mn cluster during the S1-to-S2 transition and inhibits the oxygen evolution reaction at 283 K (Tsunoda et al., 2011).

**FTIR RESULTS FOR PROTEIN LIGANDS OF THE OEC**

Fourier transform infrared studies involving isotopic labeling and site-directed mutagenesis have provided a wealth of information on dynamic structural changes of the protein backbones and amino acid side-chains during the S state transitions of the OEC (Dubus, 2008; Noguchi, 2006a). An isotope-edited FTIR study identified the D1-Ala344 carboxylate stretching modes in S2/S1, difference spectra to the α-COO⁻ group of D1-Ala344 (Chu et al., 2004b). This mode appears at ~1356 cm⁻¹ in the S1 state and at ~1339 or ~1328 cm⁻¹ in the S2 state in unlabeled wild-type PSII particles but not in D1-Ala344Gly and D1-Ala344Ser mutant PSII particles. These frequencies are consistent with unidentate ligation of the α-COO⁻ group of D1-Ala344 to the Mn₄Ca cluster in both the S2 and S1 states (Chu et al., 2004b; Strickler et al., 2005). In addition, substituting Sr for Ca did not alter the symmetric carboxylate stretching modes of D1-Ala344 (Strickler et al., 2005). The results suggested that the α-COO⁻ group of D1-Ala344 did not ligate Ca. In the 1.9 Å XRD structure, the α-COO⁻ group of D1-Ala344 shows very asymmetrical bridging between Mn3 and Ca in the cluster, with the Mn-O distance 2.6 Å and Ca-O distance 2.6 Å (Kawasaki et al., 2011). In addition, the isotopic bands for the α-COO⁻ group of D1-Ala344 showed characteristic changes during S state cycling (Kuma et al., 2005d). These results indicated that the C-terminal Ala344D1 is structurally coupled, presumably directly ligated, to the Mn ion that undergoes oxidation of Mn(II) to Mn(IV) during the S1-to-S2 transition and is reduced in reverse with the S2-to-S1 transition (Chu et al., 2004b; Kuma et al., 2005d). In contrast, mutations of D1-Asp170, D1-Glu189, and D1-Asp342 did not eliminate any carbonylate vibrational stretching modes during S-state cycling of the OEC (Dubus et al., 2005; Strickler et al., 2006, 2007). Recent computational studies suggested that vibrations of carbonylate ligands can be quite insensitive to Mn oxidation, if they are not coordinated along the Jahn–Teller axis (Spaepen et al., 2008). In their model, the only amino acid residue that is ligated along the Jahn–Teller axis of a Mn⁷⁺ ion is CP43-E354.

Of note, CP43-E354Q mutant PSII particles gave rise to characteristic spectral changes in the amide and carbonylate stretch regions of FTIR difference spectra during S-state transitions (Strickler et al., 2008, Shimada et al., 2009; Service et al., 2010). In addition, the weakly H-bonded O–H stretching modes of the active water molecule associated with the OEC were significantly altered in S3/S2 FTIR difference spectra of CP43-E354Q mutant PSII particles (Shimada et al., 2009). Furthermore, H₂¹⁸O exchange mass spectrometry experiments showed that the CP43-E354Q mutation weakened the binding of both substrate-water molecules (or water-derived ligands), particularly affecting the one with faster exchange in the S3 state (Service et al., 2010). The XRD structure of the OEC showed that coordinated water molecules were on Ca²⁺ and Mn⁴⁺, which were both not ligated by CP43-E354 (Umena et al., 2011). Presumably, CP43-E354Q mutation may induce significant structural changes to the Mn₄CaO₅ core that affects associated active water molecule(s) on the OEC during the S1-to-S2 transition. A recent time-resolved infrared study revealed the proton and protein dynamics associated with the OEC during the S-state transitions (Noguchi et al., 2012). The results suggest that during the S1-to-S2 transition, protons are greatly rearranged to form a transient state before the oxidation of the Mn₄CaO₅ cluster to lead to O₂ formation. In addition, an early proton movement was detected during the S2 → S1 transition, indicating a proton release coupled with the electron transfer reaction. Furthermore, a relatively slow carbonylate movement occurred in the S3 → S1 transition, which might reflect the protein relaxation process to stabilize the S1 state (Noguchi et al., 2012). This study demonstrates that time-resolved infrared technique is extremely useful to monitor proton and protein dynamics of the OEC during photosynthetic oxygen evolution.

**BIOINORGANIC MODELS FOR FTIR SPECTRAL INTERPRETATION**

Vibrational data from model compounds relevant to the OEC is crucial to interpret FTIR data of the OEC during S-state cycling. However, vibrational data for synthetic multinuclear Mn complexes are still limited (Gaa et al., 2003; Berggren et al., 2012). Particularly, vibrational data are needed for the Ca–Mn multinuclear cluster that models the Mn₄CaO₅ cluster (Kanady et al., 2011; Mukherjee et al., 2011). One previous study reported IR spectra and normal mode analysis of the adamantane-like complex [Mn₄OX₁(bpeca)]⁺⁺ (Visser et al., 2002). By using the electrochemical method to record the difference IR spectrum and H²¹⁸O isotopic labeling, the authors identified Mn-O vibrational modes for [Mn⁴⁺] and [Mn⁴⁺Me⁺]. Comparison with OEC data ruled out the adamantane-like complex as the possible structure.
intermediate. Nevertheless, this approach is very powerful for interpreting FTIR data for the OEC during S-state cycling.

CONCLUSIONS AND PERSPECTIVES

Light-induced FTIR difference spectroscopy has become a fruitful structural technique to study the molecular mechanisms of photosynthetic water oxidation. The new high-resolution XRD structure of the OEC has served as a crucial foundation for designing FTIR experiments and interpreting FTIR data. Combined with isotopic labeling, site-directed mutagenesis, model compound studies, and normal mode analysis, FTIR difference spectroscopy will continue to provide important structural and mechanistic insights into the water-splitting process in PSII.

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