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Modeling near edge fine structure X-ray spectra of the manganese catalytic site for water oxidation in photosystem II

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Abstract

The Mn 1s Near Edge Absorption Fine Structure (NEXAFS) has been computed by means of transition potential gradient corrected Density Functional Theory (DFT) on four Mn_4Ca clusters modeling the successive S_0 to S_3 steps of the oxygen evolving complex (OEC) in photosystem II (PSII). The model clusters were obtained from a previous theoretical study where they were determined by energy minimization. They are composed of Mn(III) and Mn(IV) atoms, progressing from $\text{Mn(III)}_3\text{Mn(IV)}$ for S_0 , to $\text{Mn(III)}_2\text{Mn(IV)}_2$ for S_1 , to Mn(III)Mn(IV)_3 for S_2 , and to

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Mn(IV)₄ for S₃, implying an Mn centered oxidation during each step of the photosynthetic oxygen evolution. The DFT simulations of the Mn 1s absorption edge reproduce the experimentally measured curves quite well. Using the half-height method, the theoretical IPE's are shifted by 0.93 eV for the S₀ to S₁ transition, by 1.43 eV for the S₁ to S₂ transition, and by 0.63 eV for the S₂ to S₃ transition. The IPE shifts depend strongly on the method used to determine them, and the most interesting result is that the present clusters reproduce the shift in the S₂ to S₃ transition obtained both with the half-height and with the second derivative methods, thus giving strong support to the previously suggested structures and assignments.

Introduction

The use of X-ray spectroscopy is commonly motivated by the localized nature of the core electrons which implies effective selection rules, valuable for mapping the electron distribution, and a chemical shift that carries conformational information. X-ray techniques have generally experienced a great revival in recent years owing to the technical development of light sources. It is now possible to correlate specific X-ray features with functional groups and even individual bonds, such that the total spectrum can be considered as a linear combination of elementary spectra - the "building block principle".¹⁻⁵ In addition to applications of this principle and other thumb rules, the general development in simulation technology has made it possible to address ever larger systems with complex X-ray spectra, such as biological molecules. Thus, computational studies of the near edge X-ray absorption fine structure (NEXAFS) spectra of amino acids and polypeptides in solution or on surfaces have become common practice.⁶⁻⁹ Moreover, structures like proteins, poly-nucleotides and DNA are nowadays addressed,¹⁰⁻¹⁵ demonstrating the ability of computations to identify particular amino acids and to use their characteristic features for chemical mapping. Computational analysis has helped to identify the origin of individual peaks and the spectroscopic assignments are obtained in terms of hydrogen bonds, tautomerism and stacking, to such an extent that absorption spectroscopy even can be utilized to refine particular structures of DNA as obtained from X-ray

crystallography.¹⁶

Our present work takes account of the aforementioned development of X-ray simulations of complex bio systems, and addresses the K-edge NEXAFS spectra of the manganese complex of photosystem II (PSII), where water oxidation takes place. PSII is a multiprotein enzyme situated in the thylakoid membrane of plants, algae and cyanobacteria. The oxygen-evolving complex (OEC) contains four manganese and one calcium atom connected by μ -oxo bridges. X-ray diffraction studies during the past seven years have considerably clarified the detailed structure of the OEC.¹⁷⁻¹⁹ In the first of these studies,¹⁷ it was shown that three of the manganese atoms and the calcium atom form a cuboidal structure, with the fourth manganese atom situated outside the cube. The amino acids most likely to be ligated to the complex were also assigned. Waters were assumed to fill up the remaining coordination sites. Since the resolution was rather low (3.5 Å), the positions of the bridging oxo groups and the metal connectivity of the ligands could only be assumed. In the more recent X-ray structures the resolution was slightly higher (2.9-3.0 Å),^{18,19} and a different ligation pattern was suggested, partly based on chemical intuition, with most of the carboxylate amino acid ligands assumed to bind bidentately between two different metal atoms. This meant that hardly any water derived ligands had to be added to saturate the metal coordination. The positions of the metal atoms were similar to the ones in the earlier X-ray structure, with the exception of the outside manganese which was placed farther out from the Mn_3Ca -cube. No positions for the oxo groups were suggested. Quite recently, a new high-resolution (1.9 Å) X-ray structure was obtained, which turned out to be very similar to a previously suggested structure obtained from calculations using density functional theory.²⁰ A simplified model of that theoretical structure has been used here for the NEXAFS analysis.

In the present study, we make use of NEXAFS as an element specific spectroscopic technique, to investigate the electronic structure of the excited atoms and the character of the OEC states, and, in particular, of special interest for this case, we analyze and exploit the spectral sensitivity to the oxidation states of the different manganese atoms involved in the complex. Water oxidation involves four flash-induced steps with intermediates denoted as S_0 to S_4 , according to a scheme

proposed by Kok.²¹ In each of the steps an electron is released from the OEC, in most cases together with a proton, and O₂ is formed in the last step.

A good starting point for discussions of the present results is the review by Yano *et al.*,²² in which the resolution capability of X-ray absorption spectra of Manganese clusters at the K edge was demonstrated and used to build a structural model for the evolution of the cluster during the photosynthesis process. Yachandra *et al.*²³ summarized data of K edge absorption of the OEC and could, together with electron paramagnetic resonance (EPR) data, draw a number of conclusions on the cluster structure, in particular on the oxidation states of the metals. Concomitant computational work has since then been carried out. An example is the recent study by Jaszewski *et al.*,^{24,25} in which the manganese complexes were studied with different ligand environments using TDDFT and where different oxidation states were correlated with the positions of the Mn K-edges.

A key issue of particular importance in the present context is whether a manganese or a ligand centered oxidation occurs in the S₂ to S₃ transition. In one set of studies,^{23,26} it was concluded that the most likely assignment of this oxidation was a bridging μ -oxo group. This conclusion was based on a combination of results from NEXAFS, EXAFS and K β XES measurements. In another set of quite similar studies it was instead concluded that the oxidation should be manganese centered.²⁷ The most recent DFT studies have supported the latter assignment.²⁸

In the following we outline the main characteristics of the theoretical model employed for X-ray absorption spectra, in particular considering complex systems of the type studied here. In order to explore the possibilities of our X-ray simulation technology and to validate parametrizations - density functionals, basis set and structural models - we carried out a set of calculations on some manganese containing complexes and compared the results with available high-resolution experimental spectra. In the next section we subsequently discuss the calculated results in relation to the oxidation state assignment. We thereafter discuss our results both in view of earlier spectroscopic work and in a general context of assessing the structure and functionality of the OEC, in the Discussion section. Some general conclusions end the paper.

Computational Methods

NEXAFS spectroscopy reflects the promotion of a core electron into an unoccupied level in the discrete or continuum parts of the N-electron spectrum. A variety of methodologies have been developed to compute such spectra, a few with the capability to address systems of the complexity and size that are studied in the present work. We use transition state theory, originally introduced by Slater,²⁹ and employed for X-ray and photoelectron spectroscopies over a long time, and which has been implemented in modern density functional theory by Chong,³⁰ Stener³¹ and Triguero³² and their coworkers. With transition state theory one obtains the relaxation contribution to the binding energy up to second order in the energy for self-consistent field optimization between ground and core hole states (Δ SCF method). Maintaining orbital orthogonality and with the spectral energies obtained as differences of transition state orbital energies, the transition state method allows a very effective construction of X-ray spectra still maintaining an accuracy that matches Δ SCF (Δ Kohn Sham) and "static exchange" levels of theory very well. For benchmarks one can refer to studies on small molecules,³² fullerenes³³ and solutions.^{34,35}

In the discrete part of the spectrum the transition potential eigen-pairs of excitation energies and moments provide a true spectral representation while in the continuum they do not represent a correct normalization. However, closely above the ionization potential the deviation from the true normalized spectrum is still minor,³⁶ growing progressively poorer for higher energies covering shape resonance and multiple scattering regions. By experience, close to the ionization potential the continuum smearing effect can be caught by empirical broadening of the primitive spectrum, see further below.

In the present paper we study the NEXAFS K edge spectrum of manganese, reflecting the promotion of the manganese 1s orbital electron into unoccupied levels of the full cluster. The transition is in the range of 5 KeV with a broadening of the 1s level of 1.0 eV. There is thus a considerable smearing out of structures also of the discrete part of the NEXAFS spectrum compared to low-Z compounds. Another difference with respect to the latter is a strong relative enhancement of the near ionization potential region (and beyond) in relation to the discrete part of the spectrum.

Combined with the large lifetime broadening this makes the edge region close to the ionization potential, and in particular the inflection point of the spectrum at the edge, the most suitable region in the search for structure-property relations. We will therefore here explore the relation between inflection point energy (IPE) and oxidation state.

NEXAFS Mn K edge spectra were generated for Mn in different oxidation states by considering Mn(II), Mn(III) and Mn(IV) reference compounds, for which high quality experimental spectra are available. These complexes, each containing a single Mn atom, are: Mn(II)(acac)₂(H₂O)₂, Mn(III)(acac)₃ and Mn(IV)(sal)₂(bipy), where acac is acetylacetonate, sal is salicylate and bipy is bipyridine. The same molecules have been used as test models for experimental measurements by Yachandra *et al.*³⁷ The structures of the molecules were optimized by using the Gaussian 09 program³⁸ at the B3LYP³⁹ level with the 6-31G(d,p) basis set.

The geometry optimized structures are shown in Figure 1. The charges on each complex are +2 for Mn(II), +3 for Mn(III) and 0 for Mn(IV). The total spin (S) of each molecule is 5/2 for Mn(II), 2 for Mn(III) and 3/2 for Mn(IV). In all complexes the Mn is hexa-coordinated. In Mn(II)(acac)₂(H₂O)₂ the distance between the Mn and the four O of the acetylacetonate ligands amounts to 2.15 Å and 2.16 Å, while the distance to the water ligands is 2.26 Å. In the Mn(III)(acac)₃ the distances to the six acetylacetonate ligands are 1.96, 1.96, 1.99, 2.02, 2.15 and 2.15 Å. In Mn(IV)(sal)₂(bipy) the distance of the Mn from the pyridine C is 2.01 Å, and the distances of Mn from the four salicylate O are 1.92, 1.92, 1.95 and 1.95 Å.

Since the recent high-resolution structure of PSII⁴⁰ was not available at the start of the present project, the model structures of the different S-states were taken from earlier model calculations.²⁸ The models were furthermore reduced to fit present capabilities for NEXAFS calculations. This meant that only ligands directly binding to the OEC were kept, which is in line with the notion of the local electronic structure dependence of X-ray transitions. The carboxylate containing ligands (aspartate and glutamate) were modeled by formate, and histidine by imidazole. The glutamine was replaced by a water. After the truncation the structures were fully optimized at the B3LYP level, using the lacvp*⁴¹ basis set. The structures are given in the supporting information. The

total spin and the charge of each of the S_0 , S_1 , S_2 and S_3 compounds are summarized in Table 1.

Table 1: The total spin and the charge of the tetra-nuclear Mn clusters S_0 , S_1 , S_2 and S_3 .

	Spin	Charge
S_0	7.5	-2
S_1	7.0	-2
S_2	6.5	-1
S_3	6.0	-1

The NEXAFS Mn K edge spectra of the Mn complexes and of the Mn tetra-nuclear intermediates S_0 , S_1 , S_2 , and S_3 were calculated with the DFT code StoBe.⁴² We have used the generalized gradient corrected exchange functional by Becke⁴³ and the correlation functional by Perdew.⁴⁴ StoBe uses a double basis set technique to minimize the energy, and an augmented diffuse basis set (19s, 19p, 19d) to calculate the excitation energies and the transition moments in the core-excited atoms.⁴⁵ The ionization potentials for the Mn 1s electrons were calculated according to the Δ Kohn Sham approach as the difference in the total energy of the compounds in the ground state, and the total energy of the compounds in the presence of a Mn 1s core hole. The different electronic configurations were energy optimized. The igloo-iii triple zeta basis of Kutzelnigg, Fleischer and Schindler⁴⁶ was employed for describing the core excited Mn atoms. For the other atoms, we used triple zeta plus valence polarization basis sets provided by the StoBe package. In the calculations of the S_0 , S_1 , S_2 and S_3 clusters, the remaining three Mn atoms not core excited were represented by an effective core potential of 13 electrons provided by the StoBe package. The total Mn K edge spectrum of each tetra-nuclear Mn complex is the result of the summation of the spectra computed for each Mn atom of the complex.

The simulated absorption spectra obtained for the Mn(II), Mn(III) and Mn(IV) reference compounds were convoluted with gaussian curves of full width at half maximum (FWHM) of 1.5 eV up to the energy position of the top of the adsorption edge. The FWHM was then linearly increased up to 20 eV over an energy interval of about 45 eV. Each of the simulated spectra of the S_0 , S_1 , S_2 and S_3 clusters were convoluted by a gaussian curve of 1.0 eV of FWHM up to the ionization potential, and linearly increased up to 20 eV in an interval of about 55 eV. Each single Mn spectrum

was aligned to the IP calculated with the Δ KS approach. The total computed spectra of S_0 to S_3 were normalized to their own maximum intensity. Thereafter, all the computed NEXAFS energies are shifted by the same amount of 34.5 eV, so that the energy scale of the theoretical curves is aligned to the experimental spectra, and this includes also the relativistic shift. We have set the energy of the half intensity of the edges of the S_0 theoretical and experimental curves to coincide. By shifting all the theoretical curves by the same amount, the relative shifts between the absorption edges obtained in the calculations are preserved. Neglect of relativistic effects implies a shift of the spectral onset, which is a few tenths of an eV for common organic NEXAFS spectra, but which for Manganese 1s IP is of the order of about 40 eV. Thus, this contribution is very chemically inert for manganese atoms of different electronic structure environments. The contribution to the IP shifts due to different chemical structure can mainly be divided into an initial potential (electrostatic) effect and a final polarization effect.^{47,48} For charged or polar neutral compounds the largest contribution originates from the former effect which also varies most with conformation or substitution, while the final state polarization, the major contribution for non-polar systems, is relatively constant and can often be estimated by pure dielectric models. By experience our contention is that the present clusters are sufficiently large to well accommodate both these major contributions, maybe except the small fraction of long distance final state polarization, which, however, is common to all states / models.⁴⁹ Further common shifting includes systematic errors, basis set and functional incompleteness common to all atoms/states, thereby laying free the IP dependence on ligand electronic structure and oxidation state.

Results

NEXAFS K edge spectra of the reference Mn compounds

In order to validate our methodology we first address NEXAFS K edge spectra of the three reference Mn compounds. In general, the oxidation states of the Mn atoms depend on the types of ligands and on the total spin and charge of the complex. To determine the oxidation states of each

of the Mn atoms in the compounds studied, we have analyzed the Mulliken spin populations computed by the StoBe code for each Mn.^{50,51} Specifically, the Mn atom in the Mn(II)(acac)₂(H₂O)₂ complex has a spin population of 4.86 electrons, and according to Ref [51] this value can be ascribed to an oxidation state of II. The Mn in Mn(III)(acac)₃ has a spin population of 4.06 electrons, and is assigned to an oxidation state of III, and the Mn in Mn(IV)(sal)₂(bipy) has a spin population of 2.85 electrons, and oxidation state IV.

In Figure 2 the computed Mn K edge NEXAFS spectra of the Mn(II), Mn(III) and Mn(IV) reference compounds are shown. The Mn K edge NEXAFS implies mainly transitions of 1s electrons into the 4p levels, but also the 3d levels are involved. The spectra are characterized by a main threshold around 6545-6555 eV, given by excitations of the Mn 1s electrons into the 4p unoccupied levels. In the spectra presented in Figure 2 the IPE can be coupled to the oxidation state of the Mn atoms, as has been previously shown by several measurements on different complexes containing Mn in different oxidation states.⁵² In our computed spectra the absorption threshold shifts towards higher energies as the oxidation state of the Mn atom increases, in good agreement with the experimental results for the same compounds performed by Yachandra *et al.*⁵³ The energy position of the threshold, which varies considerably in the three cases, is in fact translated towards increasing energies starting from Mn(II)(acac)₂(H₂O)₂ to Mn(III)(acac)₃ and to Mn(IV)(sal)₂(bipy), as is evident from a visual comparison. The IPE was estimated using two methods. As the energy at half intensity of the rising curve, with the following results: 6549.4 eV for Mn(II)(acac)₂(H₂O)₂, 6551.2 eV for Mn(III)(acac)₃ and 6553.5 eV for Mn(IV)(sal)₂(bipy). The IPE difference between Mn(II)(acac)₂(H₂O)₂ and Mn(III)(acac)₃ amounts to 1.8 eV, and between Mn(III)(acac)₃ and Mn(IV)(sal)₂(bipy) to 2.3 eV. With the IPE estimated as the zero crossing of the second derivative of the absorption threshold, we have obtained: 6549.6, 6550.5 and 6553.9 eV respectively, with differences of 0.9 and 3.4 eV. The accuracy in determining the shifts from the theoretical curves with the chosen broadening procedure is about ± 0.1 eV. The shifts are thus completely different depending on the method used to define them, the half-height or the second derivative method. This has to be borne in mind when the results below are analysed.

At lower energies, starting above 6540 eV and extending toward the threshold, a number of low intensity peaks form the so-called pre-edge region. These features originate from 1s excitations into the not fully occupied 3d levels of Mn. While the absorption edge is mainly assigned to dipole type excitations, the pre-edge peaks are usually interpreted by quadrupole transitions of 1s into 3d levels. However, in presence of symmetry breaking, the mixing of 3d and 4p orbitals can occur and transitions into these 3d-4p states can be allowed even in a dipole calculation like in our case.⁵⁴ The pre-edge peaks in our calculations are located at energies that are closer to the edge with respect to the experimental spectra.

NEXAFS K edge spectra of models of the Mn₄ complex

In Figure 3 the tetra-nuclear Mn clusters used in this work to model S₀, S₁, S₂ and S₃ are shown, and in Table 2 the oxidation states of every Mn atom in each S-complex are listed. As for the mono-nuclear complexes previously described, the oxidation states are deduced from the Mulliken spin population computed by the StoBe code on each Mn atom.⁵⁰

Table 2: Mulliken spin populations expressed in number of unpaired electrons, and oxidation states of the four Mn atoms (Mn1, Mn2, Mn3 and Mn4) in each of the tetra-nuclear Mn complexes modeling the S-states 0 to 3.

S-state	Mn1	Mn2	Mn3	Mn4
S ₀	3.80 /III	3.99 /III	3.92 /III	2.93 /IV
S ₁	3.80 /III	3.95 /III	2.95 /IV	3.04 /IV
S ₂	3.90 /III	3.06 /IV	2.86 /IV	3.01 /IV
S ₃	3.29 /IV	3.15 /IV	2.94 /IV	3.02 /IV

In Figure 4, panel A, the total Mn K edge spectra computed for each complex are displayed together with the experimental data by Messinger *et al.*²⁶ As mentioned above, the theoretical curves are the sum of the NEXAFS results calculated for each of the four Mn in the complexes. The computed absorption edges of the model complexes S₀ to S₃ follow the same order as the experimental curves of the relative samples, with the edge of S₀ being the one at the lowest energy, and the edge of S₃ at the highest. The general shape of the experimental profiles are overall well reproduced by the simulations, see Figure 4, panel B, where the curvatures of the S₀ and S₁

spectra in the edge region match very well with the experiment. The computed spectra are also able to simulate the change in shape of the S_2 and especially of the S_3 state in the same interval in the measurements. The pre-edge region represented by the two peaks at about 6541 and 6543 eV in the experiments is reproduced in the simulation although by a slightly more complex group of peaks and at higher energies. In analogy with the experiment, the model complex for S_3 has the highest intensity pre edge resonances at 6542.7 and 6544.5 eV, followed by S_2 , with two resonances at 6543.6 and 6545.3 eV. S_1 and S_0 both have two peaks at 6542.7 and 6544.6 eV.

In Figure 5 the second derivative and the theoretical total spectra for S_0 , S_1 , S_2 and S_3 are displayed. The IPE values obtained as the zero crossing of the second derivative and those estimated by the half height of the threshold of the normalized total spectra are listed in Table 3.

As for the mono-nuclear Mn compounds described in the previous paragraph, the accuracy of the IPE's for the theoretical curves is about ± 0.1 eV.

Table 3: The IPE's for the model complexes for the states S_0 to S_3 used in the DFT calculations and their differences in the transitions S_0 to S_1 , S_1 to S_2 and S_2 to S_3 . *half edge* is for the IPE estimated as the energy position at half intensity of the absorption threshold, *zero crossing* for the zero crossing of the second derivative.

S-state	S_0	S_1	S_2	S_3	S_1-S_0	S_2-S_1	S_3-S_2
half height	6551.55	6552.48	6553.91	6554.54	0.93	1.43	0.63
zero crossing	6551.04	6552.21	6554.18	6554.18	1.17	1.97	0.00

The single NEXAFS curves calculated for each of the four Mn atoms in the S_i clusters are displayed in Figure 6. A visual inspection shows that the edges of the spectra related to Mn atoms with oxidation states III and IV are energetically shifted from each other, constituting two distinct groups. However, individual differences can be seen in the energy position and in the fine structure of each curve. In Table 4 the edge energies estimated for each of the atomic Mn spectra of Figure 6 are listed. The IPE's were estimated both as the energy at half height of the raising absorption edge of the single atom spectra, which were not normalized, and as the zero crossing of the second derivative. The IPE's obtained with the first method vary between 6550.13 to 6551.35 eV for Mn(III), and between 6554.00 and 6555.27 eV for Mn(IV). The variations are 1.22 and 1.27 eV, respectively. Using the second method, the IPE's vary between 6549.97 and 6551.47 eV for

Mn(III), and between 6553.42 and 6555.48 eV for Mn(IV). In this case the variations are between 1.50 and 2.06 eV, respectively.

Table 4: The IPE's (in eV) of each single Mn atom of the S_i complexes. The energies are estimated by the energy position at half intensity of the absorption threshold, and as the zero crossing of the second derivatives. The oxidation states are also indicated.

S-state	half height				second derivative			
	Mn1	Mn2	Mn3	Mn4	Mn1	Mn2	Mn3	Mn4
S_0	6550.93 /III	6551.22 /III	6550.94 /III	6554.45 /IV	6551.2 /III	6550.32 /III	6550.89 /III	6554.84 /IV
S_1	6550.13 /III	6551.35 /III	6554.28 /IV	6554.19 /IV	6549.97 /III	6551.47 /III	6554.06 /IV	6554.43 /IV
S_2	6551.04 /III	6554.53 /IV	6554.14 /IV	6555.00 /IV	6550.88 /III	6554.70 /IV	6553.87 /IV	6554.94 /IV
S_3	6554.41 /IV	6554.00 /IV	6554.28 /IV	6555.27 /IV	6554.14 /IV	6554.22 /IV	6553.42 /IV	6555.48 /IV

Discussion

Theoretical results for Mn K edge NEXAFS

The sensitivity of the K absorption edge to the oxidation state is a known phenomenon observed in several elements and it has been experimentally verified for Mn by a large number of studies. Our theoretical approach, based on gradient corrected Kohn-Sham DFT, is clearly able to reproduce the measured increase of the absorption edge energy for samples containing Mn with higher oxidation states, as evidenced by Figure 2, Figure 4 and Figure 6. In general, previous experimental works have shown that a threshold shift to higher energy of about 1 to up to 3 eV can be attributed to a higher oxidation state on one Mn atom of a unit.^{52,55} Our computed absorption spectra of the mono-nuclear Mn(II), Mn(III) and Mn(IV) complexes, shown in Figure 2, clearly replicate this trend. The theoretical energy differences between Mn(II)(acac)₂(H₂O)₂ and Mn(III)(acac)₃ and between the latter and Mn(IV)(sal)₂(bipy) are 1.8 and 2.3 eV for the half-height method. It has to be observed that, when comparing different complexes, a precise quantitative correlation between the energy position of the absorption edge and the increase/decrease of the oxidation state is complicated by the presence of different ligands, and is more difficult when multi-nuclear clusters are considered.⁵⁵

To analyze how this topic affects our theoretical approach, we can consider the single atomic spectra of Figure 6. Overall, the NEXAFS spectra of each of the Mn(III) atoms are characterized by absorption edges lying at lower energies with respect to those of the Mn(IV) atoms. The estimated IPE's of the Mn(III) and Mn(IV) atoms are distributed over an energy interval of about 1.2 eV according to the half height method (see Table 4). We have compared the IPE computed for the mononuclear compounds to the atomic IPE's of Table 4. The IPE of the Mn(III)(acac)₃ compound lies at 6551.2 eV, and the IPE of the various Mn(III) atoms in the S-states are between 6550.1 and 6551.4 eV. The IPE of the Mn(IV)(sal)₂(bipy) compound lies at 6553.5 eV, and the IPE of the various Mn(IV) atoms in the S-states are between 6554.0 and 6555.3 eV. This shows that in our DFT computed spectra of the tetra-nuclear clusters the energy position of the edge is clearly sensitive to the Mn oxidation state, and the IPE positions are in agreement with those obtained for the mononuclear model compounds.

In Table 5 we have listed the experimental IPE's and the IPE differences obtained in previous experimental studies^{26,27,56,57} in comparison with the theoretical values calculated in this work.

Table 5: IPE's reported in experimental studies for S_i samples, and IPE obtained from DFT calculations in the present work. The energy difference between the steps S₁-S₀, S₂-S₁ and S₃-S₂ are listed. The IPE was estimated with different methods in the different works, as indicated.

S-state	S ₀	S ₁	S ₂	S ₃	S ₁ -S ₀	S ₂ -S ₁	S ₃ -S ₂
Experiment							
Ref ⁵⁶ ^a	6550.7	6551.7	6552.5	6553.7	1.0	0.8	1.2
Ref ⁵⁷ ^b	6550.1	6551.7	6553.5	6553.8	1.6	1.8	0.3
Ref ²⁷ ^c		6551.9			1.0	0.6	1.0
Ref ²⁷ ^b		6553.0			2.4	0.8	0.7
Ref ²⁷ ^a		6551.3			1.1	0.7	1.1
Ref ²⁷ ^d		6552.8			1.3	0.8	0.8
Ref ²⁶ ^b	6550.8± 0.1	6552.9± 0.1	6554.0± 0.1	6554.3± 0.1	2.1	1.1	0.3
Theory							
This work ^a	6551.55	6552.48	6553.91	6554.54	0.93	1.43	0.63
This work ^b	6551.04	6552.21	6554.18	6554.18	1.17	1.97	0.00

^a Half of the normalized height.

^b Zero intersection of the second derivative.

^c Integral method.

^d Half of the peak height.

The experimental results summarized in Table 5 provide different pictures for the evolution of the S-states. The half-height method gives reasonably stable shifts of about 1.0-1.1 eV for the

S_0 to S_1 and S_2 to S_3 transitions and slightly smaller for the S_1 to S_2 transition of 0.6-0.8 eV.^{27,56} These results suggest quite clearly that there are manganese oxidations in all three transitions. A disturbing point is that the shifts in the mononuclear reference compounds were about twice as large, showing influences of the other manganese and possibly different ligand effects in the Mn_4 -complex. In contrast, the second derivative method gives a more shattered picture with 1.6-2.4 eV for the S_0 to S_1 transition, 0.8-1.8 eV for the S_1 to S_2 transition, and only 0.3-0.7 eV for the S_2 to S_3 transition.^{26,27,57} These latter results were interpreted to suggest a ligand oxidation in the S_2 to S_3 transition in line with other results from EPR and XAS.^{26,57} Due to these different interpretations, and other results, the character of the S_2 to S_3 transition has been one of the most debated steps in the photosynthetic reaction-sequence, and it is still somewhat controversial. The oxidation state sequence is thus $S_0(III,III,III,IV)$, $S_1(III,III,IV,IV)$, $S_2(III,IV,IV,IV)$ and $S_3(IV,IV,IV,IV)$ in the former proposal and $S_0(III,III,IV,IV)$, $S_1(III,III,IV,IV)$, $S_2(III,IV,IV,IV)$ and $S_3(III,IV,IV,IV)$ in the latter. The latter assignment was also supported by $K\beta$ XES measurements and an analysis of the reasons that might have caused different IPE shifts is given in previous studies.²⁶ In general the results of the experiments critically depend on the decomposition in S states of the flash samples. It was argued that different deconvolution procedures could be the origin of the differences to Roelofs *et al.* and Iuzzolino *et al.*, while Ono *et al.* did not provide a characterization of the S-state composition.

The present computational analysis starts in the other end compared to the experiments. The clusters chosen for the different S-states were here obtained from an energy minimization procedure²⁸ and all of them have well defined oxidation states showing Mn-oxidation in each S-state transition. The IP shifts are computed both using the half-height and the second derivative methods and the main question is if the absence of shift using the second derivative method necessarily indicates an oxidation of a ligand rather than manganese, as suggested by Roelofs *et al.*

According to our theoretical absorption spectra for the model clusters, and considering the IPE's obtained at half of the normalized height, the S_0 to S_1 transition has a shift of 0.93 eV, the S_1 to S_2 transition of about 1.43 eV. Finally the shift in the S_2 to S_3 transition is slightly

smaller, amounting to 0.63 eV. The results must be concluded to agree reasonably well with the experimental results. However, some of the details are not the same showing the difficulty in obtaining theoretical spectra of very high accuracy. Very interestingly, the shift in the S_2 to S_3 transition using the second derivative method is absent (0.0 eV) in line with the small result of only 0.3 eV obtained experimentally using this method. The conclusion is clear: the absence of a shift using the second derivative method does not necessarily exclude a manganese oxidation.

The analysis of the spectral decomposition of Figure 6 clarifies the range of IPE differences obtained in our simulations. As previously noted, each theoretical single Mn absorption spectrum is characterized by a slightly different IPE and by a specific fine structure, determined by its local chemical environment, as shown in Figure 6. These features vary among the single Mn atoms and clusters. The total final profile for each S-state is influenced by the fine structure of the contributing atomic spectra, and this complicates the assignment of the Mn oxidation states in the tetra-nuclear complexes.

From Figure 6 one can see how the total spectra are affected by the changes of the atomic profiles in the vicinity of the threshold region. One can observe in Figure 4 panel A, where the absorption spectra of the clusters S_0 , S_1 , S_2 and S_3 are displayed on top of each other, that just before the edge the experimental thresholds of the spectra of S_2 and S_3 increase in intensity more slowly than the thresholds of S_1 and S_0 , resulting in different curvatures. The same effect is obtained in the theoretical simulations, and is determined by the amount of Mn(III) and Mn(IV) in each cluster. Due to the energy shifts of the edges, in the energy region at the lower part of the edge, around 6550 eV and below, the total NEXAFS curves have higher intensity the more Mn(III) are present in the cluster, and, on the contrary, lower intensity the more Mn(IV) are present in the cluster.

Dau *et al.*^{58,59} addressed the role of coordination and oxidation on the shapes of NEXAFS spectra by analyzing results from MSX $_{\alpha}$ simulations for single metal manganese water complexes. They concluded that the changes in the shape of the edge spectra observed for the S_2 - S_3 transition are explainable by the transformation from five-coordinated Mn(III) to six-coordinated Mn(IV)

complexes and that these changes therefore are associated with oxidation of a manganese atom rather than a ligand. This is an important observation made long before a high-resolution X-ray structure was available, and which is strongly supported by later DFT studies based on energy minimizations.^{20,28} These authors speculated that the higher coordination changes the local manganese p- versus d-orbital contributions to unoccupied molecular orbitals at the edge, thereby shifting the apparent absorption spectrum as governed by local X-ray selection rules (here s - p). They also discussed an indirect effect of coordination in the change of bond length and thereby IPE shifts due to changes in the "particle in the box" potential.

The simulated shift of S_2 - S_3 in Dau's analysis was about a factor of four larger than that observed experimentally, something that was explained by the fact that only one of the four manganese atoms is oxidized in this transition. This holds, of course, for any of the single oxidation steps and the fact that the S_2 - S_3 edge shift is significantly smaller in our calculations than the S_0 - S_1 and S_1 - S_2 shifts calls for some further analysis. In order to accomplish this we emphasize in the present work a more direct effect on the shape and position of the spectra, namely through the charging or de-charging of the central atom where the core excitation takes place. A quantitative interpretation model for the shifts should account for both charging and polarization, charging in the initial ground state, and polarization (relaxation) in the final state following the ionization. In fact, for inorganic and organometallic compounds a ground state charging model generally works well for predicting IP shifts, like the ESCA potential model⁶⁰ (the size of the final state polarization contribution ~ 1 eV is very similar for every atom and is thus coped with by the general spectral alignment). The shift with respect to a reference level is in this model related to the charging of the central atom (multiplied by a so-called k parameter, given empirically or by the core valence Coulomb integral) and the charges of the surrounding atoms or atom groups divided by the interatomic distance to the central atom. Typically, the effect is dominated by the one-center contribution,⁴⁷ however, if coordination involves electronegative or electropositive groups at short distances an essential contribution to the shift can be expected also from the coordinating atoms. The values of the IPE's for each Mn atom in the S_i clusters as a function of the charge on the same

atom are shown in Figure 7. The general trend we have observed is that when an Mn atom is oxidized from (III) to (IV), its charge is enhanced by about $+0.16$ to $+0.18 e^-$. The effect of changes of the charges in the near surrounding of the metal is normally quite small, but this is not the case in the S_2 to S_3 transition. The change of charge for the oxidized atom (Mn1) is also in this case relatively large ($+0.16 e^-$). Following the empirical rules, this should lead to an IP shift of about $+1.6$ eV (assuming a k-factor of 10). However, in this transition an almost unbound neutral water ligand is deprotonated forming a short Mn-OH bond to Mn1. The charge of this OH-ligand is -0.30 and the Mn-OH distance is $1.78 \text{ \AA}$. In its most simplified form this would lead to a contribution to the IP shift of -2.4 eV at Mn1, since the unbound water ligand in S_2 does not contribute at all, and this should be added to the $+1.6$ eV from the atom itself. From this simple analysis, the effect of the OH-ligand could therefore in principle contribute significantly to both the position and shape of the curves. The reason the contribution from a ligand is so large in this case, which is unusual, is the loss of the Jahn-Teller axis in the transition, leading from 5- to 6-coordination. Admittedly, this is an oversimplified description but it still makes it understandable that the IPE shift might be observed as smaller in this transition than in the other ones. A more accurate charge distribution than just a single point charge on water, would complicate the picture, as well as contributions from the other ligands on Mn1. Connecting to Dau's analysis we find that although a quantitative interpretation cannot be obtained in this simple way, this argument supports a notion that a different character of the NEXAFS curves for the S_2 - S_3 transition can be understood even though a manganese oxidation occurs in this transition.

Direct time-dependent density functional theory (TDDFT) can also be used for core level spectra.^{25,61,62} A theoretical study of Mn K edge NEXAFS based on TDDTF by Jaszewski *et al.*²⁵ proposes a "low" Mn oxidation state evolution, where the Mn_4 clusters follow a quite different oxidation pattern than obtained here, starting from S_0 as III-IV-II-II to S_1 as III-IV-III-II, to S_2 as III-IV-III-III, and finally to S_3 as III-IV-IV-III. To analyze the present results in relation to the previous TDDFT results, it is important to address the different computer modeling techniques into some detail. A common view is that TD techniques have a clear advantage over static exchange

(based on full hole or transition potential optimized states) for valence electron excitations (where the word exchange cannot be interpreted literally in case of most DFT functionals). The reason is that static exchange is a strict approximation (diagonal A Hessian matrix) with respect to TDHF (full A and B Hessian matrices) in the coupled perturbed (TD) equations. Although the availability of the B matrix in general makes only minor changes in excitation energies, it allows for a proper screening of the excitation (while static exchange energies are unscreened). It also allows for operator gauge invariance in a full basis set, which leads to "good quality" oscillator strengths also for limited basis sets - a major advantage for property calculations using TD methods. However, for core excitations the situation is completely different, something that follows from two neglected effects in TD methods: lack of orbital relaxation, which breaks the final state rule for NEXAFS,⁶³ and, in the case of DFT, the electron self-interaction error, which is very large for core electrons. In fact these two effects are chemically dependent and have different sign, with the latter generally dominating. Thus TDDFT for manganese K excitations leads to some 70 eV offset error between the core orbital energy (or TDDFT excitation) and the IP, the exact value being subtly dependent on density functional, in particular the amount of exact exchange, and also chemical environment. Even a slight change in the core density, or change in the amount of exchange in the functional, has pronounced energetic effects.^{62,64} It was recently shown by one of the authors that chemical shifts in hydrogen bonded systems could only be properly estimated using DFT core orbitals energies if these are self-energy corrected.⁶⁵ Besley *et al.*⁶² very recently presented an interesting analysis of the self-interaction error in TDDFT core excitation energies in terms of overlap character of the orbitals taking part in the excitations, much in the same manner as for the asymptotic behaviour of DFT functionals for long distance charge transfer interactions. Problems arise in particular when the ground state unoccupied orbital lacks an amplitude localized over the atom of the core hole. This makes the self-interaction induced error large, when at the same time the relaxation induced localization towards the opened core hole is neglected. Using the present static exchange technique, the core hole potential is pre-optimized (or transition potential is optimized, which is identical to Δ SCF energy up to 3rd order of perturbation theory). This technique includes orbital

relaxation around the core hole (also in general increasing overlap), and avoids the self-energy problem which appears through core orbital energies. The result is an offset on the order of an eV (non-relativistic) thus well within the scale of general chemical shifts up to a few eV, allowing for a fine assessment of spectral features in terms of small energy perturbations. The success of Δ SCF,³⁶ and somewhat more recently of Δ SCF Kohn Sham,^{30,32} is a strong indicator of the preference for the use of orbital optimized core potentials for calculating NEXAFS spectra.

Conclusions

The advent of modern synchrotron radiation sources and the concomitant development of computational methods for interpretation of X-ray spectra have made it possible to unravel important information both on structure and function of many biological systems. In the present work, the Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra have been analyzed for the active site of photosystem II (PSII), where water oxidation takes place. Particular focus has been placed on the method for assigning the oxidation states from the measured spectrum of the oxygen evolving manganese complex. We have discussed our results both in view of earlier spectroscopic and theoretical work and in a general context of structure and functionality of the PSII system. Furthermore, in order to validate parametrizations - density functionals, basis set and structural models - we carried out a set of calculations on a few manganese containing complexes and compared them with available high-resolution spectra.

A major problem in the analysis of the experimental NEXAFS spectra is the presence of overlapping atomic spectra for multi-nuclear clusters. Another problem is obviously that the manganese K edge NEXAFS transitions occur at several thousands eV's while the separation of individual states requires a theoretical resolution of fractions of an eV. At the same time the spectra are significantly broadened, homogeneously and in-homogeneously, by the underlying background that increases steeply above the IPE. In the present study a Δ SCF Kohn Sham^{30,32} method has been used in contrast to the previous study which used the TDDFT method.^{24,25} The present method was

chosen based both on its inherent superior properties and on previous experience.^{32,36} The static exchange spectrum is constructed from a fully optimized core hole or a transition potential, allowing inclusion of orbital relaxation around the core hole, and avoiding the electron self-energy problem - two factors that increase steeply as one moves down the main shells of an atom. This implies that one can maintain an offset on the order of an eV (corrected for relativistic effects) well within the scale of chemical shifts that span a few eV, allowing the addressing of spectral features in terms of chemical shifts and other small energy perturbations.

A major question in the analysis of the oxidation state pattern of the OEC during water oxidation, has been whether a manganese or a ligand centered oxidation occurs in the S_2 to S_3 transition. Earlier studies have differed both with respect to the actual oxidation states and with respect to the assignment of where this oxidation is localized. The assignments have been made experimentally in terms of a spectral analysis and theoretically in terms of optimization of geometries and electronic structure. In the present study we have employed structural models for the S-states obtained previously by energy minimization.²⁸ These structures were found to have a manganese centered oxidation in each transition without any oxidation of ligands. We find that the NEXAFS derived IPEs using the half-height method for S_0 , S_1 , S_2 and S_3 shift as 0.93, 1.43 and 0.63 eV in reasonable agreement with experimental measurements using the same method of analysis. Any single Mn absorption spectrum is here characterized by a slightly different IPE and by a specific fine structure, determined by its local chemical environment. In the S_2 - S_3 transition a different character of the spectrum has been observed experimentally.^{27,57} An analysis based on the charges and the potential model for core electron chemical shifts suggests that this is due to change from 5- to 6-coordination following a loss of a Jahn-Teller axis, in line with a previous suggestion based on experiments,^{58,59} and not due to a ligand oxidation.

One of the most important conclusions drawn from the present calculations is that the previously theoretically suggested structures and S-transitions²⁸ lead to NEXAFS (XANES) spectra in good agreement with experiments. Most interestingly, the IPE shift obtained for the S_2 - S_3 transition is very small if the second derivative method is used to identify the position of the IPE, in

line with measurements,⁵⁷ but not if it is obtained by the half-height method, also in agreement with experiments.²⁷ The present analysis thus supports the assignments and structures suggested in the previous theoretical study based on energy minimization presented in Ref. [28]. After the present study was initiated, a high-resolution structure of PSII has appeared⁴⁰ which also confirms the theoretical OEC structures with only small modifications.⁶⁶

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Supporting Information Available

Atomic coordinates for S₀, S₁, S₂ and S₃ Mn complexes. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Figure 1: (Color online) Structures of the reference compounds Mn(II)(acac)₂(H₂O)₂, Mn(III)(acac)₃ and Mn(IV)(sal)₂(bipy).

Figure 2: (Color online) Theoretical Mn K edge NEXAFS of the mononuclear reference compounds $\text{Mn(II)(acac)}_2(\text{H}_2\text{O})_2$, Mn(III)(acac)_3 and $\text{Mn(IV)(sal)}_2(\text{bipy})$. The computed second derivative for each of the spectra is shown in the lower part of the figure. The arrows indicate the zero intersection of the second derivative.

Figure 3: (Color online) Structure of the tetranuclear Mn model complex S_0 .

Figure 4: (Color online) Panel A: the theoretical spectra of Mn K edge NEXAFS of the model complexes for the S_0 , S_1 , S_2 and S_3 states of PSII, in comparison with the experimental measurements of Messinger *et al.*²⁶ Panel B: the computed spectra are superimposed to the experimental ones.

Figure 5: (Color online) Second derivative of the Mn K edge NEXAFS of the model complexes S_0 , S_1 , S_2 and S_3 . The arrows indicate the zero intersection.

Figure 6: (Color online) Theoretical spectra of Mn K edge NEXAFS for each of the four Mn atom of the model complexes S_0 , S_1 , S_2 and S_3 . Dashed line: spectra computed for single Mn atoms with oxidation state III; continuous line: spectra computed for single Mn atoms with oxidation state IV. As a comparison, lines A and B are positioned at 6551.2 eV and at 6553.5 eV, which are the theoretical IPE of Mn(III)(acac)₃ and Mn(IV)₂(sal)₂(bipy) respectively, computed as the energy of the half height of the maximum intensity of the edge.

Figure 7: (Color online) Computed IPE's of the Mn atoms in the S-states as a function of the charge in each Mn atom.

Graphical TOC Entry