Towards a comprehensive X-ray approach for studying the photosynthetic manganese complex—XANES, Kα/Kβ/Kβ−satellite emission lines, RIXS, and comparative computational approaches for selected model complexes

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Abstract. Advanced X-ray spectroscopy experiments can contribute to elucidation of the mechanism of water oxidation in biological (tetra-manganese complex of Photosystem II) and artificial systems. Although the electronic structure of the catalytic metal site is of high interest, it is experimentally not easily accessible. Therefore, we and other researchers are working towards a comprehensive approach involving a combination of methods, namely (1) quantitative analysis of X-ray absorption near-edge structure (XANES) spectra collected at the K-edge and, in the long run, at the L-edge of manganese; (2) high-resolution X-ray emission spectroscopy (XES) of Kα and Kβ lines, (3) two-dimensional resonant inelastic X-ray scattering (RIXS) spectra. Collection of these spectroscopic data sets requires state-of-the-art synchrotron radiation facilities as well as experimental strategies to minimize the radiation-induced modifications of the samples. Data analysis requires the use and development of appropriate theoretical tools. Here, we present exemplary data collected for three multi-nuclear synthetic Mn complexes with the Mn ions in the oxidation states II, III, and IV, and for MnVII of the permanganate ion. Emission spectra are calculated for the MnVII ion using both multiple-scattering (MS) approach and time-dependent density functional theory (TDDFT).

1. Introduction

In Photosystem II (PSII), water is split (oxidized) at a protein-bound Mn4Ca(µ-O)n complex. This photosynthetic water oxidation is of outstanding importance for biosphere and atmosphere. Any attractive scheme for the use of solar energy to produce fuels involves water oxidation, i.e., the extraction of electrons and protons from mere water. Consequently, the photosynthetic Mn complex and its reactivity are of interest regarding development of (bio-inspired) technological catalysts with similar properties (high efficiency, low-cost metals, self-assembly and repair). Using X-ray spectroscopy and complementary methods, we intend to contribute to elucidation of the mechanism in PSII water oxidation and recently also in artificial systems [1], other groups have worked successfully along these lines [2]. In the present contribution, a set of absorption and emission spectra as well as RIXS planes is presented for four selected Mn model compounds. The oxidation-state dependence is

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discussed. Computational approaches (DFT and scattering theory) are applied to obtain insights in the determinants of the Kβ satellite line positions.

2. Materials and methods

2.1. Mn model complexes

To illustrate oxidation-state dependencies, several six-coordinated complexes with different oxidation state of Mn were selected: MnII4 [3] containing 4 MnII atoms with 4N and 2O ligands; a tetranuclear MnIII4 complex [4] with 6O ligands, and a dinuclear MnIV2 complex [5] (LMn(µ-O)2MnL, L = 2-((2-(bis(pyridin-2-ylmethyl)amino)ethyl)(methyl)amino) acetic acid) with 3N and 3O atoms in the first coordination sphere. KMnO4 was used as an example of a MnVII ion.

2.2. X-ray absorption and emission measurements

Experiments were performed at the undulator beamline ID26 of the ESRF in Grenoble. The excitation energy was selected by a double-crystal monochromator Si(111). For Mn Kα measurements and RIXS planes, one Ge(333) analyzer crystal were used; for Kβ emission, we used four Ge(440) crystals (resolution ~1 eV); an avalanche photodiode was used as a detector. Samples were kept at 20 K (liquid-helium cryostat). To keep the rate of radiation damage at a negligible level, the beam was attenuated by Al foils (20 μm). All shown spectra were collected on ground microcrystalline samples mixed with boron nitride powder (with the sole exception of the XANES spectrum of the MnIV compound for which the shown spectrum was collected at a bending-magnet beamline for the complex dissolved in acetonitrile). In control experiments we found that, for the appropriately attenuated beam, irradiation of the dry powder samples (for up to 15 minutes) did not cause significant shifts in edge or peak positions. Moreover XANES spectra were collected at the bending magnet beamline KMC1 at BESSY (Berlin), at 20 K, and compared to the spectra collected at the ESRF (at clearly higher X-ray flux).

All emission data were normalized to the amplitude of the absorption-edge jump in a XANES spectrum measured on the same spot after the emission scan. This procedure facilitates detection of absolute changes in the magnitude of emission lines.

2.3. Simulations of X-ray emission spectra

2.3.1. Simulations with FEFF8.4 (MS). Valence-to-core X-ray emission spectra were calculated on the basis of full multiple scattering theory using the FEFF8.4 code [6] (Hedin-Lundqvist exchange potentials). To take into account the experimental resolution, in the simulation an experimental broadening of 0.6 eV (and an energy shift of 1 eV) were applied.

2.3.2. Simulations with Orca (DFT). Kβ lines were simulated using a time-dependent DFT approach as implemented in the ORCA package [7]. The lines were obtained by first carrying out spin unrestricted ground-state calculations with the BP86 functional [8] and the TZVPP basis set [9]. Following the ground-state DFT, an excited state was simulated by interchanging of the spin-up Mn-1s orbital with an unoccupied high-energy orbital, effectively making the Mn-1s orbital vacant. Time-dependent DFT calculations were performed on this state, allowing only for transitions to the vacant Mn-1s orbital. The energy scale was recalibrated by shifting the energy axes of calculated absorption and emission transitions by the same value (+167.2 eV) such that the position of the simulated pre-edge feature of MnO4− ion (at Mn K-edge) matched the experimental data.

3. Results and discussion

3.1. XANES spectra

In the recorded XANES spectra (figure 1a), an increasing shift of the edge position towards higher energies is observed with increasing oxidation state (table 1). Correlation between the formal Mn
oxidation state and the edge position has been confirmed for extended sets of model compounds (see [10] for refs.). This correlation relates to an influence of the bond length on the energy of the transition to anti-bonding orbitals with dominating 4p character (at the principal edge maximum) [10]. The pre-edge feature is found at slightly higher energies in higher oxidation states, but this pre-edge shift is clearly less pronounced than changes in the edge position. The magnitude of the pre-edge itself increases for deviations from octahedral symmetry and in the presence of short Mn-oxo bonds. Both factors result in the giant pre-edge of the permanganate ion (Mn$^{VI}$O$_4$).

Table 1. Positions of Mn K edge (from figure 1a) and emission maxima (figure 1b,c,d and figure 2b) in complexes with different oxidation states of Mn. Changes between oxidation states are also shown.

| Positions | Mn$^{II}$ (eV) | Δ (eV) | Mn$^{III}$ (eV) | Δ (eV) | Mn$^{IV}$ (eV) | Δ/3 (eV) | Mn$^{VII}$ (eV) | Average change per increment in oxidation state (eV) |
|-----------|----------------|--------|-----------------|--------|----------------|----------|----------------|-----------------------------------------------|
| K edge    | 6546.73        | 3.74   | 6550.47         | 2.42   | 6552.89        | 1.52     | 6557.44        | 2.56                                          |
| K$_{\alpha_1}$ | 5899.80        | -0.23  | 5899.57         | -0.26  | 5899.31        | -0.23    | 5898.63        | -0.24                                         |
| K$_{\alpha_2}$ | 5999.13        | -0.07  | 5888.06         | -0.02  | 5888.04        | -0.11    | 5887.71        | -0.07                                         |
| K$_{\beta_13}$ | 6492.35        | -0.47  | 6491.88         | -0.66  | 6491.22        | -0.49    | 6489.75        | -0.54                                         |
| K$_{\beta_25}$ | 6534.67        | 0.78   | 6535.45         | 0.90   | 6536.35        | 0.71     | 6538.47        | 0.80                                          |
| K$_{\beta^*}$ | 6515.05        | 3.68   | 6518.73         | 0.34   | 6519.07        | 1.16     | 6522.56        | 1.73                                          |
| L$_3$     | 639.03         | 1.49   | 640.52          | 0.89   | 641.41         | 1.00     | 644.41         | 1.13                                          |
| L$_2$     | 650.20         | 1.70   | 651.90          | 0.80   | 652.70         | 0.83     | 655.18         | 1.11                                          |

3.2. XES

After primary X-ray excitation, the created core hole is filled by a radiative transition of an electron from higher shells giving rise to X-ray fluorescence emission. X-ray emission spectra (XES) of transition metal compounds reflect oxidation state [11], ligand environment [12], and spin state [13,14].

3.2.1. K$\alpha$ lines. K$\alpha$ emission in Mn results from a 2p→1s transition filling the hole created by an absorption of an X-ray quantum with an energy well above the K edge. The line is a doublet (K$_{\alpha_1}$ and K$_{\alpha_2}$) due to the spin-orbit interaction energy between the electron spin and the 2p orbital momentum.

The K$_{\alpha_1}$ maximum shifts by ~0.24 eV per oxidation state to lower energies (table 1). The position of the K$_{\alpha_2}$ maximum shows the same trend, but the shifts are even smaller. A dependence between the number of the unpaired spin in the valence shell and Fe K$_{\alpha_1}$ FWHM has been reported [13,14], in line with our data where the FWHM of KMnO$_4$ is smaller than in the other compounds (figure 1b, inset).

3.2.2. K$\beta$ main lines. K$\beta$ lines (figure 1c) result from an electronic transition from 3p orbitals to the 1s hole (here) created by excitation at an energy well above the Mn K-edge (6900 eV). The 3p orbitals interact stronger than 2p with 3d orbitals because of the higher wave-function overlap. Consequently the K$\beta$ emission is clearly more affected by the Mn oxidation state than the K$\alpha$ emission. Since the split of the K$\beta$ main line into K$_{\beta_13}$ and K$\beta^*$ results from a large 3p-3d exchange coupling in the final state [11,15], in Mn$^{II}$ the K$_{\beta_13}$ is shifted to higher energies in comparison to KMnO$_4$ (table 1). The chemical shifts in Mn K$_{\beta_13}$ fluorescence can be large enough [11] to selectively record the XANES and EXAFS of Mn ions in different oxidation states [16].

3.2.3. K$\beta$ satellite lines. At the high energy side of the main K$\beta$ line, the satellite line (traditionally called "cross-over" transitions) can be observed. K$\beta$ satellite lines show two main features denoted K$_{\beta_25}$ and K$\beta^*$. The position of K$\beta^*$ relative to K$_{\beta_25}$ contains information about the ligand type, and its intensity is related to the number of ligand atoms and bond lengths.

The K$_{\beta_25}$ band arises from transitions that fill the 1s hole from molecular orbitals with electronic population of metal 3p or 4p and ligand 2p or 2s character. The simulations also show that the K$_{\beta_25}$ energy is determined mostly by ligand p orbitals; if different types of ligands are coordinated to the
metal, additional peaks appear in this region [17]. It has been shown that \( K\beta_{2,5} \) line-shifts can be used to estimate the oxidation state [12]. In our data, the energy of the \( K\beta_{2,5} \) feature shifts by \(-1\) eV per increment in oxidation state, in agreement with Refs. [12] and [18]. The split of this peak for the \( Mn^{II} \) and \( Mn^{IV} \) complex (figure 1d) may be explainable by a mixture of ligand types (N, O) in the first coordination sphere [17].

The \( K\beta^{''} \) satellite line is often interpreted in terms of a cross-over transition between ligand 2s and metal 1s orbitals [19]. The energies of \( K\beta^{''} \) transitions can be used to identify the elemental type of ligand, while the intensities can be used to address the number and distance of neighbouring ligands [12]. In \( KMnO_4 \), the \( K\beta^{''} \) amplitude is especially high because of short Mn-O distances (figure 1d).

### Figure 1

Absorption and emission spectra of synthetic Mn complexes with different Mn oxidation states. (a) Mn K-edge spectra; (b) Mn K\( \alpha \) emission lines; (c) Mn K\( \beta \) emission lines; (d) Mn K\( \beta \) satellite lines. The K\( \beta \) satellite line data in (d) have been additionally smoothed by a Fourier-filter procedure to minimize the noise contributions. The XANES spectrum of the Mn\( ^{IV} \) compound was collected at lower energy resolution preventing resolutions of substructures in the pre-edge feature.

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### 3.3. RIXS

Resonant excitation (here 1s\( \rightarrow \)3d) coupled to radiative decay (here 2p\( \rightarrow \)1s) is called resonant inelastic X-ray scattering (RIXS). RIXS can be used to study electronic excitations at energies much lower than that of the incident hard X-rays because the energy transfer, defined as the difference between incident and emitted photon energy, relates to low-energy electronic transitions (here 2p\( \rightarrow \)3d; L-edges) [13]. In RIXS experiments, the fluorescence intensity is recorded at various incident and emission energies. In order to assign the total energy of an electronic state to the axes of the contour plots, the energy transfer instead of emission energy is used as in [13] (figure 2a). In this way, the energy transfer axis corresponds to the excitation energy in L-edge experiments [13].

The L\( _{2,3} \)-edge spectra carry information on metal oxidation [20] and spin state [21]. L-edge type spectra from RIXS data are shown in figure 2b. The spectrum for \( KMnO_4 \), e.g., is indeed similar to its Mn L\( _{2,3} \)-edge. For the Mn complexes in various oxidation states, a clear shift is observed, much larger than that in the K\( \alpha \) emission lines measured for excitation at 6900 eV (table 1).
3.4. Simulations

Calculation of Kβ satellite lines for the tetrahedral MnO₄⁻ using MS theory and DFT (broadening of the Lorentzian curves, 5 eV FWHM) (figure 3) allow identification of the dominant orbitals. The main contribution to the Kβ₁,₃ line comes from Mn p-orbitals, whereas the satellite lines are strongly affected by s (Kβ₁') and p orbitals (Kβ₂,₅) of the O-ligands.

4. Concluding remarks

All discussed energy levels appear to exhibit an oxidation-state dependence. In preliminary studies on a more extended series of complexes, we found that typically the dependence on the O:N ratio is weak for 6-coordinated MnOₓNₙ complexes. However, when comparing Mn^{III}L₆ complexes to a Mn^{III}L₅ complex, significant differences are observed. Theoretical tools may provide the means for unraveling the relation between geometric and electronic structure (ligand types, coordination geometry, oxidation states) on one hand, and X-ray absorption and emission data, on the other.

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