Site-Selective XANES and EXAFS: A Demonstration with Manganese Mixtures and Mixed-Valence Complexes

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This paper presents the first demonstration that chemical shifts in X-ray fluorescence energies can be used to obtain site-selective X-ray absorption spectra. X-ray absorption spectroscopy (XAS) has become a powerful tool for probing both geometric and electronic structure.¹ As commonly practiced, both X-ray absorption near-edge (XANES) and extended X-ray absorption fine structure (EXAFS) techniques measure spectra that average over all species of an element in a sample. In many instances it is desirable to selectively probe different forms of the same element. Site-selective XAS has previously been accomplished using ion-desorption detection,² luminescence detection,³ X-ray standing waves,⁴ and diffraction anomalous fine structure (DAFS).⁵ However, all of these methods require specific types of samples, and they are not generally applicable to noncrystalline bulk materials.

Chemical shifts in X-ray emission have been known for many years.⁶ More recently, the line sharpening⁷ and spin selectivity⁸ gained from high-resolution fluorescence excitation spectroscopy have become appreciated.⁹ We have shown that both the energy and shape of Mn Kβ emission change with oxidation and spin state.¹⁰ This suggests that, by picking the appropriate detection energy, it should be possible to selectively probe the absorption spectrum of a particular oxidation state of Mn in a mixed-valence complex. For mixed-valence Mn systems such as

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10 batteries¹⁰ and metalloprotein clusters¹¹ site-selective XAS of Mn(II), Mn(III), and Mn(IV) sites would have many advantages. In this paper, site-selective XANES and EXAFS using high-resolution fluorescence detection are demonstrated for a physical mixture of MnF₂ and BaMnO₃·2H₂O and for a Mn³⁺, mixed-valence complex, MnO₄²⁻·C₃H₆O₆·(H₂O)₄.

The Kβ emission spectra of MnF₂, BaMnO₃·2H₂O, and their physical mixture are presented in Figure 1. As has been observed before, the Kβ emission peaks at higher energy for lower oxidation states. The physical mixture spectrum is nicely simulated by the average of the two component spectra, as is expected. On the basis of these emission results, the fluorescence analyzer was set at an energy selective for Mn(II) (64914 eV), and the excitation energy was scanned. A

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spectrum selective for the Mn(II) component of the physical mixture was obtained, as shown in Figure 1. In the region above 6540 eV, the site-selective XANES using 6491.4 eV detection is almost identical to that of the pure MnF₂. Some differences occur in the 1s → 3d region which may be due to contamination by fluorescence from the BaMnO₂H₂O and resonant Raman scattering.\(^{17}\)

To demonstrate that site selectivity can be obtained for EXAFS of mixed-valence complexes, we show the transmission, emission, and excitation spectra of MnO₄(C₂H₄)₃(py)₃(H₂O) (Figure 2). This trinuclear mixed-valence system has a single trapped-valence Mn(II) center with a different local structure from the two Mn(III) ions.\(^{18}\) The Mn(II)–Mn(III) distances are 3.36 ± 0.02 Å while the Mn(III)–Mn(III) distance is 3.21 Å. Thus, from the Mn(II) perspective, the Mn–Mn interactions are homogeneous, while the Mn(III) sites see a more disordered environment with two different Mn–Mn distances, resulting in weaker Mn–Mn EXAFS.

The Kβ emission spectrum of MnO₄(C₂H₄)₃(py)₃(H₂O) is nicely simulated by the weighted average of Mn(II) and Mn(III) component spectra (Figure 2). A good fit\(^{19,20}\) to the transmission data was obtained using either two Mn–Mn interactions at 3.32 Å or 1/2 Mn–Mn at 3.22 Å and 1/2 at 3.37 Å, as well as Mn–O components at 1.85 and 2.13 Å (Figure 2 and supplementary material).

We selectively probed the EXAFS of the Mn(II) and Mn(III) species by monitoring the Kβ fluorescence at 6492.6 and 6488.9 eV, respectively. The site-selective EXAFS oscillations are clearly different from each other (Figure 2). Although they are similar at low k to the transmission spectrum, at high k they show stronger and sharper oscillations. The Fourier transform of the Mn(II) spectrum, which reflects two Mn–Mn interactions at 3.36 Å, shows a clear peak for this interaction, while the transmission and Mn(III)-selective spectra show much broader structure in this region.

Simulations of the smoothed site-selective EXAFS\(^{19,20}\) required two Mn–O components and at least one Mn–Mn component (Figure 2). Shells of O and C at 3.0 and 3.4 Å also contribute and complicate the analysis. The Mn(II)-selective data was best fitted to a homogeneous Mn–Mn component at 3.36 Å (R\(_{\text{crystal}} = 3.36\) Å). For the Mn(III)-selective measurement, the emission from Mn(III) always overlaps that from Mn(II) and the selectivity is lower. Nevertheless, spectra taken using 6488.9 eV detection predominantly probe the Mn(III) sites. Fitting with a single Mn–Mn interaction gave an average distance of 3.29 Å (R\(_{\text{crystal}} = 3.29\) Å). A slightly better fit was obtained when the Mn(III)–Mn(III) interaction was split into two components at 3.22 Å (R\(_{\text{crystal}} = 3.21\) Å) and 3.34 Å (R\(_{\text{crystal}} = 3.36\) Å). In the future, better statistics and a wider range of data will certainly allow better discrimination between different models.

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(20) The distances reported here are from fits with coordination numbers fixed at values obtained from the crystal structure and with individual ΔEₗ values held constant at ~10 eV. An exception was made for the two short-distance oxygen shells, where the sum of the coordination numbers was fixed, and for the Mn–C interaction, where the coordination number was floated. Additional fits are presented in the supplementary material.