Pre-edge structure, selection rules and quadrupole contributions

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The features and origin of pre-edge peaks in K-edge XANES spectra of 3d transition-metal compounds are reviewed from the viewpoints of the coordination environment of a central atom, the oxidation state and the selection rule of an electric dipole transition. The contribution of the electric dipole and quadrupole transition is discussed based on group theory. The pre-edge peak intensity of four-coordinated species with $T_d$ symmetry are much larger than those of six-coordinated species for all 3d elements, and the remarkable intense pre-edge peak is confirmed for $d_0$ compounds. The peak intensity is closely related to the number of 3d electrons and is almost independent of the element. The electric dipole transition is the main component of the intense pre-edge peak, and its possibility is strictly regulated by the selection rules. The probability of transition between s and d orbitals by the electric quadrupole transition is much lower than that for s–p transition. An electric dipole transition between an s orbital and the p component of a d–p orbital would be possible if the d orbital hybridizes with the p orbital, and the availability can be qualitatively evaluated using character tables from group theory. Polarized and/or high-energy resolution experiments and their theoretical calculation could give useful information for their interpretation.

1. Introduction

The spectrum obtained from an X-ray absorption near-edge structure (XANES) experiment is generally heavily influenced by the coordination environment (within several ångströms) of the target element. Characteristic peaks that appear near the energy regions just below an absorption edge, which are called pre-edge peaks (prepeaks), have received much attention because they provide highly sensitive information about the configuration of the atom, especially relating to the symmetry of a central atom (Fig. 1). XANES spectroscopy has been widely utilized for the analysis of various target elements in order to investigate electronic and geometrical structures and oxidation states, to identify chemical species and to perform quantitative analyses (Iwasawa, 1996; Cabaret et al., 2010; van Bokhoven & Lamberti, 2015), among other things. In this chapter, we describe the characteristics of pre-edge peaks with regard to their intensity, assignment and general tendencies on the basis of the coordination symmetry and oxidation number of the target atom.

2. Coordination-number dependency

Fig. 2 shows the K-edge XANES spectra of sixfold- and fourfold-coordinated 3d transition-metal compounds. As is well known, the pre-edge peak intensities of four-coordinated species are larger than those of six-coordinated species for all elements. The pre-edge peaks of the early 3d transition
elements (vanadium, chromium and manganese) are much larger than those of the later elements (iron and copper). Pre-edge peaks have been confirmed, even for sixfold coordination, with maximum intensities as low as <0.1. The existence of multiple peaks has been clearly confirmed in the sixfold-coordination complexes of some elements, such as chromium. However, pre-edge peaks have not been confirmed in the Zn K-edge XANES spectra of any fourfold- or sixfold-coordinated compounds.

Detailed systematic experimental and theoretical studies of pre-edge peak features and coordination number have been carried out for Ti$^{4+}$ species using Ti K-edge XANES spectra (Farges et al., 1996). As shown in Fig. 3(a), the peak intensity decreases with coordination number (from six to four), with an accompanying shift to higher energy. Similar tendencies have been confirmed for vanadium (Yoshida et al., 1992), iron (Jackson et al., 2005) and nickel (Farges et al., 2001) K-edge XANES. These characteristic features, especially in the peak intensity, have been utilized as a powerful fingerprint for investigating the coordination number of a central atom in unknown samples. For example, the vanadium species in heterogeneous catalyst materials have been identified using XANES pre-edge features (Fig. 3b; Yoshida et al., 1992).

3. Dependence on the number of $d$ electrons
As shown in Fig. 2, the pre-edge peak intensity of FePO$_4$ in a fourfold coordination environment is much smaller than those of early 3$d$ transition-metal compounds. This intensity level (~0.2, normalized to X-ray absorption) is valid because various kinds of tetrahedral Fe$^{3+}$ compounds yield the same pre-edge peak intensities (Roe et al., 1984; Westre et al., 1997; Jackson et al., 2005). The weak pre-edge peak intensity has been reported to be related to the oxidation state of the element (Fig. 4; Yamamoto, 2008).

As for the general rule regulating the pre-edge peak intensity in four-coordinated tetrahedral symmetry, the intensity has been proposed to be closely related to the number of 3$d$ electrons and is almost independent of the element itself or the oxidation number (Fig. 5; Yamamoto, 2008). The $d^0$ compounds give the highest intensity peaks and

Figure 1
XANES pre-edge peaks of different coordination environments and oxidation states.

Figure 2
Pre-edge features in the K-edge XANES spectra of selected 3$d$ transition-metal compounds with fourfold- or sixfold-coordinated metal–oxygen polyhedra. CuAl$_2$O$_4$ is 66.5% $T_d$ and 33.5% O$_h$.
the intensity decreases as the number of 3d electrons increases, reaching an intensity of zero at \( d^{10} \).

4. Bond-length dependency

The bond-length dependencies for Mn and V K-edge XANES are shown in Fig. 6 (Yamamoto, 2018). Wong and coworkers have systematically investigated the pre-edge peak features of vanadium compounds with different oxidation numbers and symmetries around the central atom. They found clear empirical ‘molecular-cage’ effects; that is, the shorter the averaged bond length, the higher the pre-edge peak intensity among compounds with the same symmetry (Wong et al., 1984). The interatomic distance of a four-coordinated tetrahedral unit is generally shorter than that of a six-coordinated octahedral unit with the same oxidation number, which is due to steric hindrance. It could also be regarded that four-coordinated species with shorter bond lengths would give rise to more intense pre-edge peaks than six-coordinated species with longer bond lengths.

The interatomic distance of polyhedral units would be shorter for compounds with a higher oxidation number because the ionic radii of atoms generally decrease with an increase in the oxidation number. Recent theoretical calculations for K-edge XANES spectra of MnO₄ units gave identical pre-edge peak intensity tendencies for interatomic
Table 1
Calculated transition probabilities for copper (Kawai, 2000).

<table>
<thead>
<tr>
<th>Transition</th>
<th>Probability</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>K–L1</td>
<td>0.00000038</td>
<td>(1s–2s)</td>
</tr>
<tr>
<td>K–L2</td>
<td>0.19</td>
<td>(1s–2p_{x,y})</td>
</tr>
<tr>
<td>K–L3</td>
<td>0.37</td>
<td>(1s–2p_{z})</td>
</tr>
<tr>
<td>K–M1</td>
<td>0.000000072</td>
<td>(1s–3s)</td>
</tr>
<tr>
<td>K–M2</td>
<td>0.022</td>
<td>(1s–3p_{x,y})</td>
</tr>
<tr>
<td>K–M3</td>
<td>0.043</td>
<td>(1s–3p_{z})</td>
</tr>
<tr>
<td>K–M4</td>
<td>0.000025</td>
<td>(1s–3d_{x^2–y^2})</td>
</tr>
<tr>
<td>K–M5</td>
<td>0.000036</td>
<td>(1s–3d_{xy})</td>
</tr>
</tbody>
</table>

Distances in the range 2.01–1.63 Å (the average oxidation number increased from ~3 to 7, in accordance with decreasing distance; Bunker, 2010). This shows that the dependence of pre-edge peak intensity on interatomic distance might also be considered to be intrinsically related to a function of the number of d electrons.

5. Assignment

The transition moment related to X-ray absorption consists of an electric dipole, an electric quadrupole and magnetic dipole transitions (where the contribution of the magnetic dipole transition is negligible; Brooder, 1990). The electric dipole transition is the main component and its value is strictly regulated by electric dipole selection rules ($\Delta l = 0, \pm 1$). An intense pre-edge peak appears in cases where inversion symmetry is broken. The transition probability between s and d orbitals would be much lower than that of s–p transitions, for example by three orders of magnitude for 3d transition elements (Cotton, 1971; Bair & Goddard, 1980), as shown in Table 1 (Kawai, 2000). This tiny, but nonzero, probability is due to an electric quadrupole transition.

If a d orbital hybridizes with a p orbital, an electric dipole transition between the s orbital and the p component in a d–p orbital would be possible. The availability can be qualitatively evaluated using character tables from group theory. An irreducible representation of the character table (Cotton, 1971) for $T_d$, $O_h$, $C_{4v}$, and $D_{4h}$ point groups is shown in Table 2. For $T_d$, $p_x$, $p_y$, $p_z$, and $d_{3x^2–y^2}$, $d_{xy}$, $d_{xz}$, $d_{yz}$ orbitals belong to $T_2$. It shows that p–d hybridization could occur among orbitals lying in a similar energy range (for example 3d–4p, 5d–6p). In contrast, there are no p and d orbitals with the same symmetry for $O_h$ and $D_{4h}$, indicating that d–p hybridization would not occur. An intense pre-edge peak observed in the K-edge XANES spectra of 3d transition-metal compounds with four-coordinated tetrahedral units can then be assigned to the electric dipole transition of a 1s electron to the p component in the 3d–4p orbital. Only tiny peaks due to the quadrupole transition to a vacant 3d orbital would be visible for compounds with regular $O_h$ and $D_{4h}$ symmetry.

The five d orbitals are split into $t_{2g}$ and $e_g$ orbitals (3:2) in the presence of an octahedral crystal field. Fig. 7(a) shows the K-edge XANES spectra of rock-salt-type metal monoxides and an inverse spinel-type binary oxide, the central atom of which has $O_h$ symmetry (Yoshida & Tanaka, 1996). As expected, weak peaks due to electric quadrupole transitions to vacant split 3d orbitals were confirmed. The peak near 1 eV is now believed to contain some electric dipole component (Modrow et al., 2003; Wu et al., 2004; de Groot et al., 2009) caused by the breakage of perfect inversion symmetry owing to neighbouring atoms, the effect of the core-hole potential and so forth. Recent progress in high energy resolution XANES spectroscopy has allowed the observation and characterization of precise pre-edge structures (van Bokhoven & Lamberti, 2015). For example, the quadrupole transitions in octahedrally coordinated 3d transition-metal compounds, such as CoO, were well reproduced by theoretical calculations with a charge-transfer multiplet program, as shown in Fig. 8(b) (de Groot et al., 2009).

6. Effects of d–p hybridization

There are few compounds with completely regular symmetry. Even if the symmetry is completely regular in the first coordination sphere of a target element, the unsymmetrical lattice
vibration (vibronic coupling) and/or the outer coordination sphere would reduce the regularity (i.e., break the inversion centre). Thus, in most cases, some extent of d–p hybridization would be expected for every compound. The degree of d–p mixing would be influenced by the pre-edge peak intensity. This was first demonstrated by Roe and coworkers in Fe K-edge XANES spectra of iron complexes and theoretical calculations (Roe et al., 1984). Fig. 8 shows the pre-edge peak intensities of iron complexes plotted as a function of the estimated p fraction in the hybridized orbital. It is obvious that the inclusion of the Fe 4p character into Fe 3d orbitals enhanced the transition momentum for the electric dipole transition. This was supported by more detailed experimental and theoretical investigations (Westre et al., 1997).

The extent of 4p mixing into the Fe 3d orbitals with different central atom symmetries was also investigated theoretically for [FeCl₆]³⁻ octahedral species as a function of the axial distortion (Westre et al., 1997). As shown in Fig. 9, the 4p component was not included in cases where one of the six Fe–Cl bonds was set around 2.5 Å, but it was mixed at shorter or longer distances. This result clearly indicated that 3d–4p mixing occurred in C₄ᵥ symmetry, the extent of which increased with distortion from O₅ᵥ symmetry (ionic radii: Fe³⁺, 0.645 Å; Cl⁻, 1.81 Å). The irreducible representation shown in Table 2 suggests that orbital mixing occurred readily because both the p and d orbitals belonged to the π₁ orbital oriented in the same direction. Theoretical calculations of a series of [FeCl₆]³⁻ units for molecular orbital analysis indicated that a 1s electron transits to an π₁ orbital via the electric dipole transition (solid arrow) and to the other d orbitals via the electric quadrupole process (dashed arrow), as shown in Fig. 9.

The selection rule for the inner-shell transitions of a 2s electron is the same as that for a 1s electron. Thus, the pre-edge features for L₁-edge XANES are also expected to be equivalent to those for the K edge. In fact, the pre-edge peak intensity for W L₁-edge XANES was confirmed to be proportional to the mixing extent of W p orbitals into the 5d orbitals (Yamazoe et al., 2008), similar to the Fe K-edge XANES shown in Fig. 8. As shown in Fig. 1, the distortion of octahedral coordination for 4d⁶ (Mo⁶⁺) and 5d⁰ (W⁶⁺) compounds results in an enhancement of pre-edge peak intensity, whereas the distortions are smaller than those with T₄ symmetry. Note that no pre-edge peaks were observed in the W K-edge (69.5 keV) XANES spectra of T₄ compounds (Yamamoto, 2008), mainly owing to the intrinsically broad natural width (K, 39.9 eV; L₁, 5.61 eV; Krause & Oliver, 1979).

7. Polarized XANES for the characterization of pre-edge features

Polarized X-ray absorption experiments, including theoretical approaches, are also useful for the precise assignment of pre-edge peaks because the electron transition moment could be nonzero in cases where the electric field vector of an incident

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**Figure 7**

**Figure 8**
Dependence of the pre-edge peak area on the total Fe 4p mixing into 3d molecular orbital iron complexes with different coordination numbers. Reprinted with permission from Roe et al. (1984). Copyright 1984 American Chemical Society.
X-ray and the direction of the target orbital are the same (Brouder, 1990; Kosugi et al., 1984). For example, the polarized Cu K-edge XANES spectra of a square-planar [CuCl$_4$]$^{2-}$ complex and the dependence of the pre-edge peak intensity on the rotation angle are shown in Fig. 10 (Hahn et al., 1982). The peak intensity varies with a 90° period against the $xy$ plane. As discussed above, no $d$–$p$ hybridization occurs in regular $D_{4h}$ symmetry. This dependence on rotation angle, the shape of the $d$ orbital, clearly shows that the component of the pre-edge peak was assigned as an electric quadrupole component to the $dz^2$ orbital. Note that the extremely ‘large’ pre-edge peak, as for electric quadrupole transition, was explained by the inclusion of electric dipole transitions due to vibronic coupling.

The assignment of the three tiny pre-edge peaks of TiO$_2$ (rutile) in the Ti K-edge XANES spectrum has been studied using both polarization experiments and theoretical calculations (Joly et al., 1999). As shown in Fig. 11, weak electric quadrupole contributions were confirmed at $A_1$ in both $\varepsilon \parallel z$ and $\varepsilon \perp z$ spectra and at $A_2$ peaks in $\varepsilon \parallel z$. The band calculation revealed that the Ti $2p_z$ orbital occupied the same energy as the $A_2$ and $A_3$ peaks but was absent in the $A_1$ peak. Thus, the $A_1$ and $A_3$ peaks were assigned to pure electric quadrupolar $t_{2g}$ and electric dipole transitions, respectively. The $A_2$ peak consisted of a mixture of the quadrupolar $e_g$ and dipole transitions.

Polarization experiments could clarify the origin of pre-edge peaks associated with a specific bonding structure in some cases. Fig. 12(a) shows the pre-edge region of a polarized V K-edge XANES of a V$_2$O$_5$ single crystal and the components obtained by theoretical calculations (Šipr et al., 1999). An intense peak was experimentally observed along the $z$ axis, the intensity of which was much larger than those for the other directions (by two orders of magnitude). A theoretical calculation indicated that weak electric quadrupole transitions to the $d$ orbitals occurred in all directions of the V$_2$O$_5$ crystal structure, whereas an intense electric dipole transition appeared for the $p_z$ orbital along the $z$ direction only. Theoretical spectra for the model structure indicated that an intense peak could be reproduced only in the case where short
V—O bonds existed along the $z$ axis. In this model, the VO$_x$ units ($x = 1–5$) utilized were obtained by removing some of the O atoms from a model VO$_6$ unit and/or were modified by changing the location of the selected atoms. The main component of the intense pre-edge peak for V$_2$O$_5$ was assigned to an electric dipole transition corresponding to one V=O vanadyl group. Applying this property to characterize the catalyst material [vanadium oxide supported on the surface of a ZrO$_2$(100) single crystal] using the polarized total-reflection fluorescence XAFS technique, the V=O bonds were suggested to be tilted by about 45° from the surface normal (Shirai et al., 1994).

References