A new analysis of X-ray adsorption branching ratios: Use of Russell–Saunders coupling

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A R T I C L E  I N F O

Article history:
Received 8 October 2007
In final form 26 February 2008
Available online 2 March 2008

A B S T R A C T

The intensities of X-ray absorption peaks at core-level edges are considered in terms of Russell–Saunders multiplets. The contributions of different multiplets to the relativistic wavefunctions of the excited states are determined and the absorption intensity related to the contributions of the dipole allowed multiplets. This is a powerful method because the selection rules for multiplets are stronger than for relativistic J levels. It is also shown that differences in the radial extent of the spin–orbit split core spinors modify the intensity given by these symmetry arguments. Applications are considered for cases involving different degrees of Russell–Saunders or j–j coupling.

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The X-ray absorption near edge structure, XANES, of transition metal, TM, rare-earth, and actinide materials, typically have intense white lines at various absorption edges [1–6]. For a sufficiently large spin–orbit splitting, a doublet is observed corresponding to excitations from the 2p1/2 sub-shell into the 3d shell and a second peak, at higher photon energy, corresponding to excitation from the 2p3/2 sub-shell into the 3d shell [2]. For actinides, the NIX/V white line will be a doublet representing 4d5/2 and 4d3/2 corresponding to excitations from the partly filled 5f shell. Of course, each of these spin–orbit split core sub-shells. Thus, for example, the l2S1/2 edge for transition metals will contain a peak, at lower photon energy, described as excitation from the 2p3/2 sub-shell into the 3d shell and a second peak, at higher photon energy, corresponding to excitation from the 2p1/2 sub-shell into the 3d shell [2]. For actinides, the NIX/V white line will be a doublet representing 4d5/2 and 4d3/2 excitations to the partly filled 5f shell. Of course, each of these spin–orbit split peaks may contain additional structure, often unresolved, of individual levels resulting from the intra-shell and inter-shell angular momentum coupling of the core and valence level open shells [4,6–10]. It is tempting to assign the relative intensities of the 1 + 1/2 and 1 – 1/2 peaks, or the branching ratios, to the statistical weights of the core levels [3]. For a transition metal l2S1/2 edge, the relative intensities would be 2/3 and 1/3: for actinide NIX/V and OIX/V edges, they would be 3/5 and 2/5. However, it is well known that the angular momentum coupling strongly affects the branching ratios and the statistical values are appropriate only in special cases [9–11].

In the previous work of Thole and van der Laan [9], sum rules have been obtained that, for certain cases, allow the deviations of the branching ratios from the statistical values to be related to the spin–orbit splittings within the valence level. These sum rules have been derived using Clebsch–Gordon algebra and have not included the differences in the radial character of core orbitals for the j = 1 – 1/2 and j = 1 + 1/2 sub-shells [12]. They are based on atomic models used to describe condensed phase materials and they are applied for a range of occupations of the open valence level shell. In the present work, we also use atomic models. However, our objective is to relate transitions between Russell–Saunders, RS, multiplets [13], to transitions between the relativistic J levels that take account of spin–orbit coupling as well as of scalar relativistic effects. This approach offers physical insight into how different angular momentum couplings can affect the branching ratios since transitions between RS multiplets are easily understood from the dipole selection rules appropriate for XANES [14]. We base our work on four-component relativistic wavefunctions [15,16], WFs, that use spinors optimized separately for both the initial and the excited final states. These WFs use configuration interaction, CI, to describe the angular momentum coupling within and between the core and valence open shells and, thus, are able to properly treat the full range of intermediate coupling from RS $2^{3/2}$L multiplets to pure j–j coupling [15].

Three cases are considered. The first is for the 2p or l2S1/2 edge of V5+, where as expected [4], the states are not pure p1/2 or pure p3/2 holes, denoted p1/2 -1 and p3/2 -1 respectively, but may involve significant mixing arising from the 2p–3d multiplet splitting. Here, we are also able to compare our predictions for the V5+ cation with our XANES measurements on V2O5 where the nominal V oxidation state is V5+. The second is for the 4d or NIV/V edge of U6+, where as expected from the large 4d spin–orbit splitting of ~40 eV, the excited states are nearly either pure d5/2 -1 or d3/2 -1 configurations. The third case is for the 5d or OIX/V edge of U6+ where we show that...
RS coupling dominates the character of the excited states and that this leads to an XANES 5d edge dominated by a single peak rather than by a doublet as for the other cases.

We have computed WF's for the initial and the core excited, final states with spinors optimized with Dirac–Fock calculations for the ground and excited configurations, respectively [15]. For the excited states, these optimized orbitals were used for a CI calculation with the core–hole distributed in all possible ways over the spinors of the core level and the electron placed in all possible ways over the spinors of the initially empty valence level. The dipole transition probabilities were computed rigorously between the initial and final state relativistic WF's taking full account of the non-orthogonality between the spinors of the initial and final states using a cofactor method [17,18]; see Ref. [8] for more details. The WF calculations were performed with the DIRAC program system [16]. For the wavefunctions of the non-relativistic RS multiplets, we used an artificially large speed of light raised to 10000 a.u. from its correct value of 137 a.u. We confirmed that this gave results equivalent to using a two component formalism where the spin–orbit coupling is not included in the Hamiltonian [15]. We then project the RS multiplets that could couple to \( J = 1 \) on the relativistic WF's in order to determine the extent of the RS composition of the dipole allowed, \( J = 1 \), core-excited levels. Here again, we took full account of the non-orthogonality between the relativistic spinors and the non-relativistic orbitals [8]. Since the only dipole allowed RS multiplet is \( ^1P_1 \), the projection of this multiplet on each of the \( J = 1 \) levels should be a good guide to the relative intensity, \( I_{rel} \), of the XANES excitation. For each edge, we also tabulated several properties which indicate the electronic character of the excited state.

In addition, we report \( \mu_{\text{rel}} \) XANES spectra for single crystal \( V_2\text{O}_5 \) recorded with light from the UE56 monochromator of the BESSY II synchrotron radiation facility in Berlin. The \( V_2\text{O}_5 \) crystals were obtained from the Paul–Drude Institut in Berlin where they were grown by zone melting [19]. They were fixed onto the sample holder of an UHV apparatus using electrically conductive silver glue. High quality (001) surfaces were obtained via in vacuo cleavage of the crystals using a sharp blade. This procedure is usually successful since \( V_2\text{O}_5 \) cleaves easily along the (001) plane. Since photon irradiation induces degradation of \( V_2\text{O}_5 \) (001) a new surface was prepared from time to time. The data presented were measured in the total electron yield mode where the photocurrent emitted by the sample is measured with an electrometer as a function of the photon energy. Our use of total electron yield emphasizes the bulk XANES contribution over that from the \( V_2\text{O}_5 \) surface; more surface sensitive measurements can be made using partial electron yield [14]. However, even with partial electron yield, the contribution of the bulk to the XANES signal is still quite large; see, for example, Ref. [20].

For the L-edge of \( \text{V}^{5+} \), the initial state is a closed shell, \( J = 0 \) and \( ^3\text{S}_0 \) configuration and the dipole allowed, \( J = 1 \), excited states have the configuration \( 2p^3d^1 \). This configuration couples to six RS multiplets, \( ^2\text{F}(J = 4, 3, 2), ^2\text{D}(J = 3, 2, 1), ^2\text{P}(J = 2), ^2\text{P}(J = 2, 1, 0), \) and \(^1\text{P}(J = 1)\), where the possible \( J \) values are indicated in parenthesis after the \( ^{25}\text{S}_{1/2} \) multiplet notation. For \( J \) levels, the dipole selection rules are \( \Delta J = (J_{\text{initial}}) - (J_{\text{final}}) = 0, \pm 1 \), where if \( J_{\text{initial}} = 0 \) then \( J_{\text{final}} \) must be one. The selection rules are stronger for RS multiplets because spin must be conserved so that \( \Delta S = 0 \) and \( \Delta L = 0, \pm 1 \). Thus, the only allowed final multiplet is \( ^1\text{P}_1 \); however, this multiplet can mix into any of the three \( J \) levels. In terms of \( j-j \) coupling, the three configurations that can couple to \( J = 1 \) are: \( 2p_{1/2}^{-1}3d_{3/2}, 2p_{3/2}^{-1}3d_{3/2}, \) and \( 2p_{3/2}^{-1}3d_{5/2} \). The three relativistic \( J = 1 \) CI WF's are combinations of these \( j-j \) configurations. The \( E_{rel} \), dipole \( I_{rel} \), and the weights of the three \( j-j \) configurations are given in Table 1; the lowest \( J = 1 \) level is set to \( I_{rel} = 0 \) and the intensity of the second level is set to \( I_{rel} = 1 \); this normalization of \( I_{rel} \) is arbitrary. The first level has very little intensity, while the third is the most intense being roughly 2.5 times more intense than the second level. None of the levels is strongly dominated by a single \( j-j \) configuration although the highest level is 85% a \( 2p_{1/2} \) hole; clearly the excited states are not at the limit of \( j-j \) coupling. However, there is no basis for relating the weights of any of the \( j-j \) configurations to the \( I_{rel} \).

In order to establish this relationship, we also give in Table 1 the projections of the Russell–Saunders multiplets, coupled to \( J = 1 \), on the relativistic CI WF's. These projections are normalized so that for a given \( J = 1 \) CI WF, the projections of \(^1\text{P}_1\), \(^3\text{P}_1\), and \(^3\text{D}_3\), sum to 1; i.e., they represent 100% of the relativistic WF. An independent check of the correctness of our projection is that, with this normalization, the sum of the projections of a single RS multiplet over the three \( J = 1 \) CI WF's, a sum over one of the ‘Multiplet Character’ columns in Table 1, is also one. Furthermore, the projection of these RS multiplets on the relativistic WF’s with \( J = 1 \) is zero. For the dipole allowed \(^1\text{P}_1\) multiplet, we also normalize the contributions of this multiplet to the different \( J = 1 \) levels to one for the second level; these values are given in parenthesis and permit a direct comparison with the \( I_{rel} \). If the radial parts of the spinors for the different \( J \) values were identical, as assumed in Ref. [9] for the derivation of sum rules for branching ratios, then the relative contribution of the \(^1\text{P}_1\) multiplet should be the same as the \( I_{rel} \). We can see from Table 1 that this is nearly true for \( V \); however, as we discuss below for the XANES of \( U \), the approximation that the \( J = 1 \) \( \pm 1 \) and \( J = 1 \) \( \pm 1/2 \) spinors have the same radial character is less good for heavier atoms. While the lowest \( J = 1 \) level in the L-edge of \( \text{V}^{5+} \), which receives almost no XANES intensity, is dominated by the \(^1\text{P}_1\) multiplet, the two higher levels have significant mixing of \(^3\text{D}\) and \(^1\text{P}\) character. It is clear from the projections of the RS multiplets that WF's for the \( 2p \rightarrow 3d \) excited states of \( \text{V}^{5+} \) do not follow RS coupling with spin–orbit splitting of the \( ^{25}\text{S}_{1/2} \) multiplets [13,21].

In Fig. 1, we present the XANES absorption intensities for light incident at 70° to the surface normal near the V L edge for \( V_2\text{O}_5 \). The XANES spectra taken with light incident at 0° are somewhat different from those shown in Fig. 1; however, until we take the –O bonding and other ligand field effects into account, we cannot interpret these differences. These XANES studies are part of a broader effort [22] to identify the electronic structure of \( V_2\text{O}_5 \).

### Table 1

<table>
<thead>
<tr>
<th>Level</th>
<th>( E_{rel} ) (eV)</th>
<th>( I_{rel} )</th>
<th>Weight of ( j-j ) configurations</th>
<th>Multiplet character</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 2p_{1/2}^{-1}3d_{3/2} )</td>
<td>( 2p_{3/2}^{-1}3d_{3/2} )</td>
<td>( 2p_{3/2}^{-1}3d_{5/2} )</td>
<td>( ^1\text{P}_1 )</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.02</td>
<td>0.02</td>
<td>0.74</td>
</tr>
<tr>
<td>2</td>
<td>4.8</td>
<td>1</td>
<td>0.13</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>11.9</td>
<td>2.44</td>
<td>0.85</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The relative energy, \( E_{rel} \) in eV, is set to zero for the first \( J = 1 \) level and the relative intensity, \( I_{rel} \), is arbitrarily normalized to one for the second level. The weights of the \( j-j \) coupled \( J = 1 \) configurations and the projections, in %, of the Russell–Saunders multiplets on the relativistic CI WF’s are also given; the \(^1\text{P}_1\) multiplet projections normalized to one for the second level are given in parenthesis.

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Figure 1. XANES spectra of V$_2$O$_5$(001) for the L$_{II}$ edge of V, left hand area, and for the O 1s excitations, right hand area; the assignments are shown. The data were recorded in the total electron yield mode (see text) for a light incidence angle of $\theta = 70^\circ$ with respect to the surface normal. The shifted energy scale shown at the top was obtained by setting the energy of the first intense V 2p feature to 4.8 eV which is the energy obtained by theory for level 2; the second vertical line is at 11.9 eV in the shifted energy scale, the position obtained by theory for Level 3 (see text and Table 1).

higher energy have their origin in O 1s excitations [22]. Clearly, the theoretical spectra in Table 1 do not reproduce the details of the XANES spectra of V$_2$O$_5$(001) for the L$_{II}$,III, edge of V, left hand area, and for the O 1s excitations, right hand area; the assignments are shown. The data were recorded in the total electron yield mode (see text) for a light incidence angle of $\theta = 70^\circ$ with respect to the surface normal. The shifted energy scale shown at the top was obtained by setting the energy of the first intense V 2p feature to 4.8 eV which is the energy obtained by theory for level 2; the second vertical line is at 11.9 eV in the shifted energy scale, the position obtained by theory for Level 3 (see text and Table 1).
Finally, we turn to the O\textsubscript{IV,V} edge of U\textsuperscript{VI} where the excited configuration is 5d\textsuperscript{5}f\textsuperscript{1}. This analysis very closely parallels that for the N\textsubscript{IV,V} edge although the results, presented in Table 3, are quite different. In Table 3, the format is slightly changed and I\textsubscript{rel} for the O-edge of U is normalized to one for the intense transition to the third excited J = 1 level at E\textsubscript{rel} = 31 eV rather than to the second J level as in Table 2; the normalized \(^{1}\text{P}\) projections are also scaled to one for the third level. The only transition that carries significant intensity is to the third level and a single intense feature with a weak satellite, at lower excitation energy, from the second level should be observed, in strong contrast to the doublet predicted for the N-edge. The mixing of the j–j configurations is even greater for the O-edge excitation of U\textsuperscript{VI} than for the L-edge excitation of V\textsuperscript{V\textsuperscript{5}}; this is hardly surprising since the 5d spin–orbit splitting is small compared to the splitting of the Russell–Saunders multiplets. We estimate j = 3/2 spin–orbit splitting of 8.7 eV from the Dirac–Fock eigenvalues of the 5d\textsuperscript{3/2} and 5d\textsuperscript{5/2} spinors for the ground state of U\textsuperscript{VI}. We estimate the multiplet splitting from the energy spread in our non-relativistic calculations on the 5d\textsuperscript{5}f\textsuperscript{1} configuration where the lowest energy multiplet is \(^{1}\text{P}\) and the highest energy multiplet is \(^{1}\text{D}\); the \(^{1}\text{P}–^{1}\text{D}\) energy separation of 30.2 eV is taken as the multiplet splitting. Thus, while the multiplet splitting should be more important than the 5d spin–orbit splitting, the levels may be significantly perturbed from pure RS multiplets. We can see for this the two levels where the dominant RS multiplet is only 85% of the total WF. The XANES spectra for the O\textsubscript{IV,V} edge of UO\textsubscript{3}, with a nominal oxidation state of U(VI), have been measured \cite{25} and show a strong main peak with a very weak satellite at lower energy; this is fully consistent with our theoretical analysis.

We have shown that examining the contribution of dipole allowed X-ray adsorption multiplets to the relativistic atomic WFs for j levels of a closed shell initial state provides insight into the origin of the energies and intensities of XANES excitations. We stress that we have neglected the changes caused by the environment in condensed phases, especially ligand field effects in oxides and other ionic crystals. Because we have used atomic models, we cannot explain the fine details of the XANES edges, including energy splittings and intensity changes that arise from condensed phase effects. However, our analysis in terms of RS multiplets has made it possible to have a qualitative understanding of the number and relative intensities of the main peaks that are observed at a particular XANES edge. Furthermore, we have shown that neglect of the difference of radial matrix elements for spin–orbit split levels, as in sum rules \cite{4} and projections introduces a modest uncertainty in the branching ratio that could become larger for heavier actinides and for the edges of deeper core levels.

We have examined three cases: (1) the N\textsubscript{IV,V}-edge of U\textsuperscript{VI} with 4d \textright 5f, where j–j coupling dominates, especially for the core level; (2) the O\textsubscript{IV,V}-edge of U\textsuperscript{VI} with 5d \textright 5f where Russell–Saunders coupling dominates; and, (3) the L\textsubscript{II,III}-edge of V\textsuperscript{V\textsuperscript{5}} with 2p \textright 3d where the coupling is strongly mixed. While we have considered the case of a closed shell initial state where only a single RS excited state multiplet is dipole allowed, our logic of decomposing initial and excited state relativistic WFs into the contributions from various multiplets can be applied to more complex cases.

This research was supported, in part, by the Geosciences Research Program, Office of Basic Energy Sciences, US Department of Energy (DOE). A portion of the research was performed at the W.R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the US DOE. We acknowledge partial computer support from the National Center for Supercomputing Applications, Urbana-Champaign, Illinois.

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