Probing Chemical Bonding in Uranium Dioxide by Means of High-Resolution X-ray Absorption Spectroscopy

Permalink
https://escholarship.org/uc/item/1nz4v051

Journal
JOURNAL OF PHYSICAL CHEMISTRY C, 120(51)

ISSN
1932-7447

Authors
Butorin, Sergei M
Modin, Anders
Vegelius, Johan R
et al.

Publication Date
2016-12-29

DOI
10.1021/acs.jpcc.6b09335

License
https://creativecommons.org/licenses/by-nc-nd/4.0/ 4.0

Peer reviewed
Probing Chemical Bonding in Uranium Dioxide by Means of High-Resolution X-ray Absorption Spectroscopy

Sergei M. Butorin,∗†, Anders Modin,‡ Johan R. Vegelius,‡ Kristina O. Kvashnina,¶∥ and David K. Shuh§

†Molecular and Condensed Matter Physics, Department of Physics and Astronomy, Uppsala University, P. O. Box 516, SE-751 20 Uppsala, Sweden
‡Department of Physics and Astronomy, Uppsala University, P. O. Box 516, SE-751 20 Uppsala, Sweden
¶The European Synchrotron, CS40220, 38043 Grenoble Cedex 9, France
§Chemical Sciences Division, Lawrence Berkeley National Laboratory, MS 70A1150, One Cyclotron Road, Berkeley, CA 94720, USA
∥Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, P.O. Box 510119, 01314, Dresden, Germany

E-mail: sergei.butorin@physics.uu.se

Abstract

A systematic x-ray absorption study at the U 3d, 4d and 4f edges of UO₂ was performed and the data were analyzed within framework of the Anderson impurity model. By applying the high-energy-resolution fluorescence-detection (HERFD) mode of x-ray absorption spectroscopy (XAS) at the U 3d_{3/2} edge and conducting the XAS measurements at the shallower U 4f levels, fine details of the XAS spectra were resolved resulting from reduced core-hole lifetime broadening. This multi-edge study enabled a far more effective analysis of the electronic structure at the U sites and characterization of the chemical bonding and degree of the 5f localization in UO₂. The results support the covalent character of UO₂ and do not agree with the suggestions of rather ionic bonding in this compound as expressed in some publications.

Introduction

While it has been agreed that UO₂ is a Mott-Hubbard system,¹ where the energy gap has f − f character, the degree of localization/delocalization of the U 5f states in UO₂ is still under debate. The conclusions about the character of chemical bonding in UO₂ made by different research groups vary from ionic² to highly covalent³ compound. The important characteristic in this respect is the U 5f occupancy (n_f) in the ground state of UO₂ that is often estimated from the electronic structure calculations or x-ray spectroscopic measurements. For example, n_f was deduced to be close to 2.0 electrons from the analysis of the resonant x-ray emission spectra² at the U L₃ edge of UO₂ while the analysis of the x-ray photoemission spectroscopy (XPS) data⁴⁻⁶ suggested n_f ≃ 2.3 electrons. The latter results indicate some degree of covalency in the chemical bonding of this dioxide.

The employment of the advanced theoretical/computational formalisms, based on lo-
cal density approximation with added 5f – 5f Coulomb interaction (LDA+U), self-interaction corrected (SIC)-LDA, dynamical meanfield theory, and hybrid density functional of Heyd, Scuseria, and Enzerhof (HSE) to describe both the ground state and spectroscopic data of UO2 did not lead to consensus with respect to the character of chemical bonding in general and the value of \( n_f \) in particular. The U 5f occupancy was calculated to be both as low as 2.0 electrons and as high as 2.5 electrons. The uncertainty calls for further studies to resolve this situation, preferably with advanced experimental methods.

An advanced technique, high-energy-resolution fluorescence-detection (HERFD) mode of x-ray absorption spectroscopy (XAS), has been recently applied for measurements at the 3d \((M_4)\) edge of actinide compounds. This has allowed for a significant improvement in experimental resolution and revealed additional structures in the XAS spectra, previously not measurable. The analysis of the newly resolved structures has enabled more accurate characterization of the chemical bonding in actinide compounds. Another way to improve the experimental resolution has been demonstrated by conducting XAS measurements at the actinide 4f \((N_{6,7})\) edge. This approach probes the unoccupied 6d states of actinides, similar to the measurements at the actinide 2p\(_{3/2}\) \((L_3)\) edge, but the 4f core-hole lifetime broadening is significantly smaller, thus allowing resolution of additional spectral structures.

In this paper, we performed a systematic study of the XAS data at multiple uranium core level thresholds in UO2 and estimated the degree of covalency \((n_f)\) in the chemical bonding in this system.

### Experimental methods

The details of the measurement of the U \( M_4 \) (3d\(_{3/2}\) → 5f, 7p transitions) HERFD-XAS spectra and the UO2- and UO2(NO\(_3\))\(_2\)-6H\(_2\)O-sample preparation and characterization are described in Refs.\(^{8,12}\) The total electron yield (TEY) spectra at U 3d edges were measured under conditions described in Refs.\(^{20,21}\)

Experiments in the energy range of the U \( N_{4,5} \) (4d → 5f, 7p transitions) and \( N_{6,7} \) (4f → 6d, 5g transitions) edges of UO2 were performed at beamline 7.0.1 of the Advanced Light Source of Lawrence Berkeley National Laboratory, employing a spherical grating monochromator. \(^{22}\) U 4d and 4f XAS data were measured in the TEY mode using drain current on the sample. The incidence angle of the incoming photons was close to 90° to the surface of the samples. The monochromator resolution was set to ~150 meV at 385 eV and to ~400 meV at 740 eV during measurements at the U 4f and 4d edges, respectively. In this case, the UO2 sample was powder acquired from Alfa-Aesar which was pressed in the indium substrate.

### Computational details

For calculations, the Anderson impurity model (AIM) was used which included the 5f and core d states (3d or 4d) on a single actinide ion and a filled ligand 2p band. The total Hamiltonian of a system can be written as

\[
H = H_{\text{AIM}} + H_{\text{FI}} + H_{\text{CF}},
\]

where \( H_{\text{AIM}} \) is the AIM Hamiltonian without the multiplet-coupling effects, \( H_{\text{FI}} \) represents the Coulomb, exchange and spin-orbit interactions for free actinide ion and \( H_{\text{CF}} \) describes the crystal-field splittings.

\[
H_{\text{AIM}} = \sum_{\gamma} \epsilon_f \sum_{\mu} d_{\mu}^{\dagger} d_{\mu} + \sum_{n,\gamma} \epsilon_n p_{n\gamma}^{\dagger} p_{n\gamma} + U_{ff} \sum_{\gamma,\gamma'} f_{\gamma}^{\dagger} f_{\gamma} f_{\gamma'}^{\dagger} f_{\gamma'} - U_{fe} \sum_{\gamma,\mu} f_{\gamma}^{\dagger} f_{\gamma} d_{\mu}^{\dagger} d_{\mu} + V \sum_{n,\gamma} (p_{n\gamma}^{\dagger} f_{\gamma} + f_{\gamma}^{\dagger} p_{n\gamma}),
\]

where \( \epsilon_f, \epsilon_d, \) and \( \epsilon_n \) are one-electron energies of actinide 5f, core d (3d or 4d) and ligand 2p levels, respectively, and \( f_{\gamma}^{\dagger}, d_{\mu}^{\dagger}, p_{n\gamma}^{\dagger} \) are electron creation operators at these levels with combined
indexes $\gamma$ ($\mu$) to represent the spin and orbital states of the 5f (3d or 4d) electrons, the index $n$ runs over a number of discrete levels representing the ligand 2p band. $U_{ff}$ denotes the 5f-5f Coulomb interaction, $U_{fc}$ is the (3d or 4d) core hole potential acting on the 5f electron and $V$ is the actinide 5f–ligand 2p hybridization term.

\[
H_{FI} = \sum_{\gamma_1, \gamma_2, \gamma_3, \gamma_4} R_{ff}(\gamma_1, \gamma_2, \gamma_3, \gamma_4) f_{\gamma_1}^\dagger f_{\gamma_2} f_{\gamma_3} f_{\gamma_4} \\
+ \sum_{\gamma_1, \gamma_2, \mu_1, \mu_2} R_{fd}(\gamma_1, \mu_1, \mu_2, \gamma_2) f_{\gamma_1}^\dagger d_{\mu_1} d_{\mu_2} f_{\gamma_2} \\
+ \zeta_f \sum_{\gamma_1, \gamma_2} \langle \gamma_1 | \mathbf{l} \cdot \mathbf{s} | \gamma_2 \rangle f_{\gamma_1}^\dagger f_{\gamma_2} \\
+ \zeta_d \sum_{\mu_1, \mu_2} \langle \mu_1 | \mathbf{l} \cdot \mathbf{s} | \mu_2 \rangle d_{\mu_1}^\dagger d_{\mu_2},
\]

where the interactions between 5f electrons ($R_{ff}$) and a 5f electron and a core 3d or 4d hole ($R_{fd}$) are described in terms of Slater integrals (Ref. 24 see also Ref. 25) and spin-orbit interactions for the 5f and core d states are described with coupling constants $\zeta_f$ and $\zeta_d$ and matrix elements of the spin-orbit interaction $\mathbf{l} \cdot \mathbf{s}$ operator in the 5f and core d states.

\[
H_{CF} = \sum_{\gamma, \gamma'} Q_{\gamma \gamma'}^{CF} f_{\gamma}^\dagger f_{\gamma'},
\]

where $Q_{\gamma \gamma'}^{CF}$ is the potential provided by the crystal environment around the actinide ion which can be expanded in terms of tensor operators $C_q^k$ as

\[
Q_{\gamma \gamma'}^{CF} = \sum_{k, q} B_q^k C_q^k.
\]

where $B_q^k$ are crystal-field parameters introduced by Wybourne. The $C_q^k$ are related to the spherical harmonics as

\[
C_q^k = \sqrt{\frac{4\pi}{2k+1}} Y_q^k.
\]

For $f$ electrons, the terms in the expansion with $k \leq 6$ are nonzero. For cubic site-symmetry as in UO$_2$, only two crystal field parameters (one of rank 4 and one of rank 6) are independent. The crystal field potential can be rewritten as

\[
Q_{\gamma \gamma'}^{CF} = B_0^4[C_0^4 + \sqrt{\frac{5}{14}} (C_4^4 + C_{-4}^4)] \\
+ B_0^6[C_0^6 - \sqrt{\frac{7}{2}} (C_4^6 + C_{-4}^6)].
\]

The XAS spectra were calculated using the following equation

\[
I(\omega) = \sum_{m} |\langle m | D_1 | g \rangle|^2 \frac{\Gamma_m/\pi}{(E_m - E_g - \omega)^2 + \Gamma_m^2}(\omega)\]

where $|g\rangle$ and $|m\rangle$ are the ground and XAS final states of the spectroscopic process with energies $E_g$ and $E_m$, respectively. $D$ is the operator for the optical dipole transition with the incident photon energy represented by $\omega$ and lifetime broadening $\Gamma_m$ of the final state in terms of half-width at half-maximum (HWHM).

The required Slater integrals, spin-orbit coupling constants $\zeta$ and matrix elements were obtained with the TT-MULTIPLETS package which combines Cowan’s atomic multiplet program (based on the Hartree-Fock method with relativistic corrections) and Butler’s point-group program, which were modified by Thole, as well as the charge-transfer program written by Thole and Ogasawara.

Note that in the calculations described in this section it is difficult to reproduce accurately the absolute energies (the difference with experiment is usually on the order of a few eV) so that the calculated spectra need to be uniformly shifted on the photon energy scale for comparison with experimental data. Since no significant differences in the core-hole lifetime for final states of different symmetries throughout actinide 3d, 4d and 4f edges are expected in contrast to the actinide 5d edges, a constant core-hole lifetime broadening was applied to all transitions across the entire energy range of the calculated spectrum.
Intensity (a. u.)

width at half-maximum, FWHM) is estimated to be $\sim 0.8$ eV\textsuperscript{19} versus $\sim 3.2$ eV for the 3d core hole.

In principle, there is some difference between the $3d^95f^{n+1}$ and $4f^{13}5f^{n+1}$ multiplets in terms of the number of states and interactions between the electrons, however, the constant energy detection of emitted photons puts an additional restriction on transitions contributing to the spectra. Although, one might expect deviations in the shape of the HERFD spectra from the x-ray absorption cross-sections, it has already been shown by calculations\textsuperscript{34,35} for the $2p-4f$ quadrupole transitions in Dy\textsubscript{2}O\textsubscript{3} that the difference between the HERFD-XAS and conventional XAS (with reduced broadening) spectra is not significant when only the emitted photons with an energy of the maximum of the corresponding $2p-3d$ x-ray emission line are counted. No significant difference has been found between HERFD-XAS and conventional XAS (with reduced broadening) at the U $M_4$ edge of the U(V) systems.\textsuperscript{15} In any case, the expected differences between the $3d^95f^{n+1}$ and $4f^{13}5f^{n+1}$ multiplets are small compared to the resolution achieved by the HERFD-XAS technique in our measurements.

In Fig. 2, the U $M_4$ HERFD-XAS spectrum of UO\textsubscript{2} is compared with results of the atomic- and crystal-field multiplet and AIM calculations for the U(IV) system. Within the atomic- and crystal-field multiplet theory, the spectra were calculated for transitions between $5f^2$ and $3d^95f^3$ configurations. It is interesting in the atomic-multiplet approach for the $^3H_4$ ground state that the calculations already produce all of the structures observed in the experimental spectrum, even a small structure at $\sim 3733$ eV. While the electrostatic $F^k(5f,5f)$ and $F^k(3d,5f)$ Slater integrals were scaled down to 80% of their Hartree-Fock values in these calculations, the exchange $G^k(3d,5f)$ integrals were reduced to 50% to lessen the intensity of the shoulder at around 3726.8 eV with respect to the main peak to provide better agreement with the experiment (see a comparison with the spectrum [blue dashed curve] calculated for the “standard” $G^k$ reduction to 80% in Fig. 2). Such a significant reduction indicates weaker influence of the core hole, probably orig-

Figure 1: XAS spectra at the U $M_4$ edge of UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O measured in the TEY (blue line) and HERFD (red line) modes.

Results and discussion

3d edge

An example of the improvement of the experimental resolution, Fig. 1 displays the U $M_4$ XAS spectra of UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O recorded in the TEY\textsuperscript{20} and HERFD modes. The self-absorption/saturation effects are minimized in the TEY mode and therefore the TEY spectrum closely reflects the "true" absorption cross-section. This spectrum is similar to the XAS data published in Refs.\textsuperscript{32,33} which were also measured in the TEY or direct transmission modes. The HERFD spectrum recorded by detecting the photons with an energy corresponding to the maximum of the U $M\beta$ x-ray emission line shows much narrower lines as compared to the TEY spectrum and reveals additional structures. Besides the main line, there are three structures at $\sim 3728.9$ eV, $\sim 3732.6$ eV and $\sim 3738.3$ eV clearly resolved in contrast to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra. Although, one might expect deviations in the shape of the HERFD spectra to the spectra.
In the limit of $V \rightarrow 0$, the difference between the configuration averaged energies for the ground state can be written as $E(5f^3\upsilon^1) - E(5f^2) = \Delta$ (where $\Delta \equiv \epsilon_f - \epsilon_n$, with $\epsilon_n$ corresponding to the center of the O 2$p$ band) which is the so-called charge-transfer energy. For the final state, this difference is $E(3d^95f^4\upsilon^1) - E(3d^85f^3) = \Delta + U_{ff} - U_{fc}$. The spectra displayed in Fig. 2 were calculated with the following model parameter values: $B_0 = -0.93$ eV and $B_6 = 0.35$ eV, $\Delta = 6.0$ eV, $U_{ff} = 4.5$ eV, $U_{fc} = 6.0$ eV, $V_0 = 1.2$ eV and $V_m = 1.0$ eV. The strength of the Coulomb interaction between 5$f$ electrons in UO$_2$ has been studied and discussed in many publications and the value of $U_{ff}$ applied here corresponds well to the previously discussed values. Furthermore, the same values of $U_{ff}$ and $\Delta$ and a similar value of hybridization term $V$ were used to calculate the U 4$f$ XPS spectrum of UO$_2$. Taking into account the U 5$f$–O 2$p$ hybridization results in an appearance of some spectral weight/intensity at energies higher than 3734 eV. The intensity of this charge-transfer satellite is fairly weak because of a relatively large $\Delta$, nevertheless it may explain the extended tail observed in the experimental spectrum at corresponding energies.

Our calculations show that the $5f^3\upsilon^1$ contribution in the ground state amounts to 24%, thus resulting in a U 5$f$ occupancy of 2.24 electrons. This result agrees with estimations of the U 5$f$ occupancy in the ground state of UO$_2$ made in a number of publications where x-ray spectroscopic data were calculated. The calculations of the U 4$f$ XPS spectrum using AIM$^6$ employing similar values for model parameters resulted in the U 5$f$ occupancy value of 2.26 electrons and using the ab-initio embedded-UO$_2$-cluster approach$^{38}$ yielded 2.35 electrons. The hybrid density functional the-
ory method\textsuperscript{11} employed for a description of the valence-band photoemission data produced 2.36 electrons. Only the local-density approximation combined with the dynamical mean-field theory (LDA+DMFT) method\textsuperscript{3} used to calculate both core $U_{4f}$ and valence-band photoemission spectra of $UO_2$ yielded $U_{5f}$ occupancy of 2.5 electrons in the ground state. The latter value of $n_f$ seems somewhat large for a Mott-Hubbard system with relatively large $\Delta$, especially in comparison with highly-covalent $CeO_2$ where $Ce$ is determined to gain about 0.5 $4f$-electrons from the strong $Ce$ $4f-O$ $2p$ hybridization and charge transfer. Furthermore, in these LDA+DMFT calculations, $U_{ff}$ was set to be larger than $U_{fc}$ which is usually the other way around for the case of core-level photoemission spectroscopy.

The crystal-field parameter values $B^d_0 = -0.93$ eV and $B^d_0 = 0.35$ eV are in good agreement with those derived from the INS experiment,\textsuperscript{39} but differ significantly from the $B^d_0$ value given in Ref.\textsuperscript{40} However, the value from Ref.\textsuperscript{40} seems to be overestimated because the calculated energy separation of the lowest excited states of the $5f^2$ multiplet from the ground state is somewhat too large when compared with experiment\textsuperscript{39} and LDA+DMFT calculations.\textsuperscript{3} Table 1 compares the lowest excited states of the $U_{5f}$ multiplet obtained from our AIM calculations for a cubic crystal-field environment with those detected by INS under conditions above the ordering temperature. The agreement between theory and experiment is fairly good. The inclusion of the $U_{5f-O}$ $2p$ hybridization in the calculations was an important factor for obtaining such agreement.

$4d$ edges

Utilizing the shallow electron core levels of actinides, one might expect an improvement in resolution for x-ray absorption spectra resulting from a reduced core-hole lifetime broadening but unfortunately it is not the case for the $4d$ edges of actinides. It has been determined to be even larger ($\sim 4.2$ eV FWHM)\textsuperscript{41} than the $3d$ core-hole lifetime broadening. Therefore, the $U_{N_{4,5}}$ x-ray absorption spectrum shown in

<table>
<thead>
<tr>
<th>State</th>
<th>Experiment (INS)</th>
<th>Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_5$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td>150</td>
<td>155</td>
</tr>
<tr>
<td>$\Gamma_4$</td>
<td>170</td>
<td>178</td>
</tr>
</tbody>
</table>

Fig. 3 recorded in the TEY mode appears as two broad, nearly structureless lines at around 735.3 eV and 776.7 eV, which represent the spin-orbit $4d_{5/2}$ and $4d_{3/2}$ pair, respectively. The broad structure observed for the range of energies between $\sim 749$ and $\sim 758$ eV represents transitions to the continuum (probably $p$-like) states. The model does not include transitions to the continuum and our calculations do not take these transitions into account.

However, if high-energy resolution was attainable, one would observe that the shapes of the $N_5$ and $N_4$ edges are different. That is a direct consequence of the interaction of the $5f$ electrons with the $4d$ core hole in the final state of the spectroscopic process. This is clearly seen when comparing the experimental data with the results of calculations using the atomic multiplet, crystal-field multiplet theory and AIM for the $U(IV)$ ion in Fig. 3. In the atomic and crystal-field approach, the spectra were calculated for transitions between $5f^2$ and $4d^05f^3$ configurations. For the calculated spectra, shown in Fig. 3, the $F^k$ integrals were reduced to 80% while the $G^k$ integrals were reduced to 65% as in calculations for the $U_{4f}$ edges (see below). However, in contrast to the situation for the $M_4$ edge, the spectral shapes at the $4d$ edges are little affected by $G^k$ scaling to 50% versus “standard” scaling to 80%, probably due to (in general) significantly smaller values of the $G^k$ integrals at the $4d$ edges compared to the $3d$ edges.\textsuperscript{40} The crystal-field parameters were set to the same values as in the calculations for the $U_{M4}$ edge.

In the AIM calculations, the final state of the
Figure 3: Experimental and calculated XAS spectra at the U N_{4,5} edges of UO₂. The spectra are calculated using atomic and crystal-field multiplet theory for the U^{4+} ion and Anderson impurity model, respectively.

system was described as a mixture of 4d^5f^3 and 4d^5f^45f^1 configurations while the description of the ground state and the values of the model parameters were kept the same as in the calculations for the U M₄ edge. To more easily identify the differences between the U N₅ and N₄ edges, the calculated spectra were only slightly broadened. While already the atomic multiplet calculations demonstrate a significant contrast in the shape between the U(IV) N₅ and N₄ edges, switching on the crystal field and the U 5f−O 2p hybridization adds to the shape changes.

An important quantity discussed in connection with the 4d edges of actinides is the branching ratio of the N₅ and N₄ lines (see e.g., Refs.²,³⁰,⁴²) as a characteristic of the actinide oxidation state and 5f count n_f. The branching ratio is defined as I_{5/2}/(I_{5/2} + I_{3/2}), where I is the integrated intensity of a line. A gradual decrease of the relative N₄ intensity and a corresponding increase of the branching ratio were demonstrated on going from the n_f = 1 system (Th metal) to the n_f = 6 system (Am metal) with reference to the nominal oxidation state/5f population. However, there is disagreement on whether the branching ratio is sensitive to the crystal field symmetry and the covalency of the chemical bonds in uranium compounds, particularly for UO₂. The contradictory conclusions were made based on results of electron-energy-loss spectroscopy² and conventional XAS.²

Our calculations do not reveal a change in the branching ratio on going from the pure atomic-multiplet theory to taking into account the crystal-field interaction and the U 5f−O 2p hybridization. Even the admixture of an extra 0.24 5f-electrons accounting for the chemical-bonding covalency and U 5f−O 2p charge-transfer in the ground state and configuration mixing in the final state do not significantly affect the branching ratio. This ratio was found to be 0.68 which is in good agreement with experiment.²

The AIM spectrum which takes into account all the crystal-field multiplet effects and the U 5f−O 2p hybridization was also fully broadened to account for the 4d core-hole lifetime and the experimental resolution, and is compared with the measured spectrum in Fig. 3. One can see that for real broadenings in conventional XAS measurements at the actinide 4d edges it is very difficult to observe shape differences between the N₅ and N₄ lines. At the same time, the sensitivity of their branching ratio to oxidation state remains an issue to explore further.

4f edges

In contrast to the actinide 4d XAS edges, the improvement in spectral resolution moving to the shallower actinide 4f XAS thresholds is achieved from a significantly reduced core-hole
We have employed an alternative, many-body (multiplet coupling) approach based on AIM to describe the XAS spectra at the actinide 4f edges in this research. Fig. 4 compares the results of atomic, crystal-field multiplet and AIM theories for the U(IV) system with the experimental XAS data obtained at the U N_{6,7} edges of UO_2. The atomic and crystal-field multiplet calculations were performed for the transitions between the 5f \textsuperscript{2} (ground state) and 4f\textsuperscript{13}5f\textsuperscript{2}6d\textsuperscript{1} (final state) configurations. The F_{k} Slater integrals were reduced to 80\% of their Hartree-Fock values while the G_{k} integrals were reduced to 65\% (see below). In the crystal-field multiplet calculations, the cubic (O\textsubscript{h}) crystal field was applied to both U 5f and 6d shells with parameters set to $B_{4}^{0} = -0.93$ eV, $B_{6}^{0} = 0.35$ eV (5f shell), and $10Dq = -3.00$ eV (6d shell), respectively.

It is clear from Fig. 4 that the atomic-multiplet theory fails to describe the U N_{6,7} XAS spectrum of UO_2, while the crystal-field multiplet calculations fairly-well reproduce the major difference between the U N_{7} and U N_{6} edges, i.e., the first peak at $\sim$395.5 eV is the most prominent structure of the N_{6} edge contrasting to the N_{7} edge where the second peak at $\sim$387.7 eV is the strongest. The splittings between the peaks at $\sim$384.4 eV and $\sim$387.7 eV in the N_{7} edge and between the peaks at $\sim$395.5 eV and $\sim$398.6 eV in the N_{6} edge directly depend on the $10Dq$ parameter for the U 6d shell and is well-reproduced for $10Dq = -3.00$ eV. This value is somewhat different from those derived in Refs. \cite{8,17} because it describes the ”bare” splitting between the $e_g$ and $t_{2g}$ states without the effects of the 6d hybridization.

It turns out that the U N_{6,7} XAS spectral structures of UO_2 between 402.5 eV and 410 eV result from the exchange interaction between core and valence electrons. This is easily revealed by scaling the $G_{k}$ integrals in the calculations so that the positions of the structures move towards higher energies with increasing $G_{k}$ values. Therefore, the energy positions of these structures observed in the experimental spectrum put additional constraints on and help to accurately determine the strength of the exchange interaction. As in case of the

---

**Figure 4:** Experimental and calculated XAS spectra at the U N_{6,7} edges of UO_2. The spectra are calculated using atomic and crystal-field multiplet theory for the U\textsuperscript{4+} ion and Anderson impurity model, respectively.

lifetime broadening,\cite{18,19} thus providing more detailed information about the unoccupied 6d states of actinides compared to normal XAS experiments at the actinide L\textsubscript{3} edge.

In Ref.,\cite{17} the XAS spectra of AnO\textsubscript{2} (An = U, Np, Pu) at the An N_{6,7} edges were compared with the LDA+U-calculated unoccupied An 6d density of states. Although the results of the LDA+U calculations describe all the observed spectral structures, the spectral shapes are not accurately reproduced especially the differences in shape between the N\textsubscript{7} and N\textsubscript{6} edges. In particular for UO\textsubscript{2} (see Fig. 4), the first peak (at $\sim$384.4 eV) of the N\textsubscript{7} edge which is not so strong becomes the most intense structure (at $\sim$395.5 eV) in the N\textsubscript{6} edge.
HERFD-XAS data at the U 3d edge of UO$_2$, a significant reduction of the $G^k$ integrals is required for a proper description of the experimental XAS data at the U 4f edges of UO$_2$.

Despite a significant improvement in the description of the experimental data, the crystal-field multiplet theory does not correctly reproduce the $\sim 390.1$-eV and $\sim 401.0$-eV peaks in the measured U $N_{0,7}$ XAS spectrum of UO$_2$. Although the splitting between the $e_g$ and $t_{2g}$ orbitals is introduced in the U 6d shell, the actual 6d band shape is not modeled in this case. This is one of the possible reasons for the discrepancy between calculations and experiment. Another reason is the importance of the U 5f–O 2p hybridization and charge-transfer in UO$_2$.

The results of the AIM calculations for the U(IV) system that take into account the U 5f–O 2p hybridization and charge-transfer do reveal an enhanced spectral weight ("extra-structures") at the energies around 390.1 and 401.0 eV (see Fig. 4), although the intensities are not as large as in the experimental spectrum. Since in this case a core hole at the U site is created in the U 4f level instead of the 3d (4d) level and an electron is excited into the U 6d states, the model Hamiltonian was accordingly modified.

In $H_{AIM}$, $\epsilon_d$ and $d^\dagger_\mu$ were replaced with a one-electron energy, $\epsilon_c$, and the electron creation operator $c^\dagger_\alpha$ for the 4f level, respectively. Two extra terms were added to account for the 5f–6d Coulomb interaction ($U_{fd}$) and the 4f core-hole potential acting on the 6d electron ($U_{dc}$), such as

$$U_{fd} \sum_{\gamma,\lambda} f^\dagger_{\gamma,\lambda} f_{\alpha,\lambda} + U_{dc} \sum_{\lambda,\alpha} a^\dagger_{\lambda,\alpha} a_{\lambda,\alpha} c^\dagger_{\alpha} c_{\alpha}$$

where $a^\dagger_{\lambda}$ is an electron creation operator in the 6d level and $\lambda$ ($\alpha$) represents the spin and orbital states of the 6d (4f) electrons. The importance of the inclusion of such terms has been demonstrated for the description of the Ce $L_3$ XAS spectrum of CeO$_2$.\(^{43}\)

In $H_{FI}$ (equation 3), the 3d (4d) spin-orbit coupling and Slater integrals of the 3d(4d)–5f interaction were replaced with the 4f spin-orbit coupling and 4f – 5f and 4f – 6d interaction integrals, respectively. In addition, the 6d spin-orbit coupling and 5f – 6d interaction integrals were taken into account. In $H_{CF}$, the crystal-field term for the 6d shell was included which can be characterized by the 10D$q$ parameter under $O_h$ symmetry.

While the ground state was the same as in the AIM calculations of the XAS spectra of UO$_2$ at the U 3d and 4d edges, the final state of the XAS process at the U 4f edges was described by a mixture of the $4f^{13}5f^26d^1$ and $4f^{13}5f^3\gamma^16d^3$ configurations. In the limit of $V \to 0$, the difference between the configuration averaged energies for the final state can be expressed as $E(4f^{13}5f^3\gamma^16d^3) - E(4f^{13}5f^26d^1) = \Delta - U_{fc} - U_{dc} + U_{fd}$ (see Ref.\(^{43}\)). The values of the AIM parameters were the same as those used for calculations of the XAS spectra of UO$_2$ at the U 3d and 4d edges, except for the $V_m$ value which was set to $V_m = 0.6$ eV. The ($U_{dc} - U_{fd}$) value was found to affect the energy positions of the "extra-structures", discussed above, and was eventually set to $U_{dc} - U_{fd} = 2.0$ eV to provide better agreement with respect to experimental energy (measured structures around 390.1 and 401.0 eV). A similar ($U_{dc} - U_{fd}$) value was derived for ThO$_2$ in Ref.\(^{14}\) and $U_{dc} - U_{fd} = 1.0$ eV was estimated for Ce $L_3$ XAS edge of CeO$_2$ in Ref.\(^{43}\).

From comparison between the results of the calculations based only on crystal-field theory and the AIM calculations, which take into account the U 5f–O 2p charge-transfer, it is clear that most of the spectral weight at $\sim 390.1$ eV and $\sim 401.0$ eV originates from the transitions to the states of the $4f^{13}5f^3\gamma^16d^3$ configuration. At the same time, a comparison of the experimental spectra with the results of LDA+U calculations in Ref.\(^{17}\) suggests that the $\sim 390.1$-eV and $\sim 401.0$-eV structures correspond to the transitions to the $t_{2g}$-derived states. However, the LDA+U calculations do not really distinguish between contributions from different electronic configurations. In this situation, the polarization-dependent and temperature-dependent XAS measurements on a single crystal of UO$_2$ (in particular at low temperatures when there is a crystal-structure distortion)
could help in establishing the nature of the \( \sim 390.1 \text{-eV} \) and \( \sim 401.0 \text{-eV} \) structures.

Conclusions

A systematic XAS study of UO\(_2\), involving both advanced experimental methods, such as HERFD-XAS, and measurements at shallower U core levels in combination with the AIM calculations, has helped to better evaluate the chemical bonding and the degree of the 5\( f \) localization in this oxide. The AIM simulations of the data produced the \( n_f \) value of 2.24 electrons. The results of our study firmly support the significant degree of covalency of chemical bonding in UO\(_2\) despite the suggestions of rather ionic character of this oxide expressed by some researchers.

Acknowledgement This research was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences Heavy Element Chemistry program (D.K.S) and the Advanced Light Source is supported by the Director, Office of Science, Basic Energy Sciences; both of the US Department of Energy at Lawrence Berkeley National Laboratory under Contract DE-AC02-05CH11231.

References


(38) Bagus, P. S.; Nelin, C. J.; Ilton, E. S. Theoretical modeling of the uranium $4f$ XPS for U(VI) and U(IV) oxides. J. Chem. Phys. 2013, 139, 244704.
TOC Graphic

![Graph showing $\text{UO}_2$ M$_4$ edge with TEY and HERFD curves.](image-url)