3d-4f Resonant Inelastic X-ray Scattering of Actinide Dioxides: Crystal-Field Multiplet Description

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ABSTRACT: A theoretical overview of the core-to-core (3d-4f) resonant inelastic X-ray scattering (RIXS) spectra of actinide dioxides AnO₂ (An = Th, U, Np, Pu, Am, Cu, Bk, Cf) is provided. The 3d-4f RIXS maps were calculated using crystal-field multiplet theory and turned out to be significantly different at the An M₄ vs M₅ edges, because of selection rules and final state effects. The results of the calculations allowed for a general analysis of so-called high-energy-resolution fluorescence-detected X-ray absorption (HERFD-XAS) spectra. The cuts of the calculated RIXS maps along the incident energy axis at the constant emitted energy, corresponding to the maximum of the RIXS intensity, represented the HERFD spectra and provided their comparison with conventional X-ray absorption (XAS) spectra with a reduced core-hole lifetime broadening at the An M₄ and M₅ edges. Although the An M₅ HERFD profiles were found to depart from the X-ray absorption cross-section, the results confirm the utility of HERFD for the An chemical state determination and indicate the importance of calculating the entire RIXS process in order to interpret the HERFD data correctly.

INTRODUCTION

The application of the high-energy-resolution fluorescence detected X-ray absorption (HERFD-XAS) technique to actinide (An) compounds has led to a striking improvement in the resolution of the spectra at the An M₄ edge (4–8 times higher, according to various estimates), because of a reduced core-hole lifetime broadening in the final state of the spectroscopic process. This can be viewed as a real breakthrough in actinide research, since the enhanced sensitivity of the method allows for probing the An oxidation state, electronic, local symmetry, (non)stoichiometry, oxygen/metal (O/M) ratio, etc. with much greater capability and efficiency. For example, the long-standing questions, such as about the ground state to the intermediate states with a 3d hole and then to final states with a 4f hole, have been addressed after the employment of the HERFD-XAS technique.

However, in the light of an increasing usage of this technique by scientists involved in the actinide research, the question about how well the profiles of the HERFD-XAS spectra at the An M₄ edges follow the X-ray absorption cross-section becomes important. This is crucial for the interpretation of recorded data with help of spectra of reference systems and/or model calculations. For example, if the HERFD-XAS spectra follow the X-ray absorption cross-section, the calculations of these spectra can be greatly simplified by just calculating the An M₄ XAS with a significantly reduced broadening, instead of calculating the full-path core-to-core (3d-to-4f) RIXS process with transitions from the ground state to the intermediate states with a 3d hole and then to final states with a 4f hole. This question is especially important for the case when states with a significant degree of localization in the valence and conduction bands are involved in the spectroscopic process (in our case, 5f states), i.e., when the multiplet approach is appropriate. For example, Tanaka et al. found some differences between the calculated Dy(III) L₃ XAS spectrum with a reduced core-hole lifetime broadening and the calculated HERFD-XAS spectrum for the region of quadrupole 2p−4f transitions. Moreover, the X-ray fluorescence yield spectra at the L₂,₃ edges of 3d transition metal systems were shown to depart from the X-ray absorption cross-section.

The paper presents the results of the calculations using the crystal-field multiplet theory, which address the questions about...
Table 1. Ab Initio Hartree–Fock Values of Slater Integrals and Spin-Orbit Coupling Constants in the Ground-State Configurations

| Element | Slater Integrals (eV) | Spin-Orbit Coupling Constants (eV) |
|---------|---------------------|-----------------------------------|
|          | $f^{5}g^{5}$ | $f^{5}d^{5}$ | $f^{5}f^{5}$ | $\zeta$ | $f^{5}d^{5}$ | $f^{5}f^{5}$ | $G_{f^{5}}$ | $G_{d^{5}}$ | $G_{f^{5}}$ | $\zeta(3d)$ |
| Th(IV)  | 0.233            | 2.192             | 1.008           | 1.694 | 1.022           | 0.714           | 66.004               |
| U(IV)   | 0.301            | 2.564             | 1.190           | 2.003 | 1.211           | 0.847           | 73.384               |
| Np(IV)  | 0.338            | 2.741             | 1.277           | 2.151 | 1.301           | 0.910           | 77.308               |
| Pu(IV)  | 0.377            | 2.915             | 1.362           | 2.296 | 1.390           | 0.973           | 81.395               |
| Am(IV)  | 0.418            | 3.085             | 1.447           | 2.439 | 1.478           | 1.035           | 85.649               |
| Cm(IV)  | 0.461            | 3.251             | 1.529           | 2.578 | 1.563           | 1.095           | 90.076               |
| Bk(IV)  | 0.506            | 3.410             | 1.607           | 2.710 | 1.645           | 1.152           | 94.681               |
| Cf(IV)  | 0.553            | 3.568             | 1.685           | 2.844 | 1.727           | 1.210           | 99.468               |

In the RIXS calculation, the Slater integrals were reduced to 80% of these values.

Table 2. Ab Initio Hartree–Fock Values of Slater Integrals and Spin-Orbit Coupling Constants in the Intermediate-State Configurations

| Element | Slater Integrals (eV) | Spin-Orbit Coupling Constants (eV) |
|---------|---------------------|-----------------------------------|
|          | $f^{5}g^{5}$ | $f^{5}d^{5}$ | $f^{5}f^{5}$ | $\zeta$ | $f^{5}d^{5}$ | $f^{5}f^{5}$ | $G_{f^{5}}$ | $G_{d^{5}}$ | $G_{f^{5}}$ | $\zeta(3d)$ |
| Th(IV)  | 0.233            | 2.192             | 1.008           | 1.694 | 1.022           | 0.714           | 66.004               |
| U(IV)   | 0.301            | 2.564             | 1.190           | 2.003 | 1.211           | 0.847           | 73.384               |
| Np(IV)  | 0.338            | 2.741             | 1.277           | 2.151 | 1.301           | 0.910           | 77.308               |
| Pu(IV)  | 0.377            | 2.915             | 1.362           | 2.296 | 1.390           | 0.973           | 81.395               |
| Am(IV)  | 0.418            | 3.085             | 1.447           | 2.439 | 1.478           | 1.035           | 85.649               |
| Cm(IV)  | 0.461            | 3.251             | 1.529           | 2.578 | 1.563           | 1.095           | 90.076               |
| Bk(IV)  | 0.506            | 3.410             | 1.607           | 2.710 | 1.645           | 1.152           | 94.681               |
| Cf(IV)  | 0.553            | 3.568             | 1.685           | 2.844 | 1.727           | 1.210           | 99.468               |

In the RIXS calculation, the Slater integrals were reduced to 80% of these values.

The relationship between HERFD and conventional XAS spectra. The choice to apply these calculations to systems such as An dioxides is understandable, because An dioxides are the most commonly used materials in the nuclear industry. Mixed An dioxides are considered to be good candidates for innovative fuels in Generation IV reactors to recycle major actinides, such as U and Pu, and reduce the radioactive waste by partitioning and transmuting the minor ones, such as Np, Am, and Cm. For the optimized fuel performance, handling, and storage, it is important to gain insight on the An chemical state and cation charge distribution and on the oxygen/metal (O/M) ratio as key parameters to assess thermodynamic, chemical, and physical properties of the fuels. Furthermore, mixed-oxide systems cannot be fully understood without a thorough understanding of each binary oxides in the mix. Advanced X-ray spectroscopic tools, such as HERFD-XAS, with enhanced sensitivity help to link the changes in the electronic structure to specific macroscopic properties of the materials in question.

**Computational Details**

The crystal (ligand)-field multiplet approach was used in the calculations, which included the 5f and core 3d or 4f states on a single An ion in cubic symmetry.

The total Hamiltonian of a system can be written as

$$H = H_{FI} + H_{CF}$$

where $H_{FI}$ represents the Coulomb, exchange, and spin–orbit interactions for a free actinide ion and $H_{CF}$ describes the crystal-field splittings.

$$H_{FI} = \sum_{\gamma}(\gamma)\sum_{a}(\gamma)a^\dagger(\gamma)a(\gamma)$$

$$+ \sum_{\gamma}(\gamma)\sum_{a}(\gamma)a^\dagger(\gamma)a(\gamma)$$

$$+ \sum_{\gamma}(\gamma)\sum_{a}(\gamma)a^\dagger(\gamma)a(\gamma)$$

$$+ \zeta(\gamma)\sum_{\gamma}\sum_{a}(\gamma)a^\dagger(\gamma)a(\gamma)$$

$$+ \zeta(\gamma)\sum_{\gamma}\sum_{a}(\gamma)a^\dagger(\gamma)a(\gamma)$$

$$+ \zeta(\gamma)\sum_{\gamma}\sum_{a}(\gamma)a^\dagger(\gamma)a(\gamma)$$

where the interaction between 5f electrons ($R_{5f}$) and between a 5f electron and a core 3d hole ($R_{5f}$) or a core 4f hole ($R_{4f}$) is described in terms of Slater integrals, while the spin–orbit interaction for the 5f and core 3d or 4f states is described with coupling constants $\zeta(5f)$, $\zeta(3d)$, and $\zeta(4f)$, respectively, and matrix elements $h$, $l$, and $p$ of the spin–orbit coupling operator. $a^\dagger$ is an electron creation operator and $a^\dagger$, $a$, and $l$ are combined indices to specify the spin and orbital degeneracies of $5f$, $3d$, and $4f$ states, respectively.

$$H_{CF} = \sum_{\gamma}Q_{\gamma}^{CF}a^\dagger(\gamma)a(\gamma)$$

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

$$Q_{\gamma}^{CF} = \sum_{k,q}b_{\gamma,k}^{\gamma}$$

where $b_{\gamma}^{\gamma}$ are Wybourne's crystal-field parameters. The $C_{\gamma}^{\gamma}$ are related to the spherical harmonics as

$$C_{\gamma}^{\gamma} = \frac{4\pi}{2k + 1} Y_{\gamma}^{k}$$

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

$$Q_{\gamma}^{CF} = b_{0}^{\gamma}4^{\gamma} + \frac{5}{14}(C_{4}^{\gamma} + C_{4}^{\gamma}) + b_{2}^{\gamma}4^{\gamma} - \frac{7}{2}(C_{6}^{\gamma} + C_{6}^{\gamma})$$

To calculate the An HERFD spectra at the $M_{4}$ (3d_{1/2} → 5f_{5/2}) transitions and $M_{5}$ (3d_{3/2} → 5f_{7/2,5/2}) transitions, the core–to-core (3d-to-4f) RIXS maps around the An $M\beta$ ($A_{f_{2}}$ → $3d_{1/2}$)
Table 3. Ab Initio Hartree–Fock Values of Slater Integrals and Spin-Orbit Coupling Constants in the Final-State Configurationsa

| Parameter | Slater Integral (eV) | Spin-Orbit Coupling Constant (eV) |
|-----------|---------------------|----------------------------------|
| $P^f(5f,5f)$ | $P^f(5d,5f)$ | $P^f(5s,5f)$ | $\zeta^f(5f)$ | $P^f(4f,5f)$ | $P^f(4d,5f)$ | $G^f(4f,5f)$ | $G^f(4s,5f)$ | $G^f(4p,5f)$ | $\zeta^f(4f)$ |
| Th(IV) | 0 | 0 | 0 | 0.227 | 4.577 | 1.950 | 1.200 | 1.211 | 1.494 | 1.161 | 0.905 | 2.662 |
| U(IV) | 9.963 | 6.534 | 4.804 | 0.294 | 5.209 | 2.255 | 1.394 | 1.380 | 1.721 | 1.343 | 1.050 | 3.078 |
| Np(IV) | 10.332 | 6.782 | 4.989 | 0.330 | 5.503 | 2.398 | 1.485 | 1.457 | 1.827 | 1.509 | 1.182 | 3.538 |
| Pu(IV) | 10.687 | 7.020 | 5.167 | 0.368 | 5.787 | 2.536 | 1.573 | 1.531 | 1.927 | 1.509 | 1.182 | 3.538 |
| Am(IV) | 11.031 | 7.250 | 5.339 | 0.409 | 6.062 | 2.670 | 1.658 | 1.601 | 2.024 | 1.588 | 1.245 | 3.785 |
| Cm(IV) | 11.365 | 7.474 | 5.505 | 0.451 | 6.328 | 2.799 | 1.740 | 1.707 | 2.119 | 1.665 | 1.306 | 4.044 |
| Bk(IV) | 11.690 | 7.691 | 5.667 | 0.495 | 6.588 | 2.926 | 1.821 | 1.736 | 2.210 | 1.739 | 1.365 | 4.315 |
| Cf(IV) | 12.008 | 7.903 | 5.826 | 0.542 | 6.843 | 3.050 | 1.900 | 1.801 | 2.300 | 1.813 | 1.423 | 4.600 |

aIn the RIXS calculation, the Slater integrals were reduced to 80% of these values.

Table 4. Values of Wybourne’s Crystal-Field Parameters Used in the RIXS Calculation

| Parameter | Value (eV) | Ref(s) |
|-----------|------------|--------|
| $B_0^f$ | $-1.30 \times 10^{-3}$ | 11, 13 |
| $B_0^g$ | 0.55 | 12, 13, 14 |
| ref(s) | 13, 15, 16 |

aThe HERFD-XAS spectrum is represented by a linear cut of half-maximum (HWHM) of the Lorentzian function. Operators for optical dipole transitions $D$ are expressed in terms of spherical tensor operators $C_{l}^{(1)}$. For a transition to the intermediate state:

$$D_1 = \hat{e} \cdot \mathbf{r}$$

$$= r \left[ -\frac{1}{\sqrt{2}} (\epsilon_{\pi} - i\epsilon_{\sigma}) C_{1}^{(1)} + \frac{1}{\sqrt{2}} (\epsilon_{\pi} + i\epsilon_{\sigma}) C_{-1}^{(1)} + \epsilon_{0} C_{0}^{(1)} \right]$$

(8)

where $\epsilon = (\epsilon_{\pi}, \epsilon_{\sigma}, \epsilon_{0})$ is the polarization vector of a photon and $r$ is the position operator. For a transition to the final state, $D_2$ is a Hermite conjugate of $D_1$ $(D_2 = D_1^*)$, which results in a complex conjugate for $e$. In present RIXS calculations, the 90°-scattering geometry was used, which is usually applied in HERFD experiments. The incident photons were chosen to propagate along the $z$-axis with linear polarization along the $x$-axis and parallel to the propagation direction of scattered photons ($x$-polarized incident photon beam with the polarization vector in the scattering plane). For these settings, the dipole transition operators become:

$$D_1 = r \left[ -\frac{1}{\sqrt{2}} C_{1}^{(1)} + \frac{1}{\sqrt{2}} C_{-1}^{(1)} \right]$$

(9)

and

$$D_2 = r \left[ \frac{i}{\sqrt{2}} C_{1}^{(1)} + \frac{i}{\sqrt{2}} C_{-1}^{(1)} \right]$$

(10)

The HERFD-XAS spectrum is represented by a linear cut of such a RIXS map (see, for example, ref 1) along the diagonal of the plane defined by the incident energy axis and energy transfer axis or parallel to the incident energy axis at a constant emitted energy (the energy of the RIXS intensity maximum in this case) in the plane of the emitted versus incident energies.

The conventional XAS spectra which represent the 5f transitions $3d^{2}f^{0} \rightarrow 3d^{5}f^{3+1}$ transitions were calculated using the following equation:

$$I_{XAS}(\omega) = \sum_{m} |l(m)D_{l}|^{2} \frac{\Gamma_{m}/\pi}{(E_{m} - E_{g} - \omega)^{2} + \Gamma_{m}^{2}}$$

(11)

transitions) and An $M_{a}(4f^{7/2,5/2} \rightarrow 3d_{9/2})$ transitions X-ray emission lines were calculated. In terms of electronic configurations, the $S^{0} \rightarrow 3d^{5}f^{0} \rightarrow 4d^{5}f^{0}$ excited states of the spectroscopic process with energies neglected. In the actual multiplet calculations, the Slater integrals were set to 0.001 eV. The Slater integrals and spin–orbit coupling constants are given in Table 4, along with references from 37, 11 12, 13 14 13, 15 13, 16

| Parameter | Value | Ref(s) |
|-----------|--------|--------|
| $B_0^f$ | $-1.30 \times 10^{-3}$ | 11, 13 |
| $B_0^g$ | 0.55 | 12, 13, 14 |
| ref(s) | 13, 15, 16 |

where $l(g, l, m)$ and $|f \rangle$ are the ground, intermediate, and final states of the spectroscopic process with energies $E_{g}, E_{m},$ and $E_{f}$, respectively. $\omega$ and $\omega'$ are the energies of the incident and scattered/lost emissions with polarizations $q_{1}$ and $q_{2}$, respectively, and $\Gamma_{m}$ and $\Gamma_{f}$ are the lifetime broadenings of the intermediate and final states, in terms of half width at half-maximum (HWHM) of the Lorentzian function. Operators for optical dipole transitions $D$ are expressed in terms of spherical tensor operators $C_{l}^{(1)}$. For a transition to the intermediate state:

$$D_1 = \hat{e} \cdot \mathbf{r}$$

$$= r \left[ -\frac{1}{\sqrt{2}} (\epsilon_{\pi} - i\epsilon_{\sigma}) C_{1}^{(1)} + \frac{1}{\sqrt{2}} (\epsilon_{\pi} + i\epsilon_{\sigma}) C_{-1}^{(1)} + \epsilon_{0} C_{0}^{(1)} \right]$$

(8)

where $e = (\epsilon_{\pi}, \epsilon_{\sigma}, \epsilon_{0})$ is the polarization vector of a photon and $r$ is the position operator. For a transition to the final state, $D_2$ is a Hermite conjugate of $D_1$ $(D_2 = D_1^*)$, which results in a complex conjugate for $e$. In present RIXS calculations, the 90°-scattering geometry was used, which is usually applied in HERFD experiments. The incident photons were chosen to propagate along the $z$-axis with linear polarization along the $x$-axis and parallel to the propagation direction of scattered photons ($x$-polarized incident photon beam with the polarization vector in the scattering plane). For these settings, the dipole transition operators become:

$$D_1 = r \left[ -\frac{1}{\sqrt{2}} C_{1}^{(1)} + \frac{1}{\sqrt{2}} C_{-1}^{(1)} \right]$$

(9)

and

$$D_2 = r \left[ \frac{i}{\sqrt{2}} C_{1}^{(1)} + \frac{i}{\sqrt{2}} C_{-1}^{(1)} \right]$$

(10)

The HERFD-XAS spectrum is represented by a linear cut of such a RIXS map (see, for example, ref 1) along the diagonal of the plane defined by the incident energy axis and energy transfer axis or parallel to the incident energy axis at a constant emitted energy (the energy of the RIXS intensity maximum in this case) in the plane of the emitted versus incident energies.

The conventional XAS spectra which represent the 5f transitions $3d^{2}f^{0} \rightarrow 3d^{5}f^{3+1}$ transitions were calculated using the following equation:

$$I_{XAS}(\omega) = \sum_{m} |l(m)D_{l}|^{2} \frac{\Gamma_{m}/\pi}{(E_{m} - E_{g} - \omega)^{2} + \Gamma_{m}^{2}}$$

(11)
The required Slater integrals $F^k$, $G^k$, spin–orbit coupling constants $\zeta$, and transition-matrix elements were obtained with the TT-MULTIPLETS package including Cowan’s atomic multiplet program$^{17}$ (based on the Hartree–Fock method with relativistic corrections) and Butler’s point-group program,$^{18}$ which were modified by Thole.$^{19}$ In the RIXS calculations, $\Gamma_m$ and $\Gamma_f$ were set to values of 1.6 and 0.25 eV, respectively.$^{20}$ To simulate the experimental response function, the calculated spectra were additionally broadened with Gaussian with HWHM of 0.25 eV. The conventional XAS spectra are represented by calculated isotropic spectra with the reduced core–hole lifetime broadening ($\Gamma_m = 0.25$ eV) and 0.25 eV HWHM Gaussian convolution.

The results and discussion

Figures 1–8 show the results of the calculations at the An $M_5$ edges and Figures 9–16 show the results of the calculations at the An $M_4$ edges. These figures display the 3d-to-4f RIXS maps by using for the $x$-axis the incident energy scale and, for the $y$-axis, the energy transfer (panel (a)) and emitted energy (panel (b)) scales. Panel (c) makes a comparison between the calculated conventional XAS spectrum at the An $M_5$ or $M_4$ edge with a HERFD cut (red curve) of the 3d-to-4f RIXS map along the incidence energy axis at an emitted energy corresponding to the RIXS maximum. This cut is indicated by a dashed line in panel (b). The spectra in panel (c) are normalized to a main maximum.

All spectra were calculated for the lowest state of the ground-state configuration. The population of states due to finite temperature was not considered.

Figure 1. 3d-to-4f RIXS map of ThO$_2$ with the incident energy on the $x$-axis and the (a) energy transfer or (b) emitted energy on the $y$-axis. The incident energy varies across the Th $M_5$ edge. (c) Comparison between the calculated conventional XAS spectrum (black curve) at the Th $M_5$ edge with a reduced core–hole lifetime broadening and a HERFD cut (red curve) of the 3d-to-4f RIXS map along the incidence energy axis at an emitted energy corresponding to the RIXS maximum. This cut is indicated by a dashed line in panel (b). The spectra in panel (c) are normalized to a main maximum.

Figure 2. 3d-to-4f RIXS map of UO$_2$ with the incident energy on the $x$-axis and the (a) energy transfer or (b) emitted energy on the $y$-axis. The incident energy varies across the U $M_5$ edge. (c) Comparison between the calculated conventional XAS spectrum (black curve) at the U $M_5$ edge with a reduced core–hole lifetime broadening and a HERFD cut (red curve) of the 3d-to-4f RIXS map along the incidence energy axis at an emitted energy corresponding to the RIXS maximum. This cut is indicated by a dashed line in panel (b). The spectra in panel (c) are normalized to a main maximum.
reduced core-hole lifetime broadening (0.25 eV HWHM) and a HERFD cut through the $3d$-to-$4f$ RIXS map along the incidence energy axis at an emitted energy corresponding to the RIXS maximum. These cuts are indicated by dashed lines in panel (b). The spectra in panel (c) are normalized to a main maximum.

In contrast to earlier systematic XAS calculations at the $d$-edges of actinides, where only an atomic multiplet approach was used, it is clear that, for the spectra with a significantly improved resolution, the crystal-field interaction must be included in the calculations. This interaction affects the shape of the spectra, as has been already shown for ThO$_2$, as an example. However, the crystal field influence becomes less pronounced for dioxides of late actinides, because the crystal-field strength is reduced. Other effects may also play a role, such as the increasing relativistic correction and degeneracy lifting of the energy levels with increasing $Z$.

While there are several publications where the crystal field strength in UO$_2$, NpO$_2$, and PuO$_2$ is determined theoretically or from the analysis of various experimental data, much fewer publications related to the crystal field strength in AmO$_2$ and CmO$_2$ can be found. To set the values of crystal-field parameters $B^{(4)}_0$ and $B^{(6)}_0$ in our calculations for AmO$_2$ and CmO$_2$, a combination of the data for Am(III) and Cm(III), respectively, incorporated into the ThO$_2$ lattice and of the $B^{(4)}_0$ and $B^{(6)}_0$. 
estimations within the unified approach for An dioxides, presented in ref 13 was used. We could not find the experimental data related to the crystal-field strength in BkO₂ and CfO₂; therefore, it was decided to use, in the spectral calculations for these dioxides, the same B₀⁴ and B₀⁶ values as those for CmO₂.

In panel (a) in Figures 1−8, the spectral structures, representing X-ray scattering on the 4f₁³5fⁿ⁺¹ multiplet states via virtual 3d⁻¹⁻⁵fⁿ⁺¹ excitations, appear on the constant energy transfer with the varying incident energy throughout the M₅ edge. The energy separation between the intensity maxima of transitions to the 4f⁷/₂¹³5fⁿ⁺¹ (associated with M₅₁) and 4f⁵/₂⁻⁵fⁿ⁺¹ (associated with M₅₂) components, defined by the 4f spin−orbit interaction, gradually increases from ∼9 eV to ∼18 eV when going from ThO₂ to CfO₂.

It has been shown²²−²⁴ for the 3d transition-metal (TM) compounds that the constant-incident-energy cut along the energy-transfer axis through the quadrupole part of the 1s−2p RIXS map of TM, which involves the 1s³3dⁿ⁺¹ excitations, can provide “TM-2p-edge-like” information, because the final state configuration includes the 2p³3dⁿ⁺¹ multiplet. In our case, a constant-incident-energy cut through the RIXS maximum in panel (a) in these figures will not represent the XAS spectrum at the An 4f edge,⁷,²⁵ which includes 4f⁻¹⁻⁵fⁿ⁺¹ multiplet, but rather the 4f→5f transition part of the energy-electron-loss (EELS)²⁶ or nonresonant inelastic X-ray scattering (NIXS)²⁷ spectra at this edge.

For the An M₄ edges, the 3d-4f RIXS maps (panel a) in Figures 9−16) appear, overall, to be significantly different from
those for the An $M_5$ edges. While no separation into the two transition groups is expected, because of the $4f$ spin–orbit interaction (only the $4f^{13/2}S_{1/2}^{\text{av}}$ multiplet is involved), some calculated (although weak) transitions appear at a quite few eV below and above the main RIXS intensity maximum on the energy-transfer scale. For example, for UO$_2$ (Figure 10), such transitions can be found at the energy transfer of around 385.9 and 398.8 eV, while the maximum is located at $\sim$390.5 eV. This cut is indicated by a dashed line in panel (b). The spectra in panel (c) are normalized to a main maximum.

By plotting the 3$d$-to-4$f$ RIXS map on the emitted energy scale as in panel (b) in Figures 1–16, a connection is made to how the measurements of the HERFD-XAS spectra are performed, when the scattered photons are counted with a X-ray emission spectrometer at a fixed emitted energy while scanning the incident energy across the X-ray absorption edge. Horizontal cuts of the maps in panel (b) in these figures allow one to compare the RIXS profile with the conventional XAS spectrum. Panel (c) in Figures 1–16 provide such a comparison, using a cut through the RIXS intensity maximum (see horizontal white dashed lines in panel (b)), as a representation of the HERFD-XAS spectrum. At the An $M_5$ edges of dioxides, for actinides from Th to Cm, a clear trend in differences between calculated conventional XAS
and HERFD is observed when the HERFD spectra are lacking some intensity on the low-incident-energy side of the main line and show the extra intensity on the high-incident-energy side, compared to conventional XAS spectral shapes. This becomes especially pronounced for CmO$_2$ (see Figure 6). A lack of some intensity on the low-energy side can be understood from the considerations similar to those described in ref 28. The high-spin states of the $3d^{95}f^{1}$ multiplet at the An $M_4$ edge have a tendency to be at a lower energy than the low-spin states. Such high-spin states have a tendency to elastically scatter/decay to states at the low energy transfer, so that the inelastic scattering weight is minimized. This is, in a way, similar to an observation of the relatively lower intensity on the low-energy side of the fluorescence-yield spectra as compared to XAS (see ref 9). On the other hand, the low-spin states have a tendency to scatter inelastically.

The origin of the extra intensity on the high-incident-energy side of the main line in the HERFD spectra can be understood from the analysis of the ThO$_2$ spectra (Figure 1), as an example. In the calculated conventional Th $M_4$ XAS spectrum of ThO$_2$, the XAS transition to the highest state of the $3d^95f^1$ multiplet is observed at 3341.5 eV and contributes to the main XAS peak, while the calculated Th $M_4$ HERFD spectrum shows, in addition, some structure at $\sim$3343.0 eV. An inspection of Figure 17 can explain the appearance of this structure. The figure includes two $3d$-$4f$ RIXS spectra calculated at incident energies of 3341.5

![Figure 9](image-url) **Figure 9.** $3d$-$4f$ RIXS map of ThO$_2$ with the incident energy on the $x$-axis and the (a) energy transfer or (b) emitted energy on the $y$-axis. The incident energy varies across the Th $M_4$ edge. (c) Comparison between the calculated conventional XAS spectrum (black curve) at the Th $M_4$ edge with a reduced core–hole lifetime broadening and a HERFD cut (red curve) of the $3d$-$4f$ RIXS map along the incidence energy axis at an emitted energy corresponding to the RIXS maximum. This cut is indicated by a dashed line in panel (b). The spectra in panel (c) are normalized to a main maximum.

![Figure 10](image-url) **Figure 10.** $3d$-$4f$ RIXS map of UO$_2$ with the incident energy on the $x$-axis and the (a) energy transfer or (b) emitted energy on the $y$-axis. The incident energy varies across the U $M_4$ edge. (c) Comparison between the calculated conventional XAS spectrum (black curve) at the U $M_4$ edge with a reduced core–hole lifetime broadening and a HERFD cut (red curve) of the $3d$-$4f$ RIXS map along the incidence energy axis at an emitted energy corresponding to the RIXS maximum. This cut is indicated by a dashed line in panel (b). The spectra in panel (c) are normalized to a main maximum.
and 3343.0 eV (spectra A and B, respectively), which are displayed on the emitted energy scale. The spectra represent transitions to the states of the 4\(f\)\(^{135}\)f\(^{1}\) multiplet. Since the vertical line in Figure 17 corresponds the emitted energy of the M\(_5\) HERFD cut in Figure 1, one can see that spectrum B still has a significant intensity at this emitted energy when the incident energy is 3343.0 eV. That is because the states of the 4\(f\)\(^{135}\)f\(^{1}\) multiplet show a wider spread in energy than the states of the 3d\(^{9}\)f\(^{1}\) multiplet, because of larger F\(_{2,4,6}(4f,5f)\) and G\(_{2,4,6}(4f,5f)\) integrals, thus still offering the possibility for the excited state to decay by emitting a photon with the energy used for the detection of the HERFD spectrum. Therefore, the ~3343.0 eV structure in the calculated Th M\(_5\) HERFD spectrum of ThO\(_2\) (Figure 1) can be considered as the final state effect of the 3d-4f RIXS process.

Overall, one can say that profiles of the An M\(_5\) HERFD spectra do not follow the X-ray absorption cross-section at the An M\(_5\) edges of An dioxides well and exhibit some extra structures, which are absent for the dipole transitions from the ground state to the states of the 3d\(^{9}\)f\(^{1}\) multiplet. Furthermore, the Cf M\(_5\) HERFD spectrum of CfO\(_2\) was found to be very different from the 3d-4f RIXS map along the incidence energy axis at an emitted energy corresponding to the RIXS maximum. This cut is indicated by a dashed line in panel (b). The spectra in panel (c) are normalized to a main maximum.
small variations in the chemical state (e.g., because of covalency), because the main maxima of the HERFD and XAS spectra coincide rather well (for UO₂, noticeable shift of ∼0.3 eV is found between HERFD and XAS maxima), regardless of the CfO₂ case.

On the other hand, at the An M₄ edges of dioxides (Figures 9–16), the calculated HERFD spectra reproduce the main structures of the XAS spectra (except for AmO₂), although the relative intensities of these structures vary between HERFD and XAS spectra for some dioxides. In particular, the main peak at ∼3742.5 eV in the U M₄ HERFD spectrum of UO₂ (Figure 10) is much stronger than other structures, while it is not the case for the U M₄ XAS spectrum. Nevertheless, the results of calculations for the An M₄ edges demonstrate overall better agreement between the HERFD and XAS spectra than that for the An M₅ edges. At the M₄ edge, the contribution of the states of the 3d⁹5fⁿ⁺¹ multiplet (which are the intermediate states in the 3d-4f RIXS process) to the XAS spectrum is more rich, in terms of observable structures, and is spread over a larger energy range, compared to that at the M₅ edge. Therefore, the final state effects due to the 4f³5fⁿ⁺¹ multiplet involvement are less pronounced at the M₄ edge in the HERFD-XAS spectra (except for the significantly separated-in-energy, weak structures appearing quite a few eV below and above of the main RIXS intensity maximum, which were discussed above). Furthermore, the high- and low-spin states of the 3d⁹5fⁿ⁺¹ multiplet are more intermixed in energy at the M₄ edge, compared to those at the M₅ edge.
where high-spin states have a tendency to group on the low-energy side. In addition, the high-spin states are even preferentially distributed to the $3d_{5/2}$ manifold, compared to the $3d_{3/2}$ manifold.

XAS for the $\pi$-polarized incident beam was also calculated, since such polarization was used in RIXS calculations. A large difference between the calculated conventional XAS spectrum (black curve) at the Bk $M_4$ edge with a reduced core–hole lifetime broadening and a HERFD cut (red curve) of the $3d$-to-$4f$ RIXS map along the incidence energy axis at an emitted energy corresponding to the RIXS maximum. This cut is indicated by a dashed line in panel (b). The spectra in panel (c) are normalized to a main maximum.

For other An $M_5$ and $M_4$ edges of An dioxides, negligible or no changes were found between the calculated $\pi$-polarized and isotropic XAS spectra. The incident and emitted energy scales shown in all figures use the ab initio Hartree–Fock values obtained in the calculations. For comparison with experimental spectra, some uniform shifts in energy will be required since these Hartree–Fock values worse. On the other hand, the structure at $\sim 4375.2$ eV in the $\pi$-polarized Bk $M_4$ somewhat decreases, becomes more separated from the main peak and appears similar, shape-wise, to the corresponding ($\sim 4375.3$ eV) structure in the HERFD spectrum, thus improving an agreement with the HERFD spectrum, compared to the isotropic XAS spectrum. For other An $M_5$ and $M_4$ edges of An dioxides, negligible or no changes were found between the calculated $\pi$-polarized and isotropic XAS spectra.

The incident and emitted energy scales shown in all figures use the ab initio Hartree–Fock values obtained in the calculations. For comparison with experimental spectra, some uniform shifts in energy will be required since these Hartree–Fock
calculations were performed for actinide ions and do not take into account all the solid-state effects. Considering the available experimental data, recorded with high resolution, we find a fairly good agreement in the spectral shape between calculated and measured HERFD spectra for the Th $M_4$ edge of ThO$_2$, for the U $M_4$ and $M_5$ edges of UO$_2$, and for Np $M_5$ edge of NpO$_2$. However, all of the main structures of the experimental Pu $M_5$ and $M_4$ HERFD spectra of PuO$_2$ are reproduced by the crystal-field multiplet calculations; the agreement between calculated and measured spectra becomes somewhat worse than that observed for dioxides of other early actinides. That is because, for PuO$_2$, AmO$_2$, CmO$_2$, BkO$_2$, and CfO$_2$, the An 5f-O 2p interactions are significant.

Table 5. Calculated Ground State of Each An Dioxide

| An | Ground State | $\Gamma_1$ |
|----|--------------|------------|
| Th(IV) | $\Gamma_1$ |
| U(IV) | $\Gamma_5$ |
| Np(IV) | $\Gamma_1$ |
| Pu(IV) | $\Gamma_1$ |
| Am(IV) | $\Gamma_1$ |
| Cm(IV) | $\Gamma_1$ |
| Bk(IV) | $\Gamma_1$ |
| Cf(IV) | $\Gamma_1$ |

Since the finite exchange field is applied along the z-axis, the notation is for $C_{4h}$ symmetry.

Table 6. Energies of Calculated Lowest 50 States of the Ground-State Configuration

| An | U(IV) | Np(IV) | Pu(IV) | Am(IV) | Cm(IV) | Bk(IV) | Cf(IV) |
|----|-------|--------|--------|--------|--------|--------|--------|
| Th(IV) | 0.000437 | 0.000116 | 0.140209 | 0.000005 | 0.540210 | 0.002403 | 0.000690 |
| U(IV) | 0.000874 | 0.000869 | 0.140427 | 0.043055 | 0.540711 | 0.003639 | 0.006657 |
| Np(IV) | 0.162052 | 0.000976 | 0.140628 | 0.043840 | 0.541201 | 0.003895 | 0.007043 |
| Pu(IV) | 0.162059 | 0.050629 | 0.281582 | 0.044352 | 0.941752 | 0.004333 | 0.007659 |
| Am(IV) | 0.186396 | 0.050801 | 0.282453 | 0.045177 | 0.942714 | 0.006920 | 0.029101 |
| Cm(IV) | 0.186404 | 0.051268 | 0.283337 | 0.045773 | 0.942714 | 0.009694 | 0.068869 |
| Bk(IV) | 0.186433 | 0.051448 | 0.337378 | 0.046381 | 0.943685 | 0.012176 | 0.096718 |
| Cf(IV) | 0.201998 | 0.216236 | 0.337380 | 0.047089 | 0.944659 | 0.014657 | 0.120518 |

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charge-transfer effects become significant and must be taken into account in calculations of X-ray spectroscopic data.\textsuperscript{31} Furthermore, the calculations of the Slater integrals specifically for compounds in question, using, e.g., the density functional theory approach instead of using the scaled atomic values of the Slater integrals for actinide ions, should improve the agreement between RIXS/HERFD calculations and the experiment. Note that the Am dioxide is claimed\textsuperscript{32} to be hyperstoichiometric without high oxygen pressure, which makes it difficult to perform a comparison using the results of present calculations.

\section*{SUMMARY}

The results of crystal-field multiplet calculations of 3d-4f RIXS of An dioxides indicate that the 3d-4f RIXS profiles significantly differ for the An $M_3$ and $M_4$ edges. Both of the selection rules, when the 4f$_{7/2}$ and 4f$_{5/2}$ components are involved in the $5f_n^m \rightarrow 3d^{3}\text{S}^{m+1}$ excitation−de-excitation process at the $M_4$ edge, whereas only the 4f$_{4/2}$ component is involved at the $M_4$ edge, and the final state effects of the RIXS process due to the 4f-5f interaction are contributing to the calculated differences.

The simulation of the HERFD spectra by making cuts across the 3d-4f RIXS maps along the incident energy axis at the emitted energy, corresponding to the maximum of the RIXS results of calculations for the An dioxides, keeping in mind the restricted HERFD resolution, indicates that, in some instances, it will be crucial to calculate the entire 3d-4f RIXS process in order to interpret the HERFD spectra.

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\section*{Notes}

The author declares no competing financial interest.

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