

Crystal-field splitting strength of U-6*d* orbitals in NaUO₃, KUO₃ and RbUO₃

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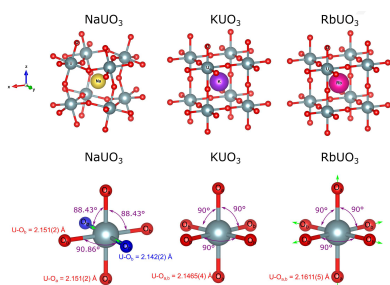
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Here, the uranium valence electronic structures in the perovskite-based ternary uranate systems NaUO₃, KUO₃ and RbUO₃ are reported on the basis of high-energy resolved fluorescence-detected X-ray absorption spectroscopy experiments at the U *L*₃ edge and relativistic quantum chemistry calculations based on density functional theory. Advanced theoretical simulations allowed us to identify the origin of spectral features and to assess the impact of structural distortion within the oxygen octahedra. The octahedral crystal-field strength extracted from both experiments and calculations is reported for all three compounds.

1. Introduction

Uranium compounds have been triggering scientific interest for many decades, not only for their nuclear energy applications but also for more fundamental aspects. Indeed, uranium shows very versatile physicochemical properties due to the wide range of its possible oxidation states, and due to the rather complex behavior of its 5*f* electrons, the origins of which are not yet clearly understood. Uranium 5*f* electrons show an apparent duality in localization, being often found in radially dispersed and hybridized bands in the vicinity of the Fermi level, whereas sometimes they remain localized (Guziewicz *et al.*, 2004; Teterin *et al.*, 1981; Teterin & Teterin, 2004). Consequently, they can simultaneously participate in the conduction band and remain localized, producing a mixed covalent/ionic character of the uranium bonding (Kaltsoyannis, 2013). When working with a significant amount of uranium, dedicated laboratories or specific safety measures are usually required to safely handle the natural radioactivity of uranium, but despite that a large amount of crystallographic, physical, chemical and thermodynamic data is available today (Grenthe *et al.*, 2006); however, the uranium electronic structure is not yet completely understood. The experimental difficulties are also reflected in the complexity of accurate theoretical calculations because of comparable magnitudes of the crystal field, spin–orbit coupling and the electron–electron repulsion interactions affecting simultaneously the electronic structure. Fortunately, one can significantly reduce such a complexity by exploring pure pentavalent



U(V) compounds, where no electron–electron repulsion interactions are expected within the $5f$ shells.

The pentavalent U(V) state has essentially been identified in oxidation products of UO_2 , such as U_4O_9 , U_3O_7 and U_3O_8 . However, with the exception of the pure pentavalent U_2O_5 phase, which has been reported to exist only under very specific conditions (Hoekstra *et al.*, 1970; Gouder *et al.*, 2018), pentavalent uranium always occurs as a mixture with tetra- or hexa-valent uranium in those compounds (Kvashnina *et al.*, 2014; Leinders *et al.*, 2017, 2021).

Pure pentavalent uranium compounds are also commonly observed in ternary systems of uranium and oxygen with one additional cation, *e.g.* from the alkali metal group, or certain alkaline earth and transition metals, as well as some of the rare earth elements (Selbin & Ortego, 1969). Often stable, these ternary compounds may sometimes suffer from slight oxygen non-stoichiometry, leading to a mixed-valence character (Grenthe *et al.*, 2006).

Within the alkali metal uranates MUO_3 series (with M being Li, Na, K, Rb and Cs), a pure U(V) valence state has been confirmed by experimental and theoretical studies for Li, Na, K and Rb, while the CsUO_3 compound was reported as non-existing (Kovba & Golubenko, 1960; Aravamudan *et al.*, 1978; Cordfunke & Ouweltjes, 1981; Chippindale *et al.*, 1989; Ball, 1992; Soldatov *et al.*, 2007; Misra *et al.*, 2008; Liu *et al.*, 2009; Azam & Reshak, 2014; Butorin *et al.*, 2016; Leinders *et al.*, 2017; Lopez *et al.*, 2017; Sanyal *et al.*, 2017; Dorbane *et al.*, 2019; Leinders *et al.*, 2020; Bes *et al.*, 2022).

The series is related to perovskites, as suggested by their chemical formulae MUO_3 , and shows an interesting gradation in structural property and stability. The stability of perovskites is often discussed in terms of a Goldschmidt derived tolerance factor t , based only on the chemical formula, here MUO_3 , and the ionic radii, r_i , of each ion (M , U, O). This tolerance factor is given by

$$t = \frac{r_M + r_O}{\sqrt{2}(r_U + r_O)}. \quad (1)$$

The closer t is to unity, the more stable the regular perovskite structure is, while distorted variants are more likely when t is deviating from unity. Using Shannon's crystal radii for six-coordinated uranium and oxygen, and 12-coordinated alkali, tolerance factors of 0.87, 0.91, 1.00, 1.02 and 1.07 are reported for MUO_3 perovskites with M being Li, Na, K, Rb and Cs, respectively (Ball, 1992; Bartel *et al.*, 2019). CsUO_3 has a tolerance factor that is significantly greater than unity. As discussed by Ball (1992), one would thus expect alternative structures such as that of hexagonal-close-packed BaNiO_3 to be adopted, but no stable CsUO_3 has been reported yet. Having a tolerance factor very close to unity, KUO_3 and RbUO_3 both crystallize in a prototypical undistorted perovskite-type structure in space group $Pm\bar{3}m$, but differ in the value of the lattice constant, *i.e.* 4.2930 (6) Å for KUO_3 and 4.3222 (9) Å for RbUO_3 . The U–O distances are thus slightly longer in RbUO_3 than in KUO_3 with 2.1611 (5) Å and 2.1465 (4) Å, respectively (Van den Berghe *et al.*, 2004).

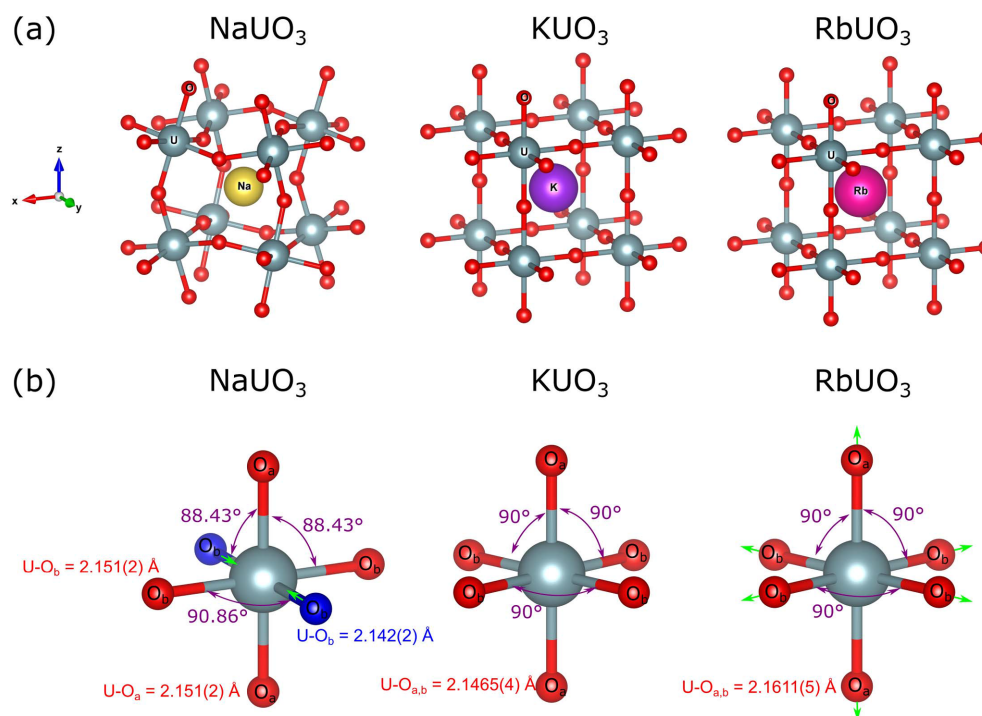
However, NaUO_3 and LiUO_3 have values of t that are significantly less than unity, leading to distorted structures. LiUO_3 adopts the lithium niobate structure, which can be regarded as a heavily distorted perovskite structure, while NaUO_3 crystallizes in an orthorhombically distorted perovskite structure, described in space group $Pbnm$, with lattice constants $a = 5.7739$ (2) Å, $b = 5.9051$ (2) Å, and $c = 8.2784$ (2) Å. The bi-pyramid geometry of the oxygen octahedra observed in KUO_3 and RbUO_3 is slightly distorted in NaUO_3 , forming an oblique bi-pyramid with a parallelogram base (Van den Berghe *et al.*, 2004). For the sake of clarity, Fig. 1 compares the structural changes (bond length and angles) observed in the oxygen octahedra between NaUO_3 , KUO_3 and RbUO_3 . In NaUO_3 , the distances between uranium and two opposite oxygen atoms of the base O_b are 2.142 (2) Å and 2.151 (2) Å, the latter being equal to the distance between uranium and each of the oxygen atoms forming the apices of the bi-pyramid O_a . The square base of the regular bi-pyramid is not maintained, but distorted into a parallelogram with angles of 89.14 (3)° and 90.86 (3)°, instead of 90°. As a result, angles between the four atoms of the base and the apices of the bi-pyramid, $\text{O}_b\text{--U--O}_a$, are no longer 90° but 91.44 (8)°, 91.57 (8)°, 88.43 (8)° and 88.56 (8)°. However, the angles between two opposite oxygen atoms relative to uranium are still equal to 180°.

The bond length and angle distortions of the oxygen octahedra are likely to affect the strength of the crystal field, producing noticeable changes in the uranium electronic structure. Indeed, when the ligand–metal bond length increases, the crystal-field splitting energy generally decreases owing to the overlap between the metal d -orbitals and the ligand orbitals becoming weaker as the distance increases. Similarly, structural distortions likely weaken the metal–ligand orbital overlapping and thus the crystal-field splitting. Therefore, by studying the uranium electronic structure behavior along the alkali MUO_3 series, we are aiming at a better understanding of the electronic properties of uranium. In this paper, we report the results of our study on the uranium valence electronic structure in the prototypical perovskite systems KUO_3 and RbUO_3 , and in the distorted perovskite NaUO_3 , by means of uranium L_3 -edge high-energy resolution/resolved fluorescence-detected X-ray absorption spectroscopy (HERFD-XAS) and state-of-the-art relativistic quantum chemistry calculations based on density functional theory (DFT). The results are found to complement the insights obtained previously on KUO_3 (Bes *et al.*, 2022) using multi-edge HERFD-XAS (uranium L_1 , L_3 and M_4 edges) combined with DFT calculations.

2. Materials and methods

2.1. Sample preparation

Polycrystalline powders of NaUO_3 , KUO_3 and RbUO_3 were prepared following the same methodology for all compounds. Firstly, a batch of U_3O_8 powder was prepared by treating depleted nuclear-grade (according to ASTM C

**Figure 1**

(a) Representation of the cubic arrangement of the eight nearest UO_6 bi-pyramids around the alkali metals in NaUO_3 , KUO_3 and RbUO_3 . The projection view is along the normal of the (723) plane. (b) Representation of the oxygen bi-pyramid around uranium for NaUO_3 , KUO_3 and RbUO_3 . For an easy comparison between all three uranates, all the apices are oriented along z , *i.e.* without the expected tilt shown in (a), but the rotation of the base around the z axis is shown. The distortion in terms of U–O distances (contraction and elongation) is marked with light green arrows, relative to KUO_3 . Nonequivalent distances between uranium and each of the oxygen atoms forming the apices O_a and the base O_b of the bi-pyramid are shown, using the same color as the oxygen atoms they refer to (*e.g.* blue and red O_b in the case of NaUO_3). Main angles between atoms are also indicated. This figure was partially created using the VESTA 3 software (Momma & Izumi, 2011).

753-04) UO_{2+x} powder at 500°C for 4 h in a muffle furnace under normal atmospheric conditions ($\text{N}_2/21 \text{ vol.}\% \text{ O}_2$). Stoichiometric amounts of U_3O_8 were then intimately mixed with the carbonate powder of each respective alkali metal, *i.e.* NaCO_3 , KCO_3 and RbCO_3 ($\geq 99.0\%$ purity according to ACS Reagent), in a small excess (2 wt%), using a zirconia mortar and pestle. Each powder mixture was transferred into Al_2O_3 crucibles and an annealing was performed in a tubular furnace at 800°C for 10 h. A reducing atmosphere (-400 kJ mol^{-1} at 800°C) was applied by flushing the furnace with a gas mixture of $\text{Ar}/0.5 \text{ vol.}\% \text{ O}_2$ (519 ml min^{-1}) and $\text{Ar}/5 \text{ vol.}\% \text{ H}_2$ (481 ml min^{-1}). The used gases were of high purity (99.9992%) and flow rates were accurately controlled using Bronkhorst EL-FLOW mass-flow controllers.

X-ray powder diffraction was performed on each sample to verify phase purity. A PANalytical X'Pert Pro equipped with a Cu LFF X-ray tube and operating in Bragg–Brentano geometry was used. The beam path consisted of a fixed divergence slit (0.5°), a 10 mm beam mask, 0.02 rad Soller slit assemblies and a Ni filter. Diffraction patterns were measured over the angular range $19\text{--}144^\circ 2\theta$ using a position-sensitive detector (PANalytical X'Celerator) with a window of $2.2^\circ 2\theta$. Data assessment, including Rietveld refinement, was performed using the *HighScore Plus* (v4) software. The diffraction patterns obtained from each sample were in accordance with the corresponding calculated patterns from the crystallographic information reported in the literature

(Van den Berghe *et al.*, 2004). Small amounts of a UO_2 impurity phase could be detected in the powder samples of NaUO_3 ($3 \pm 1 \text{ wt}\%$) and RbUO_3 ($5 \pm 1 \text{ wt}\%$). No impurity phase could be detected in the KUO_3 powder sample. The diffraction patterns and resulting Rietveld fits of each sample are available in the supporting information. In the supporting information, a qualitative study of the UO_2 impurity effect on the high-energy resolution fluorescence-detected X-ray absorption near-edge structure (HERFD-XANES) spectral features is available. It demonstrates that the presence of this impurity does not affect the conclusions drawn hereafter.

2.2. High-energy resolution fluorescence-detected X-ray absorption spectroscopy

Uranium L_3 -edge XAS measurements were performed at the Rossendorf Beamline (BM20) (Matz *et al.*, 1999; Scheinost *et al.*, 2021) of the European Synchrotron Radiation Facility (ESRF) operating at an electron-beam energy of 6 GeV in Grenoble, France. The incident energy was scanned using a Si(311) monochromator. HERFD-XAS spectra were collected at room temperature using an X-ray emission spectrometer equipped with five Si(220) crystal analyzers with 1 m bending radius, and a silicon drift X-ray detector in a vertical Rowland geometry (Kvashnina & Scheinost, 2016). The spectrometer was tuned to the maximum of the U $L_3\text{O}_{4,5}$ ($L\beta_5$, $2p_{3/2}\text{--}5d_{5/2}$ transition at 17.063 keV) X-ray emission line using the 10 10 0

reflection at a Bragg angle of 71° (Leinders *et al.*, 2025). The detected intensity was normalized to the incident flux. The estimated beam size was $50\ \mu\text{m}$ (vertically) and $2\ \text{mm}$ (horizontally). A total experimental energy broadening (incident energy convoluted with emitted energy and core-hole lifetime broadening) of $2.2\ \text{eV}$ was achieved, well below the core-hole lifetime broadening of the U L_3 edge ($\sim 8.2\ \text{eV}$). This value is greatly improved compared with the $3.6\ \text{eV}$ achieved in our previous study using a Si(111) monochromator and collecting the U L_3M_5 emission line ($L\alpha_1, 2p_{3/2}-3d_{5/2}$ transition) (Bes *et al.*, 2022). During the experiment reported here, spectra were also collected using the U L_3M_5 emission line for comparison, using the 880 reflection at a Bragg angle of 72° . Energy calibration was achieved through the K -edge excitation energy ($17.038\ \text{keV}$) of a metallic yttrium foil placed in the beam path. The MUO_3 powder was directly inserted and sealed with Kapton foil inside a small recess of a polypropylene sample holder. The total measurement time was $\sim 3\ \text{h}$ per sample. The integration time was $5\ \text{s}$ per point, and 30-min long scans were repeated six times and then merged.

2.3. Electronic structure calculations

Relativistic quantum chemistry calculations were performed using the *Finite Difference Method for Near-Edge Structure* (FDMNES) code (Bunău & Joly, 2009). Atomic clusters of $9\ \text{\AA}$ were used in self-consistent-field calculations using the Dirac–Slater approach. The Poisson equation was solved to obtain the Coulomb potential from the superposed self-consistent atomic densities in the considered cluster. The energy-dependent exchange–correlation potential was evaluated using the local density approximation, and constructed using both the real Hedin–Lundqvist and Von Barth formulations. These calculations were based on static atom supercells of hundreds of atoms, and thermally induced disorder was not considered. Because of the presence of heavy nuclei (U), spin–orbit effects were taken into account, but no spin-polarization effect was noticed from the comparison of spin-polarized spectra. Finally, calculations were performed with and without the quadrupolar transition probability in order to account for the $5f$ contribution on the final spectra at the U L_3 edge.

3. Results and discussion

Fig. 2 shows the obtained HERFD-XAS spectra of NaUO_3 , KUO_3 and RbUO_3 using the U $L_3O_{4,5}$ emission line, together with the spectra collected using the U L_3M_5 emission line and the simulated spectra using the FDMNES code. Superimposed experimental spectra, as well as their comparison with their corresponding simulated but convoluted spectra, are available in the supporting information.

Thanks to the tremendous gain in energy resolution when using the U $L_3O_{4,5}$ emission line compared with the spectra collected using the U L_3M_5 emission line, the crystal-field splitting of the uranium $6d$ orbitals is well resolved in all three uranates. For all three compounds, the maximum of the white

line occurs at $17172.9 \pm 0.5\ \text{eV}$, while the maximum of the first derivative, which corresponds to the uranium L_3 -edge energy position E_0 , is found at $17169.9 \pm 0.5\ \text{eV}$. Therefore, no energy shift in the edge position is observed between all three compounds.

The occurrence of a quadrupolar transition of $2p \rightarrow (n)f$ has been previously reported on many uranium compounds.

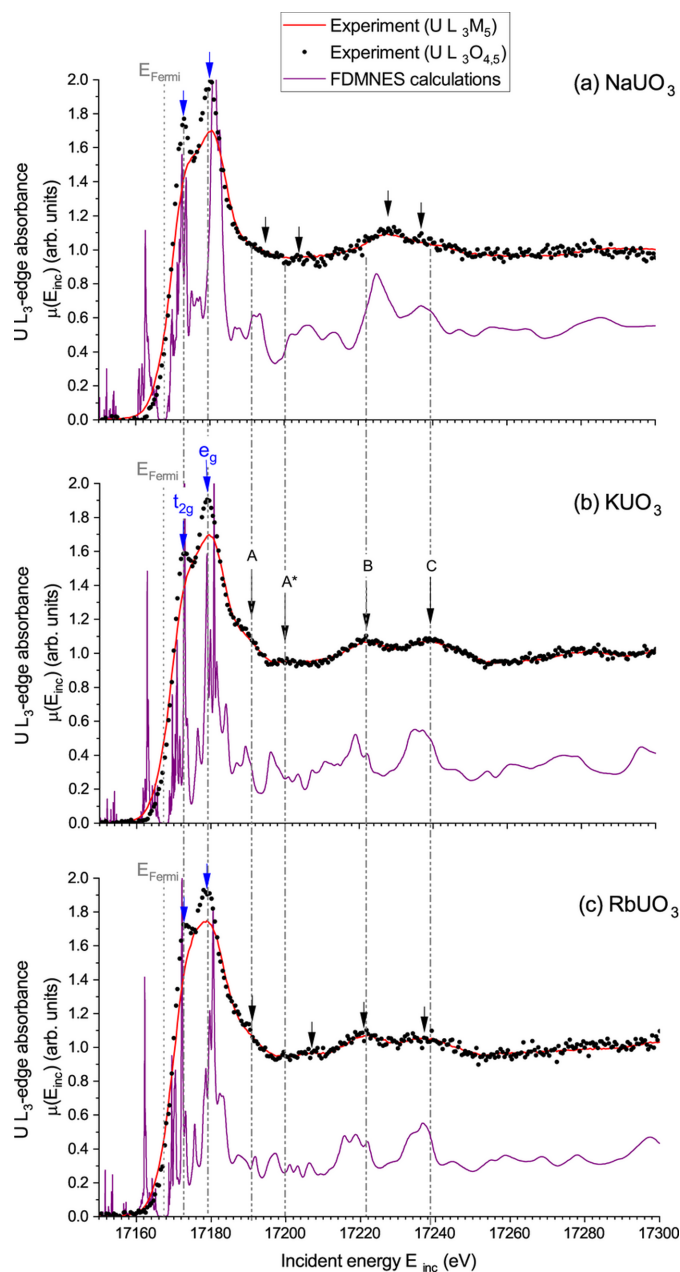


Figure 2

Uranium L_3 -edge HERFD-XAS and the corresponding simulated spectrum using FDMNES for NaUO_3 , KUO_3 and RbUO_3 . The calculated spectra account for both dipolar and quadrupolar transitions (see the supporting information for comparison of simulated spectra with and without the quadrupolar transition). The Fermi energy level is indicated with a vertical dotted line. Vertical dashed–dotted lines indicate the positions of features A, A*, B and C, as experimentally observed in KUO_3 , to guide the eye. Blue arrows highlight the crystal-field splitted U- d orbitals (t_{2g} and e_g), while black arrows indicate the positions of the post-edge observed features.

Vitova *et al.* (2010) first observed such a transition as a shoulder in the rising edge on UO_2 , $[\text{UO}_2\text{py}_5][\text{KI}_2\text{py}_2]$ and $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$. Later on, Kvashnina *et al.* (2014) reported a similar observation on U_4O_9 and U_3O_8 , while the same observation was also made on $[\text{Ni}(\text{H}_2\text{O})_4]_3[\text{U}(\text{OH}, \text{H}_2\text{O})(\text{UO}_2)_8\text{O}_{12}(\text{OH})_3]$ (Bès *et al.*, 2016). Nevertheless, no quadrupolar transition is observed in our experimental spectra. As previously discussed for KUO_3 (Bes *et al.*, 2022), this is essentially a consequence of both the partial overlap between U-5*f* and U-6*d* electrons, being also separated by about 2 eV in NaUO_3 and RbUO_3 , and the weak strength of the quadrupolar transition relative to the dipolar one, as confirmed by our calculations (see the supporting information). The weak quadrupolar feature thus remains hidden within the white line for all three uranates.

The splitting of the U-6*d* orbitals follows the expected trends when comparing KUO_3 and RbUO_3 : the crystal-field strength is weakened when increasing the ligand–metal distance. However, if the structural distortions in NaUO_3 are expected to break the symmetry of the O octahedra, this will reduce the strength of the crystal-field splitting. Nevertheless, the symmetry break is probably not enough in NaUO_3 because one may observe a slight increase of the U-6*d* splitting when comparing KUO_3 and NaUO_3 spectra. This increase is the probable consequence of the shortening of some of the ligand–metal distances, having more effect on the crystal-field strength compared with the bonding angle distortions.

In addition to the split white line, several features are clearly visible in the post-edge region. The same features A, A*, B and C, as already reported earlier for KUO_3 (Bes *et al.*, 2022), are also observed in NaUO_3 and RbUO_3 , but they appear at slightly different energy positions. All these observed spectral features are reproduced by the calculations in terms of number and relative intensity, but with a few electronvolt discrepancies on their positions. Therefore, a very good agreement between experiments and calculation is demonstrated. A comparison between the experimentally observed and calculated energy positions of the spectral features is reported in Table 1.

The spectra of KUO_3 and RbUO_3 are very close to each other, as expected given their structural similarities. The longer U–O distance, however, seemingly affects the position of the A* feature, shifting it to higher energies by 8 eV relative to A* in KUO_3 . A closer look at the calculated spectra gives another explanation for such a surprisingly large energy shift. Indeed, a weak feature situated nearby the expected energy is observed, which is likely to be the missing A* feature. A* is probably not observed in the experimental spectrum of RbUO_3 because of the occurrence of a new feature, A**, situated about 10 eV above A* and because of statistical uncertainties. In addition to their weak intensities, the energy difference between the calculated positions of A and A* is reduced to 5.3 eV compared with the 7.2 eV observed in KUO_3 , making them more difficult to distinguish. Structural distortion in NaUO_3 has a stronger effect on the spectral features. A and A* are shifted to higher energies but remain separated by about 9 eV. B is also shifted to higher energies

Table 1

Energy positions of experimentally observed and calculated uranium L_{3-} edge HERFD-XAS spectral features for NaUO_3 , KUO_3 and RbUO_3 .

Differences between the experimental and calculated values, $\Delta_{\text{exp-cal}}$, are also given for convenience.

Uranate	Feature	Experimental	Calculated	$\Delta_{\text{exp-cal}}$
NaUO_3	t_{2g}	17172.9 ± 0.5 eV	17173.5 ± 0.2 eV	−0.6 eV
	e_g	17179.7 ± 0.5 eV	17180.3 ± 0.2 eV	−0.6 eV
	A	17195 ± 1 eV	17192.3 ± 0.2 eV	2.7 eV
	A*	17204 ± 1 eV	17204.9 ± 0.2 eV	−0.9 eV
	B	17228.0 ± 0.5 eV	17224.8 ± 0.2 eV	3.2 eV
	C	17236.9 ± 0.5 eV	17237.3 ± 0.2 eV	−0.4 eV
KUO_3	t_{2g}	17172.9 ± 0.5 eV	17173.3 ± 0.2 eV	−0.4 eV
	e_g	17179.2 ± 0.5 eV	17180.2 ± 0.2 eV	−1.0 eV
	A	17191 ± 1 eV	17189.9 ± 0.2 eV	1.1 eV
	A*	17200 ± 1 eV	17197.1 ± 0.2 eV	2.9 eV
	B	17222.0 ± 0.5 eV	17219.5 ± 0.2 eV	2.5 eV
	C	17239.2 ± 0.5 eV	17236.6 ± 0.2 eV	2.6 eV
RbUO_3	t_{2g}	17172.9 ± 0.5 eV	17172.7 ± 0.2 eV	0.2 eV
	e_g	17179.1 ± 0.5 eV	17180.0 ± 0.2 eV	−0.9 eV
	A	17191 ± 1 eV	17191.6 ± 0.2 eV	−0.6 eV
	A*	–	17196.9 ± 0.2 eV	–
	A**	17207 ± 1 eV	17206.3 ± 0.2 eV	0.7 eV
	B	17220.9 ± 0.5 eV	17220.4 ± 0.2 eV	0.4 eV
	C	17237.1 ± 0.5 eV	17237.0 ± 0.2 eV	0.1 eV

Table 2

Energy difference of experimentally observed, Δ_{exp} , and calculated, Δ_{cal} , spectral features for NaUO_3 and RbUO_3 relative to KUO_3 .

Uncertainties are ± 1 and ± 0.4 eV for experiments and calculations, respectively.

Uranate	Feature	Δ_{exp}	Δ_{cal}
NaUO_3	t_{2g}	0 eV	0.2 eV
	e_g	0.5 eV	0.1 eV
	A	1 eV	2.4 eV
	A*	4 eV	7.8 eV
	B	6 eV	5.3 eV
	C	2.3 eV	0.7 eV
RbUO_3	t_{2g}	0 eV	−0.6 eV
	e_g	−0.1 eV	−0.2 eV
	A	1 eV	1.7 eV
	A*	–	−0.2 eV
	B	−1.1 eV	0.9 eV
	C	−2.1 eV	0.4 eV

while C is moved to lower energies, reducing their energy difference from ~ 17 to 9 eV. The energy differences of the positions of the spectral features for NaUO_3 and RbUO_3 relative to KUO_3 are reported in Table 2. In this table, despite the large uncertainties associated with some reported values, the effect of the structural distortion in NaUO_3 is clearly visible for the A* and B features, where values of Δ_{exp} and Δ_{cal} are significantly different from 0.

Figs. 3 and 4 show the calculated U-*d* and O-*p* density of states, respectively. We refer to the supporting information for the other U-related density of states, as well as the counter-ion density of states. To gain more insight into the nature of the spectral features, these partial densities of states are represented as cubic harmonics. The U-*d* and O-*p* orbitals involved in each of the features are reported in Table 3, where individual orbitals are mentioned only when a significant contribution is observed in Fig. 3 or in Fig. 4. When considering the crystal field in an octahedral geometry, the U-*d* orbitals are

divided into two degenerated groups: t_{2g} , composed of $U-d_{xy}$, $U-d_{yz}$ and $U-d_{zx}$ orbitals; and e_g , composed of $U-d_{z^2}$ and $U-d_{x^2-y^2}$ orbitals. The former is pulled to lower energy, while the latter is pushed to higher energy. These two groups are clearly visible for KUO_3 and $RbUO_3$ for which a perfect overlap of the orbitals expected in each group is observed in the calculations. For $NaUO_3$, the perfect octahedral symmetry is broken as a consequence of the structural distortion, releasing the degeneracy of the orbitals initially involved in t_{2g} and e_g . However, such a release is not very strong, and two groups of almost overlapping orbitals remain visible despite the occurrence of a larger density of states observed in between t_{2g} and e_g . Another surprising finding is the group exchange of the $U-d_{xy}$ and $U-d_{x^2-y^2}$ orbitals. One plausible explanation for this exchange is found by considering that the octahedra are approximately rotated by 45° around the z axis (*i.e.* the O_a – O_a axis) when passing from KUO_3 to $NaUO_3$. The main difference between the $U-d_{xy}$ and $U-d_{x^2-y^2}$ orbitals originates from the directions where the lobes are pointing to: along the referential x and y axes or in between. Therefore, a 45° rotation is switching from one to the other.

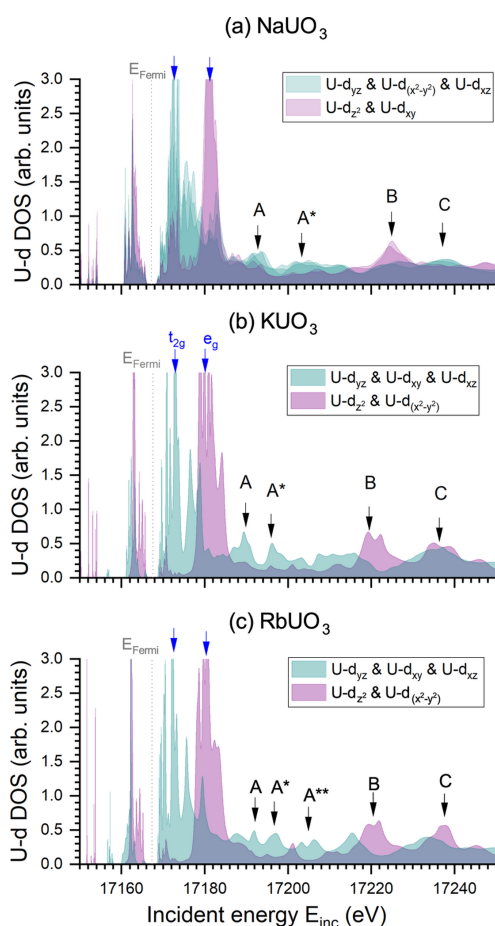


Figure 3
Calculated $U-d$ partial density of states (DOS), here expressed as cubic harmonics, for (a) $NaUO_3$, (b) KUO_3 and (c) $RbUO_3$. The Fermi energy level is indicated with a vertical dotted line. Blue arrows highlight the crystal-field split $U-d$ orbitals (t_{2g} and e_g). The positions of the post-edge features A, A^* , A^{**} , B and C from the simulated spectra are indicated by black arrows.

Table 3

The $U-d$ and $O-p$ cubic harmonics contributing to the spectral features.

Uranate	Feature	Main $U-d$ cubic harmonics	Main $O-p$ cubic harmonics
KUO_3	t_{2g}	$U-d_{xy}, U-d_{xz}, U-d_{yz}$	$O-p_x$
	e_g	$U-d_{z^2}, U-d_{x^2-y^2}$	$O-p_y, O-p_z$
	A	$U-d_{xy}, U-d_{xz}, U-d_{yz}$	$O-p_x$
	A^*	$U-d_{xy}, U-d_{xz}, U-d_{yz}$	–
	B	$U-d_{z^2}, U-d_{x^2-y^2}$	$O-p_y, O-p_z$
$NaUO_3$	C	All	$O-p_x$
	t_{2g}	$U-d_{x^2-y^2}, U-d_{xz}, U-d_{yz}$	$O_a-p_x, O_a-p_y, O_b-p_z$
	e_g	$U-d_{z^2}, U-d_{xy}$	$O_b-p_x, O_b-p_y, O_a-p_z$
	A	$U-d_{x^2-y^2}, U-d_{xz}, U-d_{yz}$	O_b-p_z
	A^*	$U-d_{x^2-y^2}, U-d_{xz}, U-d_{yz}$	–
$RbUO_3$	B	$U-d_{z^2}, U-d_{xy}$	–
	C	$U-d_{x^2-y^2}, U-d_{xz}, U-d_{yz}$	–
	t_{2g}	$U-d_{xy}, U-d_{xz}, U-d_{yz}$	$O-p_x$
	e_g	$U-d_{z^2}, U-d_{x^2-y^2}$	$O-p_y, O-p_z$
	A	$U-d_{xy}, U-d_{xz}, U-d_{yz}$	$O-p_x$
	A^*	$U-d_{xy}, U-d_{xz}, U-d_{yz}$	–
	A^{**}	$U-d_{xy}, U-d_{xz}, U-d_{yz}$	–
	B	$U-d_{z^2}, U-d_{x^2-y^2}$	$O-p_y, O-p_z$
	C	$U-d_{z^2}, U-d_{x^2-y^2}$	$O-p_x$

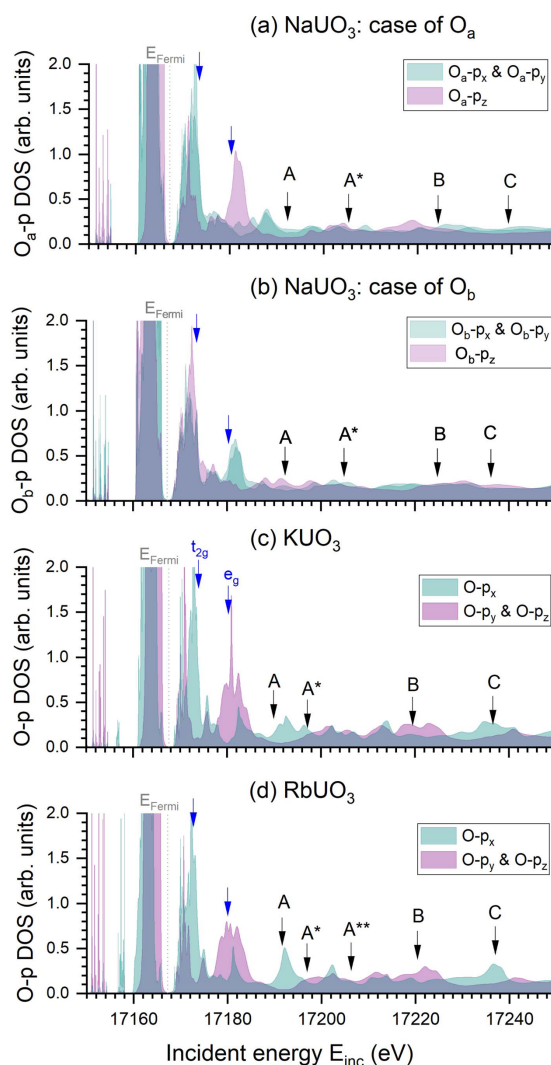


Figure 4
Calculated $O-p$ partial density of states, here expressed as cubic harmonics, for (a) the apices oxygen O_a from $NaUO_3$, (b) the base oxygen O_b from $NaUO_3$, (c) KUO_3 and (d) $RbUO_3$. The Fermi energy level is indicated with a vertical dotted line. Blue and black arrows highlight the calculated positions of the spectral features from Fig. 3.

The crystal-field strength, $10Dq$, can be deduced from the energy separation between t_{2g} and e_g (see Table 1). Corresponding experimental values of 6.8 ± 1 eV, 6.3 ± 1 eV and 6.2 ± 1 eV, as well as calculated values of 6.8 ± 0.4 eV, 6.9 ± 0.4 eV and 7.3 ± 0.4 eV, were estimated for NaUO_3 , KUO_3 and RbUO_3 , respectively. These values do not clearly differ from each other within the uncertainty range. Thus, no significant effect of the longer U–O distance or the slight structural distortion of the octahedra are noticeable. This is in line with the experimental and theoretical crystal-field strengths of 6 ± 2 eV and 8.2 ± 0.4 eV, respectively, reported in FeUO_4 , which exhibits strong structural distortion of the oxygen octahedra (Yomogida *et al.*, 2022). However, on the sole basis of our calculations, the effects of the spin–orbit coupling, the p – d multiplet interaction or the $2p$ core hole in the observed splitting cannot be ruled out and may somehow compensate the changes in the crystal field. Further theoretical studies are therefore required to unravel the potentially intricate roles of these effects and the crystal field in these uranates.

If no significant difference is surprisingly observed in the U- $6d$ splitting strength of all three uranates, the electronic structure still differs in the post-edge. According to the calculations, feature A originates mainly from U- d states U- d_{yz} , U- d_{xy} and U- d_{xz} for KUO_3 and RbUO_3 ; and from U- d states U- d_{yz} , U- $d_{x^2-y^2}$ and U- d_{xz} for NaUO_3 . No significant contribution from O- p states is noticed for KUO_3 , but the O- p_z state slightly contributes for NaUO_3 and the O- p_x state strongly contributes for RbUO_3 . Feature A* also originates mainly from U- d states, with no significant contribution from O- p states in KUO_3 and RbUO_3 . In RbUO_3 , A** is similar to A*. In NaUO_3 , slight contributions of the O- p_x , O- p_y and O- $a-p$ states are observed in A*. Feature B is essentially related to U- d_{z^2} and U- $d_{x^2-y^2}$ (U- d_{z^2} and U- d_{xy} for NaUO_3), with also a significant contribution of O- p_x in KUO_3 and RbUO_3 . In the case of NaUO_3 , the O- p contribution is less clear, with no significant peak observed in the O- p density of states, except for O- $a-p_x$. Feature C appears to result from a mixture of all U- d electrons in KUO_3 , but this is not the case for RbUO_3 and NaUO_3 . In the former compound, U- d_{z^2} and U- $d_{x^2-y^2}$ start to dominate, while in the latter compound, it is U- d_{yz} , U- $d_{x^2-y^2}$ and U- d_{xz} that dominate. Moreover, contributions of O- p_y and O- p_z are observed for KUO_3 and RbUO_3 . The contribution of O- p states in NaUO_3 is less clear, but a probable inversion is observed between O_b and O_a in terms of which orbital contributes. The U- s , U- p and U- f orbitals were found to not have a significant contribution to the observed features (see the supporting information). Similarly, the potential binding interactions of the counter ion were ruled out based on their calculated density of states (available as well in the supporting information), with no significant energy overlap between the observed spectral features and the calculated density of states. This result was also confirmed through comparison of the calculated spectra of NaUO_3 and RbUO_3 with and without the counter ion replaced by K without changing the structure of the uranates (also available in the supporting information).

4. Conclusions

Here, we reported HERFD-XAS data obtained at the uranium L_3 edge of NaUO_3 , KUO_3 and RbUO_3 . By collecting the U $L_3O_{4,5}$ emission line, an overall resolution of 2.2 eV was achieved, allowing the separation of the split U- $6d$ orbitals to become visible. The experimental data were compared with theoretical calculations to identify the nature of the U- d and O- p orbitals contributing to the observed spectral features. These calculations are in very good agreement with the experiments. More insight into the nature of the spectral post-edge features was obtained by using U and O partial density of states projected into cubic harmonics. The strength of the crystal-field splitting of the U- $6d$ states was evaluated experimentally to 6.8 ± 1 eV, 6.3 ± 1 eV and 6.2 ± 1 eV, and theoretically to 6.8 ± 0.4 eV, 6.9 ± 0.4 eV and 7.3 ± 0.4 eV, for NaUO_3 , KUO_3 and RbUO_3 , respectively. No significant difference was observed here despite the structural differences existing between all three uranates. One possible hypothesis is that the crystal-field strength may be compensated due to opposite effects on orbitals by, for example, spin–orbit coupling, p – d multiplet interaction or the $2p$ core hole. If preliminary studies tend to demonstrate that the core hole slightly enhances the crystal field, the reason behind our observations remains to be clarified by further studies, supported by more advanced theories. The four post-edge features already observed in KUO_3 are also present in NaUO_3 and RbUO_3 , but their character in terms of U- d and O- p cubic orbital mixtures is affected by the U–O distance and the structural distortion of the oxygen octahedra around uranium atoms.

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