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Study of the electronic structure of the actinide tetrabromides ThBr₄ and UBr₄ using ultraviolet photoelectron spectroscopy and density functional calculations

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Ultraviolet photoelectron spectra of UBr₄ and ThBr₄ have been recorded in the gas-phase and interpreted using relativistic density functional calculations. For ThBr₄, eight bands were observed which are interpreted as ionization from the five Br 4*p* symmetry orbitals of a Br₄ unit in T_d symmetry, with three of the bands [the $(4t_2)^{-1}$, $(1t_1)^{-1}$, and $(3t_2)^{-1}$ ionizations] each being split into two by spin-orbit interaction. The observed splittings are rationalized in terms of the Th 6*p* and Br 4*p* contributions to the orbitals and by comparison with the known ultraviolet photoelectron spectra of ThF₄ and ThCl₄. The first vertical ionization energy (VIE) of ThBr₄ was measured as (10.92 ± 0.03) eV. UBr₄ shows a very similar photoelectron spectrum with an extra band at (9.65 ± 0.02) eV VIE. This is associated with a $(5t_2)^{-1}$ (U 5*f*,6*d*) ionization. Supporting matrix isolation infrared experiments were also carried out under very similar vaporization conditions to those used in the photoelectron spectroscopy experiments to check the composition of the vapor beams used. In these experiments, the T_2 stretching modes of ThBr₄ and UBr₄ have been measured as 230 ± 2 and 239 ± 2 cm⁻¹, respectively. Both the photoelectron and infrared matrix isolation spectra are consistent with an effective tetrahedral geometry for UBr₄ and ThBr₄. © 2001 *American Institute of Physics*. [DOI: 10.1063/1.1370945]

I. INTRODUCTION

The uranium and thorium tetrahalides play important roles in nuclear fuel enrichment and reprocessing¹ and they have been studied in some detail both in the solid state and the gas phase. Uranium tetrafluoride is of particular importance in the nuclear industry as it acts as a precursor for both uranium metal and UF₆ required for isotope enrichment processes. UF₄ is usually prepared from UO₂, extracted from uranium ore, by reaction with HF at 850 K in a fluidized-bed reactor. It is then directly fluorinated to produce UF₆ for isotope separation. Similarly thorium tetrafluoride is a key intermediate for the reprocessing and recovery of thorium metal.¹

The investigation of the electronic structure of the uranium and thorium tetrahalides provides a good opportunity to study the role of metal 5*f* electrons in chemical bonding.^{2–6} The gas-phase He(I) photoelectron spectra of UF₄, ThF₄, UCl₄, and ThCl₄ have been recorded previously.² The spectra were first interpreted using nonrelativistic multiple-scattering SCF-X α calculations² and later reinterpreted using relativistic Hartree–Fock–Slater (HFS) density functional calculations.⁷ For each tetrafluoride or tetrachloride, the results are consistent with an effective tetrahedral geometry with no evidence of any Jahn–Teller distortion away from tetrahedral symmetry. In the uranium tetrahalides, a distortion from tetrahedral symmetry is possible because of the open-shell degenerate ground state and gas-phase electron diffraction studies indicated a structure of C_{2v} symmetry with equal metal-halogen bond lengths.⁸ Recently a density functional study of the ground states of the thorium tetrahalides has also provided estimates of equilibrium bond lengths and harmonic vibrational frequencies of ThX₄ (X=F, Cl, Br, and I).⁹ These tetrahalides were all found to have tetrahedral minimum energy geometries in their ground states. In summary, although reasonably detailed experimental studies have been undertaken to probe the electronic structure of the uranium and thorium tetrafluorides and tetrachlorides, relatively little work has been undertaken on the corresponding tetrabromides, UBr₄ and ThBr₄.

Electron-impact high temperature mass spectrometric studies of the uranium and thorium halides^{10–12} have measured the appearance energy of ThBr₄⁺ from ThBr₄ as (10.4 \pm 0.3) eV (Ref. 10) and UBr₄⁺ from UBr₄ as (9.6 \pm 0.3) eV.¹¹ These represent the only available values for the first ionization energies of these molecules.

The aim of this present work was to record He(I) photoelectron spectra of ThBr₄ and UBr₄ in the vapor phase using a high temperature photoelectron spectrometer which uses radio frequency induction heating to vaporize a solid sample.^{13–15} It was proposed to compare the photoelectron spectra obtained for ThBr₄ and UBr₄ with those previously recorded for UF₄, ThF₄, UCl₄, and ThCl₄. Relativistic density functional calculations of vertical ionization energies (VIEs) were also performed for all six MX₄ tetrahalides (M =Th, U; X=F, Cl, Br). Comparison with experimental VIEs should allow ionic state assignment to be achieved for the tetrabromides and trends in ionization energies and ionic

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TABLE I. Comparison of the unit cell parameters used to reproduce the x-ray diffraction pattern obtained from a UBr_4 single crystal prepared in this work, with those reported in the literature (Ref. 18).

Crystal parameter	Values from single crystal diffraction pattern ^a	Reference parameters Ref. 18
Space group	C2/m	C2/m
a	11.01	11.04(2)
b	8.77	8.76(2)
С	7.06	7.04(1)
α	90.00	90.00
β	94.24	94.05(8)
γ	90.00	90.00

^aSingle crystal data were obtained using the Nonius COLLECT software, incorporating the DENZO Package (Refs. 38 and 39).

state spin-orbit splittings in the metal tetrahalides deduced as the halide ligand gets heavier. Supporting matrix isolation experiments were also carried out under very similar vaporization conditions in order to confirm the composition of the vapor and obtain infrared spectra of the MBr₄ species.

II. EXPERIMENT

ThBr₄ was commercially available as an anhydrous solid (Pfaltz and Bauer, 99.5%). It was used as received, but samples were kept in a desiccator prior to use and loaded into a furnace under nitrogen prior to transfer to the photoelectron spectrometer. This reduced, but did not eliminate, hydration of the sample.

UBr₄ was prepared from UO₂ (Strem Chemicals) using an existing preparative route.¹⁶ This involved passing bromine in dry nitrogen over a heated UO₂/C mixture at 1300 K. The product, which was collected downstream of the solid UO₂/C mixture in a long reaction tube, was initially identified as UBr₄ by its appearance as a tan colored powder¹⁷ which distinguished it from the main likely impurity, UO₂Br₂, which is a brick-red color.

A small sample of the product was sealed in a Lindemann capillary and examined by x-ray diffraction using a Nonius Kappa CCD diffractometer with Mo $K\alpha$ radiation (λ =0.710 69 Å). A good powder pattern was obtained from a single one degree image, but this also showed single crystal reflections. Following recording of a further ten one degree images, it proved possible to index all observed reflections, as one set, to give a cell analogous to that previously reported for UBr₄ (Ref. 18) (see Table I). The powder lines were all compatible with this cell, indicating a homogeneous sample.

The general features of the matrix isolation equipment used for this work have been described previously.¹⁹ Matrix isolation infrared studies on UBr₄ and ThBr₄ involved vaporization of the samples in the temperature range 720–800 K and subsequent co-condensation with argon onto a cesium iodide window cooled to ~12 K. The bromide samples were contained in silica holders and extensively degassed at ~600 K in order to remove traces of HBr, arising from hydrolysis. Final purification was by sublimation immediately prior to co-condensation with argon. Pure samples of solid UBr₄ were yellow-brown in color, while those of ThBr₄ were white. Deposition times were typically 1-2 h and the argon matrix was estimated to be at least 1000-fold in excess relative to the metal tetrabromide in the final matrix used for spectroscopic study. Infrared spectra were recorded over the range 4000–180 cm⁻¹ using a PE983 infrared spectrometer, supported by standard data processing facilities.

In the photoelectron experiments, the actinide tetrabromide molecules, UBr_4 and $ThBr_4$, were produced in the gas phase by vaporizing a solid sample from an inductively heated graphite furnace.^{13,14} ThBr₄ and UBr₄ are known to vaporize congruently.^{10–12} The temperature range over which vaporization occurred, and over which photoelectron spectra were recorded with reasonable signal-to-noise ratios, was 870-1000 K for ThBr₄ and 820-970 K for UBr₄ as estimated from measurements made with a chromel-alumel thermocouple attached to the furnace. For both tetrabromides, it was found necessary to bake the sample on the photoelectron spectrometer, initially at 550 K for 1 h to remove residual water and hydrogen bromide. Any MO₂Br₂ (M=Th or U) that may have been present as a minor impurity in the MBr₄ samples would have decomposed (probably to less volatile MO₂ and MBr₄) at the temperatures at which photoelectron spectra were obtained.1,17,20

In a typical photoelectron experiment, a solid MBr_4 sample was loaded into a graphite furnace in a glove bag under dry nitrogen. This was then transferred as quickly as possible to the photoelectron spectrometer, which was immediately evacuated to minimize exposure to air. Both ThBr₄ and UBr₄ hydrolyze in air with UBr₄ appearing to hydrolyze more rapidly. The photoelectron spectrometer and inductively heated furnace system used in this work have been described previously.^{13–15} The typical resolution of the spectrometer under the conditions at which He(I) (21.22 eV) photoelectron spectra were recorded was 25-35 meV full width at half maximum (FWHM), as measured for the $(3p)^{-1}$ He(I) ionization of argon. Spectra were calibrated using argon, methyl iodide, nitrogen, carbon monoxide, and hydrogen bromide. The transmission of the spectrometer, which varies linearly with pass energy, was checked regularly using oxygen. Under conditions at which the MBr₄ spectra were recorded, it was found to be acceptable, as the fifth band of oxygen could be observed with reasonable intensity relative to the other four oxygen bands. Hence, the relative band intensities in the MBr₄ spectra presented in this work are not unduly affected by loss of intensity at lower kinetic energy.

III. COMPUTATIONAL DETAILS

Relativistic density functional theory (DFT) calculations of vertical ionization energies were carried out for the actinide tetrahalides MX_4 (M=U, Th; X=F, Cl, Br) to facilitate a complete valence ionic state assignment of their ultraviolet photoelectron spectra.

Calculations for the actinide halides ThF_4 , $ThCl_4$, $ThBr_4$, UF_4 , UCl_4 , and UBr_4 were carried out using the Amsterdam Density Functional (ADF) program²¹ on the Columbus machine at the Rutherford Appleton Laboratories.²² The $ThBr_4$ and UBr_4 results presented here assumed a tetrahedral geometry with metal–bromine bond lengths being

taken from gas-phase electron diffraction studies⁸ (2.73 Å for ThBr₄ and 2.69 Å for UBr₄).

For both uranium and thorium tetrabromide, a relativistic frozen core was used. Calculations were carried out using the metal core (a) frozen up to the 6p level, and (b) frozen up to the 5*d* level. This allowed the effect of having the metal 6porbitals frozen or unfrozen on the computed VIEs to be investigated. For the bromine atoms, the 4s and 4p orbitals were in the valence region in these calculations, while the lower-lying orbitals were in the frozen core. Including the Br 3d orbitals in the valence region was found to have negligible effect on computed VIEs. Therefore, with the metal 6s and 6p orbitals not frozen, the valence space contained the metal 6s, 6p, 7s, and 5f orbitals and the bromine 4sand 4p orbitals. A triple zeta plus polarization (TZ+P) Slater-type basis set was used. Also, the gradient-corrected BLYP functional, which includes the uniform electron gas exchange, the Becke 88 correction to exchange²³ and the Lee-Yang-Parr correlation functional²⁴ was utilized. Relativistic effects are taken into account using a relativistic frozen core and a perturbation treatment in the valence region.^{25,26} This method has been shown to give reliable minimum energy geometries and ionization energies for compounds containing heavy elements.²⁷⁻²⁹ In order to calculate VIEs, the transition state method was used. This involved half an electron being removed from each orbital, in turn, and the negative of the orbital energy of the resulting partially filled orbital, obtained from a converged calculation, being equated to the VIE. These VIEs were then compared with the experimentally measured VIEs. The transition state method has been shown to give results which are equivalent to Δ SCF calculations^{30,31} and this was confirmed by performing transition state and Δ SCF calculations on VIEs on ThBr_4 .

IV. RESULTS AND DISCUSSION

A. Matrix isolation studies

Figure 1 shows the argon matrix infrared spectra obtained from samples of UBr₄ and ThBr₄ in the frequency region 300-200 cm⁻¹. One band is observed for each tetrabromide, and this feature is assigned in each case to the T_2 stretching mode of the T_d monomer. The only other absorptions present in these spectra were bands arising from traces of adventitious water at \sim 3700 and 1600 cm⁻¹, and a number of sharp, weak features in the region $2300-2600 \text{ cm}^{-1}$ which may be assigned to HBr and its oligomers. These latter features appeared at considerably lower vaporization temperatures than the metal tetrabromide absorptions, and their positions corresponded very closely to the absorptions previously reported for HBr in argon over a range of concentrations.³² It is particularly significant that no absorptions were observed in the U-O (or Th-O) stretching region (typically 700–1000 cm^{-1}) indicating that under the vaporization conditions used, no uranium (or thorium) oxybromides were produced.

Previous studies on UBr₄ have assumed T_d symmetry in the gas-phase.^{8,33,34} In an experimental gas-phase infrared study, a single infrared-active band has been reported at



FIG. 1. Infrared spectra of the 200–300 cm⁻¹ spectral region obtained for UBr₄ and ThBr₄ isolated in argon matrices at 12 K.

 233 ± 3 cm⁻¹, and assigned as the T_2 stretch.³⁴ This value is in very satisfactory agreement with the results obtained in this present work (239 ± 2 cm⁻¹, see Fig. 1), when one considers that the gas phase band contour would be expected to include an appreciable contribution from a hot band.

There appears to be no published infrared spectral data for molecular ThBr₄, but the experimental value of 230 ± 2 cm⁻¹ for the T_2 stretching mode observed here compares very favorably with the recommended value of 227 cm⁻¹ obtained from density functional calculations with a B3LYP functional.⁹

There are no other infrared active stretching modes predicted for T_d UBr₄ and ThBr₄ and the infrared active T_2 bends are anticipated to lie at ~45 cm⁻¹ (Refs. 8 and 9), which is well below the lower limit of the infrared spectrometer used. There is no evidence from these results of any significant distortion from T_d symmetry, and indeed, it can be shown that if a static C_{3v} distortion of more than ~5° in bond angle were present in these tetrabromides, the effect would be to split the observed " T_2 " stretching modes by ~8 cm⁻¹, which would be clearly visible in the matrix infrared spectra.

These matrix isolation infrared measurements therefore provide support for the purity of the tetrabromide effusive beams used in these studies, and for the T_d symmetry of molecular UBr₄ and ThBr₄. They also provide the first experimental measurement of the T_2 stretching mode in ThBr₄.

B. Photoelectron spectra

If the actinide tetrabromides, UBr₄ and ThBr₄, have tetrahedral geometries then the transformation properties of the metal 7s, 6p, and 6d orbitals and the halogen 4s and 4p orbitals can be readily determined. Also, metal 5f orbitals in T_d symmetry transform as a_1 , t_1 , and t_2 . One way of understanding the valence energy level ordering as well as the character of each valence level in these MBr₄ molecules is to compute the valence energy levels of the Br₄ group, at the geometry it has in the MBr₄ neutral molecule, and study the



FIG. 2. Computed orbital energies for M, Br, Br₄, and MBr₄ obtained from non-relativistic density functional calculations for (a) M=Th and (b) M=U. The $1a_1$ molecular orbital in the MBr₄ compounds is essentially a metal 6s orbital. It is the lowest energy molecular orbital in the MBr₄ compounds and is too low in energy to be shown in (a) and (b).

effect of the introduction of the central metal M. This has been done for ThBr₄ and UBr₄. The eigenvalues obtained from non-relativistic ADF density functional calculations have been plotted for M, Br_4 , and MBr_4 (for M=Th and U) in Figs. 2(a) and 2(b).

The following order of the Br4p symmetry orbitals was obtained for the Br₄ unit



FIG. 3. He(I) photoelectron spectrum obtained for (a) ThBr₄ and (b) UBr₄.

 $3t_2 < 1e < 1t_1 < 3a_1 < 4t_2$.

These symmetry orbitals interact with the orbitals of the central atom, i.e., $6p(t_2)$, $5f(a_1+t_1+t_2)$, $6d(e+t_2)$, and $7s(a_1)$ and the order changes to

 $3a_1 < 3t_2 < 1e < 1t_1 < 4t_2$.

In ThBr₄, these are the outermost occupied five levels. Mulliken analysis of the occupied levels in ThBr₄ shows that the next deepest levels, the $2t_2$ and $2a_1$ levels, are essentially ligand 4s symmetry combinations with the $2t_2$ level having some metal $6p(t_2)$ character. The next lowest level, the $1t_2$ level, is almost completely composed of Th $6p(t_2)$ orbitals. UBr₄ has two more electrons than ThBr₄ and these go into the $5t_2$ level which has metal 5f and 6d character.

The experimental He(I) photoelectron spectra of UBr_4 and ThBr₄ are shown in Figs. 3(a) and 3(b). The 10.0–13.5 eV ionization energy regions of these spectra exhibit a remarkable similarity and each spectrum shows eight reproducible band maxima, labeled A-H in Fig. 3. UBr₄ shows an extra band which is not present in the ThBr₄ spectra. This has a vertical ionization energy (VIE) of (9.65 ± 0.02) eV and an adiabatic ionization energy (AIE) (band onset) of (9.35) ± 0.10) eV. These values compare with the only previously determined value for the first AIE of UBr₄, from electron impact mass spectrometry, of (9.6±0.3) eV.11 The corresponding values in ThBr₄, the band maximum and band onset of band A in Fig. 3(a), are (10.92±0.02) eV and (10.28 ± 0.05) eV, which compare with the earlier value, from electron impact mass spectrometry of (10.4 ± 0.3) eV.¹⁰ Scans in the higher ionization energy region (13.5–21.0 eV) showed no bands that could be attributed to these tetrabromides, although it was noted that the bands in the 10.0-13.5

TABLE II. Comparison of experimental and computed VIEs (in eV) of ThBr4, with band assignments.

Orl	bital			Th 5 <i>d</i> core		
Non relativistic	Relativistic	Th 6 <i>p</i> core	Th 5 <i>d</i> core	Shifted values	Experiment	Assignment
4 <i>t</i> ₂	6 <i>u</i> _{3/2}	10.83	10.82	10.92	10.92	А
$4t_2$	$4e_{5/2}$	10.86	11.08	11.18	11.23	С
1 t ₁	$5u_{3/2}$	11.02	11.00	11.10	11.12	В
1 t ₁	$4e_{1/2}$	11.19	11.16	11.26	11.33	D
1 e	$4u_{3/2}$	11.60	11.56	11.65	11.85	Е
$3t_2$	$3u_{3/2}$	12.01	11.93	12.02	12.11	F
$3t_2$	$3e_{5/2}$	12.23	12.23	12.32	12.40	G
$3a_1$	$3e_{1/2}$	12.43	12.40	12.50	12.67	Н
$2t_2$	$2u_{3/2}$	23.35	22.84	22.94	а	
$2t_2$	$2e_{5/2}$	23.37	23.39	23.49		
$2a_1$	$2e_{1/2}$	23.59	23.56	23.66		
$1t_2$	$1 u_{3/2}$		26.33	26.43		
$1t_2$	$1e_{5/2}$		32.67	32.77		
$1a_{1}$	$1 e_{1/2}$		49.87	49.97		

^aBands outside the photon energy range used.

eV region were lower in intensity than the corresponding bands observed for the tetrafluorides and tetrachlorides, and hence any weak metal tetrabromide bands in the 13.5–21.0 eV region would be difficult to detect.

Tables II and III show the computed VIEs for ThBr₄ and UBr₄ with the metal orbitals (a) frozen up to the 6*p* level (the M 6*p* core in Tables II and III) and (b) frozen up to the 5*d* level (the M 5*d* core in Tables II and III). As can be seen, the computed VIEs are all slightly too low. This is attributed to (i) the use of a relatively small basis set, (ii) the use of a frozen core, and (iii) the use of the transition-state method which neglects some electron correlation energy change on ionization, although the gradient corrected functional includes some electron correlation in each state involved in the ionization process. In order to compare computed and experimental VIEs, for both tetrabromides the computed VIE of band A [the first $(4t_2)^{-1}$ VIE] was shifted to match the experimental VIE of band A, and this shift was then applied

to all computed VIEs. This shift was 0.10 eV for ThBr₄ and 0.08 eV for UBr₄. The spread in the computed VIEs, both with and without the metal 6*p* orbitals in the valence region, for bands A–H (1.60 and 1.58 eV for ThBr₄, 1.73 and 1.70 eV for UBr₄) compares very favorably with the experimental spread (1.75 eV for ThBr₄ and 1.70 eV for UBr₄) for both metal tetrabromides (see Tables II and III).

The assignment of the bands shown in Figs. 3(a) and 3(b) relies on the computed VIEs of ThBr₄ and UBr₄ shown in Tables II and III and the assignment achieved previously for the UV photoelectron spectra of the uranium and thorium tetrafluorides and tetrachlorides,⁷ which is also based on VIEs computed with relativistic density functional calculations.

It is well established that the spin-orbit splitting of the outermost occupied t_2 level in ThF₄ and ThCl₄, the $4t_2$ level, is responsible for the first two bands in their UV pho-

Orbital				U 5d core		
Non relativistic	Relativistic	U 6 <i>p</i> core	U 5 <i>d</i> core	Shifted values	Experiment	Assignment
5 <i>t</i> ₂	$7u_{3/2}$	9.46	9.30	9.37	9.65	U(5 <i>f</i> ,6 <i>d</i>)
$4t_2$	$6u_{3/2}$	10.88	10.91	10.99	10.99	А
$4t_2$	$4e_{5/2}$	10.88	11.17	11.25	11.28	С
$1t_1$	$5u_{3/2}$	11.10	11.09	11.16	11.18	В
$1 t_1$	$4e_{1/2}$	11.30	11.27	11.34	11.42	D
1 e	$4u_{3/2}$	11.64	11.61	11.68	11.88	Е
$3t_2$	$3u_{3/2}$	12.03	11.99	12.06	12.12	F
$3t_2$	3e _{5/2}	12.24	12.28	12.35	12.42	G
$3a_1$	$3e_{1/2}$	12.61	12.61	12.68	12.69	Н
$2t_2$	$2u_{3/2}$	23.41	23.08	23.16	а	
$2t_2$	2e _{5/2}	23.42	23.51	23.58		
$2a_1$	$2e_{1/2}$	23.69	23.67	23.74		
1 <i>t</i> ₂	$1 u_{3/2}$		27.17	27.25		
$1t_2$	1 e _{5/2}		34.48	34.56		
$1a_1$	$1 e_{1/2}$		54.74	54.81		

TABLE III. Comparison of experimental and computed VIEs (in eV) of UBr₄, with band assignments.

^aBands outside the photon energy range used.

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FIG. 4. Comparison of the ultraviolet photoelectron spectra of ThF_4 , ThCl_4 , and ThBr_4 , and correlation of the ionic state assignment of the bands.

toelectron spectra. This arises because the $4t_2$ level contains a small amount of thorium 6p character and the Th 6p orbital shows a large spin-orbit splitting (the spin-orbit splitting in the $1t_2$ level of ThBr₄, which is mainly Th 6p in character, is 6.3 eV; similar values are also obtained for this splitting in the other uranium and thorium tetrahalides). For ThF_4 , $ThCl_4$, and $ThBr_4$ the experimental spin-orbit splitting of the outermost t_2 level stays approximately constant at (0.35 ± 0.06) eV with values of 0.41, 0.35, and 0.31 eV being measured. Table II confirms the origin of this splitting as it is only reproduced when the metal 6p orbitals are not frozen and included in the valence space. The $1t_1$ level is almost completely halogen in character, and the computed spin-orbit splittings in ThF₄, ThCl₄, and ThBr₄ are 0.03, 0.05, and 0.16 eV. This splitting is only resolved in the photoelectron spectra of ThBr₄ and UBr₄ and these components are assigned to bands B and D. Although the $4t_2$ level is split into $u_{3/2}$ and $e_{5/2}$ levels with the $u_{3/2}$ level lying lower (expected degeneracy ratio 2:1) and the $1t_1$ level is split into $u_{3/2}$ and $e_{1/2}$ levels with the $u_{3/2}$ level lying lower (expected degeneracy ratio 2:1), the bands A, B, C, and D in the experimental UBr₄ and ThBr₄ spectra are not sufficiently well resolved to estimate the A:C relative intensity (the $4t_2$ components) and the B:D relative intensity (the $1t_1$ components). The 1elevel is $u_{3/2}$ relativistically and ionization from this level is assigned to band E in ThBr₄ (and UBr₄). The $(3t_2)^{-1}$ ionization is expected to give two components $u_{3/2}$ and $e_{5/2}$, degeneracy ratio 2:1. Bands F and G in Figs. 3(a) and 3(b) are assigned to these ionizations and support for this assignment is provided by the fact that the intensity ratio of these



FIG. 5. Comparison of the ultraviolet photoelectron spectra of UF_4 , UCl_4 , and UBr_4 and correlation of the ionic state assignment of the bands.

bands is approximately 2:1. This splitting is not resolved in the ThF₄ and ThCl₄ spectra (or the UF₄ and UCl₄ spectra). The computed separations of the $u_{3/2}$ and $e_{5/2}$ components in ThF₄, ThCl₄, and ThBr₄ are 0.08, 0.10, and 0.30 eV consistent with a large halogen p and a small metal 6p contribution to this level. The measured splitting of bands F and G in the UBr₄ and ThBr₄ spectra are 0.30 and 0.29 eV, consistent with the computed splittings of 0.29 and 0.30 eV obtained from calculations with the metal 6p orbitals in the valence region. These computed splittings reduce slightly, to 0.21 and 0.22 eV, on putting the metal 6p orbitals in the core. Band H is assigned to ionization from the $3a_1$ orbital, which is $3e_{1/2}$ relativistically.

A comparison of the assignment of the ThF_4 , $ThCl_4$, and ThBr₄ spectra, and the UF₄, UCl₄, and UBr₄ spectra are presented in Figs. 4 and 5. Apart from the extra band seen in the uranium tetrahalide spectra at low ionization energy, which arises in each case from ionization from the outermost $5t_2(7u_{3/2})$ level, the assignments of the uranium and thorium spectra are remarkably similar. The splitting of the ionic states that arise from the $(4t_2)^{-1}$ ionization in ThF₄, ThCl₄, and ThBr₄ (0.41, 0.35, and 0.31 eV) and in UF₄, UCl₄, and UBr₄ (0.30, 0.36, 0.29) are approximately constant, consistent with it being associated with a spin-orbit splitting arising from a metal 6p contribution to the $4t_2$ level. In contrast, the $1t_1$ and $3t_2$ levels have spin-orbit splittings which are expected, from the computed VIEs, to increase on going along the series MF_4 , MCl_4 , MBr_4 (with M=Th or U) consistent with these levels being halogen np in origin. This is consistent with the spectra, as these splittings are only resolved in the tetrabromides.

If the $1t_1$ level in each tetrahalide is composed solely of halogen np valence orbitals, then neglecting off-diagonal spin-orbit interactions, the ${}^{2}T_{1}(u_{3/2}-e_{1/2})$ splitting is just $-3/4 \zeta$, where ζ is the spin-orbit coupling constant for the free halogen ion.^{35,36} The negative sign implies that the splitting is inverted with the $u_{3/2}$ component lying lower than the $e_{1/2}$ component, consistent with Hund's third rule as the t_1^{5} shell in the tetrahalide ion is more than half full. ζ values can be readily evaluated for $F^{+},\ Cl^{+},\ and\ Br^{+}$ from atomic tables as 0.04, 0.08, and 0.32 eV giving calculated $1t_1$ spinorbit splittings in the uranium and thorium tetrafluorides, tetrachlorides and tetrabromides of 0.03, 0.06, and 0.24 eV. The only observed $1t_1$ splittings occur for ThBr₄ and UBr₄ with values of 0.21 and 0.24 eV being measured, in good agreement with the value of 0.24 eV obtained from this simple model. The $1t_1$ splittings in the tetrafluorides and tetrachlorides are unresolved experimentally and are therefore expected to be <0.10 eV. The $1t_1$ splittings computed for ThF₄, ThCl₄, and ThBr₄ by relativistic density functional calculations are 0.03, 0.06, and 0.16 eV in good agreement with the above values derived from atomic halogen ion splittings. The $3t_2$ levels show splittings of 0.29 and 0.30 eV in ThBr₄ and UBr₄ which are slightly greater than the corresponding splittings in the $1t_1$ levels. The $3t_2$ splittings are unresolved in the tetrafluorides and tetrachlorides.

The simple atomic spin-orbit model cannot be so readily applied to the t_2 ionic states, as the t_2 molecular orbitals contain a larger number of contributions, notably halogen *ns*, halogen $np\sigma$, halogen $np\pi$, metal 6*d*, metal 5*f*, and metal 6p orbitals.^{35–37} The density functional computed values of the $3t_2$ spin-orbit splitting for ThF₄, ThCl₄, and ThBr₄ are, however, 0.02, 0.10, and 0.30 eV. These values are very similar to the splittings computed by relativistic density functional calculations for the $1t_1$ levels, consistent with the $3t_2$ levels also being composed of mainly halogen np valence orbitals. However, the computed $3t_2$ values are slightly larger and this is probably due to a small metal 6pcontribution to these levels. It is particularly notable that when the metal 6p level is included in the core, the computed $3t_2$ spin-orbit splitting reduces to the spin-orbit splitting of the $1t_1$ level (from 0.29 to 0.22 eV in ThBr₄).

In summary, the photoelectron and infrared matrix isolation results obtained in this work are consistent with effective tetrahedral geometries for UBr₄ and ThBr₄. The photoelectron spectrum of ThBr₄ exhibits eight bands which arise from ionization of the five outermost orbitals derived from the Br 4p symmetry combinations in a Br₄ tetrahedral unit, with three of the bands split by spin-orbit interaction. The UBr₄ spectrum is very similar but it also exhibits a weak band at lower ionization energy arising from ionization of a $5t_2$ orbital, which is unfilled in ThBr₄ and has two electrons in it in UBr₄. The origin of the observed spin-orbit splittings can be understood on the basis of this combined experimental and theoretical study but improved calculations of ionization energies of the uranium and thorium tetrahalides that give improved agreement with experimental values would be valuable.

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