F1s X-ray emission spectroscopy of UF₄

J.G. Tobin*, Sung Woo Yu, Ruimin Qiao, Wan Li Yang, Corwin H. Booth and David K. Shuh

*aUniversity of Wisconsin-Oshkosh, Oshkosh, WI, USA; bLawrence Livermore National Laboratory, Livermore, CA, USA; cLawrence Berkeley National Laboratory, Berkeley, CA, USA

The experimentally measured F K (1s) X-ray Emission from a Uranium Tetrafluoride sample is presented and discussed, including comparison to the results of an earlier cluster calculation by Ryzhkov and coworkers. It is shown that the F K (1s) spectrum is dominated by emission from the bulk UF₄, but a small secondary peak can be associated with the Uranyl Fluoride produced during surface degradation.

Keywords: actinides; x-ray emission; fluorine; uranium; synchrotron radiation

1. Introduction

Uranium Tetrafluoride has become an important material for control experiments underpinning the investigation of more complicated materials. For example, it has: (1) provided the ionic limiting case behavior in the demonstration of 5f covalency in uranium dioxide [1-4]; (2) served as the n(5f) = 2 boundary in RXES studies of mixed valent systems [5,6] and URu₂Si₂ [7]; (3) and it has helped resolve the misunderstanding of the 5f occupation in uranium oxides. [5,8,9] Here, a careful examination of the F K (1s) x-ray emission from uranium tetrafluoride will be performed, confirming and supporting the earlier reports. [1,10,11]

2. Experimental

The synchrotron-radiation-based measurements were carried out at Beamline (BL) 8.0 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). [1,11,12] Details of the BL 8.0 characteristics can be found in Reference 13. Data were collected at room temperature (near 300 K). The uranium tetrafluoride was a single-crystalline sample, with significant surface degradation [1,11]. The synchrotron-radiation-based experiments include X-ray Absorption Spectroscopy (XAS) and X-ray Emission Spectroscopy (XES) [1]. XES was also performed at Lawrence Livermore National Laboratory, using an in-house spectrometer and an electron gun as the excitation source [10,14].

After the generation of a core hole in the F 1s level, by either bombardment with high energy electrons or the absorption of a photon, the F K (1s) x-ray emission is produced by the decay process of filling the core hole. Of course, the decay process is dominated by electric dipole transitions, thus making the F K (1s) XES a good measure of the occupied density of states (ODOS) the F2p levels. The F2p levels are important because they participate in the formation of bonds with the cation, in this case the uranium. A series of F 1s spectra are shown in the left column of Figure 1. Similar spectra for the O K (1s) are in the right column of Figure 1 [10,15].

3. Results and discussion

Because the F K (1s) should be a measure of the 2p Occupied Density of States (ODOS), it is useful to compare the experimental XES results with another experimental technique with a parallel sensitivity and with computational predictions of the theoretical ODOS. Such a comparison is shown in Figure 2.

It is clear that the earlier XPS and cluster ODOS results are consistent with the more recent XES spectra. XPS is a powerful probe of electronic structure [16-18]. Within the constraints of cross sectional variations, photoelectron diffraction and other intensity modulating effects, it can provide a measure of the occupied density of states (ODOS). However, it generally does not have an elemental specificity in direct valence band measurements. Thus, not only is the peak associated with the F2p states observed, but so is the U5f peak. In reality, each of these peaks includes an admixture of contributions from the F2p and U5f states, as well as other states, but to a large extent, the one near BE = 2 eV is dominated by the U5f contribution and the one near BE = 7 eV is dominated by the F2p contribution.

(© 2018 Atomic Energy Society of Japan. All rights reserved.)
Figure 1. The oxidant K(1s) XES for UF₄, UO₂ and CeOxide. The F1s emission peak is at $h\nu = 675$ eV and the O1s emission peak is at $h\nu = 524$ eV. The spectra are as follows: (a) UF₄ and collected at LLNL using an electron gun for excitation [10]; (b) UF₄ collected at ALS using photon absorption for excitation ($h\nu_{EX} = 810$ eV), with emission at approximately 80 degrees from the surface normal [1]; (c) UF₄, collected at ALS using photon absorption for excitation ($h\nu_{EX} = 810$ eV), with emission at approximately 60 degrees from the surface normal [1]; (e) CeOxide, collected at LLNL with electron excitation and a series of slit widths (60 μm or 20 μm) and excitation energies (1.5 keV and 3.0 keV). The two arrows denote (1) the main peak, from the near-surface CeOxide layer, and (2) the shoulder, from the true surface oxygen [15]; and (f) UO₂, collected at LLNL with electron excitation, for an “as is” sample and a sample which had been “sputtered,” i.e. cleaned with ion bombardment [10]. (d) Model of the UF₄ sample [1,11]. More detail can be found in the references.

Electric dipole selection rules, the XES provides a sensitivity to only the F2p states. It is important that the overall envelopes of the XES peak near $h\nu = 675$ eV and XPS F2p peak near BE = 7 eV agree so well with each other and with the histogram ODOS from the cluster calculation [17].
The ODOS histogram was produced by taking the results of the cluster calculation and plotting the sum of the percentages of F2p contributions at each energy, in 1/10 eV steps, versus the relative energy of the states. Almost all of the F2p occupied density is grouped together in a 5 eV range, between ODOS Energy = 3 and 8 eV. However, there is also a vanishingly small contribution near ODOS Energy = 0 eV, consistent with the mixture of F2p character into the mainly 5f peak near BE = 3 eV.

Figure 2. Comparison of the XES results for UF₄ with the X-ray Photoelectron Spectroscopy (XPS) of UF₄ from Thibaut et al. [16] and the ODOS derived from the calculations of Ryzhkov [17], for a (UF₈)⁴⁻ cluster. Note that while the energy steps are identical, each of the x-axes can be shifted relative to the others. The XES peak is at hv = 675 eV. The XPS measurements of Teterin et al. [17] confirm the Thibaut result. XPS is not element specific.

It is tempting to associate the small XES peak near hv = 680 eV with 2p hybridization of the U5f states. However, a closer examination will show that this is not the case: it instead is indicative of the contribution of F from a second site, probably the uranyl fluoride discussed in an earlier publication [11]. Below are the reasons for this conclusion.

i. Experimentally, there is no corresponding feature in the O1s XES of UO₂, plotted in Figure 1f. It is well known that the valence band XPS of UF₄ and UO₂ are very similar, almost identical, differing in essentially only one way, a rigid shift in Binding Energy. [8] If the XPS are so similar, why then are the XES different? It should be noted that the UO₂ specimen was very carefully analyzed, using a variety of spectroscopic probes, the result of which was the demonstration that the UO₂ was a single site sample[19].

ii. In the case of CeOxide, where there were two sites, the second minority site could be found as a shoulder, at a higher photon energy. This result is reproduced in Figure 1, panel e.

iii. The results of the (UF₈)⁴⁺ calculation show essentially no F2p density over this range, with only a vanishingly small contribution. One might wonder whether this reflects a limitation in the cluster calculation, where the small result is merely a quantitative error and that is representative of a larger contribution. To further test the quality of the cluster calculation, it is possible to compare the prediction of the F2p Unoccupied Density of States (UDOS) to the measurement of the F2p UDOS via X-ray Absorption Spectroscopy (XAS). This comparison is shown in Figure 3. Clearly, the cluster calculations do very well. (Previously, the division into 2p-5f and 2p-6d regimes had been established using multiple experimental measurements. Please see References 1-3.) The cluster calculations reconstruct the experimental determination of the separation into regimes of 5f and 6d dominance, as well as the F1s peaks, and thus F2p densities, themselves. Thus, nothing is obviously wrong here.

iv. In a series of earlier reports [1,10,11], it was demonstrated that the UF₄ sample was bulk UF₄ with a surface region that was depleted of U but also a subsurface layer that had a uranyl component, possibly UO₂F₂. (See Figure 1d.) It seems likely that the weak shoulder at hv = 680 eV in the F1s XES is from the proposed UO₂F₂ contaminant, part of the surface degradation of the UF₄ single crystal.

It is a valid question to ask whether there should be an angular dependence to the XES emission from the two sites. Unfortunately, because both sites are buried, the bulk and the subsurface, and the because of the long attenuation lengths associated with photons [11], it is very unlikely that a relative effect between the two peaks would be observed. This interpretation is consistent with the near identically of the two XES
spectra in panels b and c of Figure 1.

4. Conclusions
A systematic evaluation of the F K (1s) XES of uranium tetrafluoride has been performed, including a comparison to the results of a $(\text{UF}_4)^{-}$ cluster calculation. The analysis confirms the results of several earlier studies and identifies the small contaminant feature as belonging to uranyl fluoride. The $\text{UOF}_2$ is a part of the surface corruption of the $\text{UF}_4$ single crystal, in a subsurface layer below the U depleted surface.

Acknowledgements
Lawrence Livermore National Laboratory (LLNL) is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration, under Contract DE-AC52-07NA27344. Work at Lawrence Berkeley National Laboratory (LBNL) (D.K.S.) was supported by the Director of the Office of Science, Office of Basic Energy Sciences (OBS), Division of Chemical Sciences, Geosciences, and Biosciences (CSGB), Heavy Element Chemistry (HEC) Program of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The ALS is supported by the Director of the Office of Science, Office of Basic Energy Sciences (OBS), Division of Chemical Sciences, Geosciences, and Biosciences (CSGB), Heavy Element Chemistry (HEC) Program of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The UF$_4$ sample was originally prepared at Oak Ridge National Laboratory and provided to LLNL by J. S. Morrell of Y12.

References
[1] J.G. Tobin, S.-W. Yu, R. Qiao, W.L. Yang, C.H. Booth, D.K. Shuh, A.M. Duffin, D. Sokaras, D. Nordlund and T.-C. Weng, Covalency in oxidizeduranium, Phys. Rev. B 92 (2015), p.045130.
[2] J.G. Tobin and S.-W. Yu, Orbital specificity in the unoccupied states of UO$_2$ from resonant inverse photoelectron spectroscopy, Phys. Rev. Lett. 107 (2011), p.167406.
[3] S.-W. Yu, J.G. Tobin, J.C. Crowhurst, S. Sharma, J.K. Dewhurst, P. Olalde-Velasco, W.L. Yang and W.J. Siekhaus, $t$-$t$- origin of the insulating state in uranium dioxide: X-ray absorption experiments and first-principles calculations, Phys. Rev. B 83 (2011), p.165102.
[4] J.G. Tobin, C.H. Booth, W. Siekhaus and D.K. Shuh, EXAFS investigation of UF$_4$, J. Vac. Sci. Tech. A 33 (2015), p.033001.
[5] J.G. Tobin, S.-W. Yu, C.H. Booth, T. Tyliszczak, D.K. Shuh, G. van der Laan, D. Sokaras, D. Nordlund, T.-C. Weng and P.S. Bagus, Oxidation and crystal field effects in uranium, Phys. Rev. B 92 (2015), p.035111.
[6] P. Söderlind, A. Landa, J.G. Tobin, P. Allen, S. Medling, C.H. Booth, E.D. Bauer, J.C. Cooley D. Sokaras, T.-C. Weng and D. Nordlund, On the valence fluctuation in the early actinide etals, J. Electron Spectroscopy and Rel. Phen. 207 (2016), p.14.
[7] C.H. Booth, S.A. Medling, J.G. Tobin, R.E. Baumbach, E.D. Bauer, D. Sokaras, D. Nordlund and T.-C. Weng, Probing 5f-state configurations in URu2Si2 with U LIII-edge resonant x-ray emission spectroscopy, Phys. Rev. B 94 (2016), p.045121.
[8] J.G. Tobin, The apparent absense of chemical sensitivity in the 4d and 5d X-ray absorption spectroscopy of uranium compounds, J. Electron Spectroscopy and Rel. Phen. 194 (2014), p.14.
[9] G. Kalkowski, G. Kaindl, W.D. Brewer and W. Krone, Near-edge x-ray-absorption fine structure in uranium compounds, Phys. Rev. B 35 (1987), p.2667.
[10] S.-W. Yu and J.G. Tobin, Multi-electronic effects in uranium dioxide from X-ray Emission Spectroscopy, J. Electron Spectroscopy and Rel. Phen. 187 (2013), p.15.
[11] J.G. Tobin, A.M. Duffin, S.-W. Yu, R. Qiao, W.L. Yang, C.H. Booth and D.K. Shuh, Surface degradation of uranium tetrafluoride, J. Vac. Sci. Technol. A 35 (2017), p.03E108.
[12] S.-W. Yu, J.G. Tobin, P. Olalde-Velasco, W.L. Yang and W.J. Siekhaus, Energy calibrations in the x-ray absorption spectroscopy of uranium dioxide, J. Vac. Sci. Tech. A 30 (2012), p.011402.
[13] J.J. Jia, T.A. Calcott, J.Yurkas, A.W. Ellis, F. J.Himpsel, M.G. Samant, J. Stohr, D.L. Ederer, J.A. Carlisle, E.A. Hudson, L.J. Terminello, D.K. Shuh and R.C.C. Perera, First experimental results from IBM/TENN/TULANE/LLNL/LBL undulator beamline at the advanced light source, Rev. Sci. Instrum. 66 (1995), p.1394.
[14] S.-W. Yu, J.G. Tobin and B.W. Chung, First experimental results from IBM/TENN/TULANE/LLNL/LBL undulator beamline at the advanced light source, Rev. Sci. Instrum. 82 (2011), p.093903.
[15] J.G. Tobin, S.W. Yu, B.W. Chung, G.D. Waddill, E. Damian, L. Duda and J. Nordgren, Observation of strong resonant behavior in the inverse photoelectron spectroscopy of Ce oxide, Phys. Rev. B 83 (2011), p.085104.
[16] E. Thibaut, J.-P. Boutique, J.J. Verbist, J.-C. Levet and H. Noel, Electronic structure of uranium halides and oxyhalides in the solid state. An x-ray photoelectron spectral study of bonding ionicity, J. Am. Chem. Soc. 104 (1982), pp.5266-5273.
[17] A.Yu. Teterin,Yu. A. Teterin, K.I. Maslakov, A.D. Panov, M.V. Ryzhkov and L. Vukcevic, Electronic structure of solid uranium tetrafluoride UF4, Phys. Rev. B 74 (2006), p.045101.
[18] J.G. Tobin and D.K. Shuh, Electron spectroscopy of the oxidation and aging of U and Pu, J. Electron Spectroscopy and Rel. Phen. 205 (2015), p.83.
[19] S.-W. Yu and J.G. Tobin, Confirmation of sample quality: X-ray and ultraviolet photoelectron spectroscopies of uranium dioxide, J. Vac Sci. Tech. A 29 (2011), p.021008.