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# Surface degradation of uranium tetrafluoride

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A detailed analysis of a single crystal of uranium tetrafluoride has been carried out. The techniques include x-ray absorption spectroscopy, as well as x-ray photoelectron spectroscopy and x-ray emission spectroscopy. Evidence will be presented for the presence of a uranyl species, possibly  $\text{UO}_2\text{F}_2$ , as a product of, or participant in the surface degradation. © 2017 American Vacuum Society.

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## I. INTRODUCTION

In a sense, uranium tetrafluoride ( $\text{UF}_4$ )<sup>1–7</sup> is the simplified version of uranium dioxide ( $\text{UO}_2$ ).<sup>1–11</sup> While  $\text{UO}_2$  is widely used as a nuclear fuel and is a key participant in nuclear storage scenarios,<sup>12</sup> it is interlaced with complexity, including issues of 5f covalency.<sup>6</sup> On the other hand,  $\text{UF}_4$  tends to the more ionic limit.<sup>6</sup> While the uranium species in both are iso-electronic, being  $\text{U}^{4+}(5f^2)$  if completely oxidized, the degree of oxidation depends on the oxidizing agent, with fluorine being the better oxidant. Uranium tetrafluoride does have the complication of lower symmetry and two inequivalent uranium sites per unit cell, but the  $\text{UL}_3(2p_{1/2})$  extended x-ray absorption fines structure (EXAFS) measurements points toward essentially identical bond lengths between uranium and the oxidant.<sup>4</sup> Thus, it is useful to pursue a spectroscopic interrogation of  $\text{UF}_4$ , with the intent to better understand both  $\text{UF}_4$  and its more complicated cousin,  $\text{UO}_2$ .

In the process of carrying out this investigation of  $\text{UF}_4$ , some rather peculiar but interesting qualities were observed in the surface degraded parts of the single crystalline sample. The chief of these is the possible presence of a uranyl structure such as uranyl fluoride [ $\text{U}(\text{VI})\text{O}_2\text{F}_2$ , with a  $\text{UO}_2^{2+}$  (VI) moiety] in a near-surface, but subsurface region (Fig. 1). However, it should be noted that the surface analysis presented herein is a bit unusual. In most surface analyses, one prepares a clean surface and then permits it to degrade, by monitoring the process. In the case of a radioactive sample at a user facility such as the advanced light source (ALS), there are concerns about the dissemination of radioactive debris. Thus, the experiment was pursued in a different approach, using a combination of photon and electron based probes to vary the sampling depth. In fact, one might liken this type of surface analysis to a forensics study, where the sample remains intact. The spectroscopic analysis will follow after a brief description of the experimental details.

## II. EXPERIMENT

The x-ray absorption spectroscopy measurements were carried out at beamline (BL) 8.0 at the ALS at Lawrence Berkeley National Laboratory. For BL 8.0, energy calibrations were performed at the Fe  $2p_{3/2}$  white line (710 eV for iron oxide) for the beamline monochromator. This calibration is reflected in the energy scale used in the regime around 700 eV: a 10 eV shift is invoked. However, it is less clear how to apply this shift to the energy regime near the OK (1s) threshold, around 500 eV. Thus, instead, we will quote the original energy scale of the beamline monochromator and then shift the spectra to place them on the same scale as spectra taken from the literature, as denoted below. Details of the BL 8.0 characteristics can be found in Ref. 13. Data were collected at room temperature (300 K). The uranium tetrafluoride was a single-crystalline sample, with significant surface degradation.<sup>6</sup>

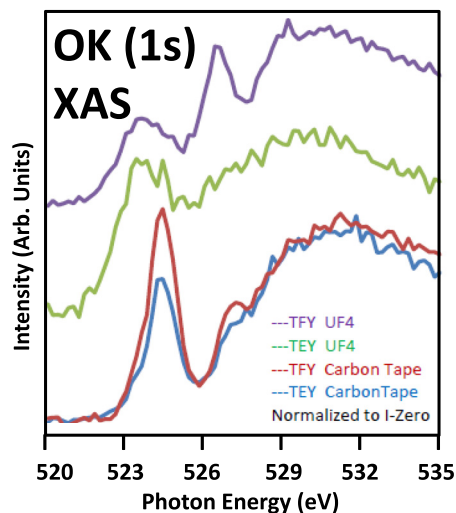


Fig. 1. (Color online) Shown here is a series of OK (1s) x-ray absorption spectra for the uranium tetrafluoride sample and the carbon tape, using TFY and TEY detection. These data were smoothed and corrected for  $I_0$ .

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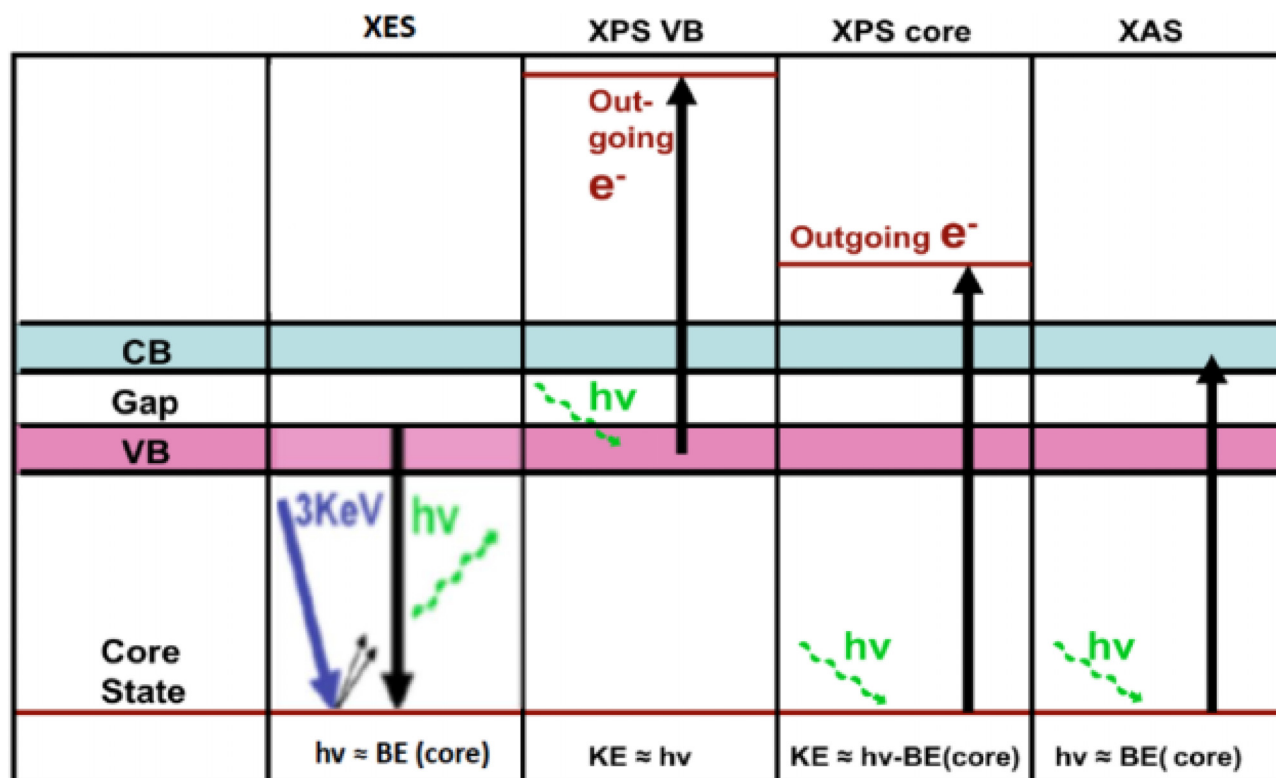


FIG. 2. (Color online) Processes of XES, XPS and x-ray absorption spectroscopy in a schematic fashion. See text for details.

The measurements to be discussed include x-ray absorption, x-ray emission, and x-ray photoelectron spectroscopy (XPS), the processes of which are shown schematically in Fig. 2. Because core level electrons are involved in these processes, there is a fundamental elemental specificity to the analysis. The specifics of each measurement will be briefly discussed in connection with the spectroscopic data in the figures below.

In the case of x-ray absorption spectroscopy, two variants will be utilized: total fluorescence yield (TFY) and total electron yield (TEY). In our case, the TEY was performed using a channeltron for electron detection.<sup>6,13</sup> The experimental arrangements for these variants are shown diagrammatically in Fig. 3.

For the experiments on BL 8.0, the  $\text{UF}_4$  sample was mounted on a sample platen with carbon tape, as shown in Fig. 4. This provided sufficient conductivity to avoid sample charging and allowed unhindered access to the  $\text{UF}_4$  sample. Despite the blackish corrosion, note the hints of blue-green color from the underlying  $\text{UF}_4$ . The carbon tape was also used to determine background emission, as will be discussed below.

### III. RESULTS AND DISCUSSION

#### A. Summary of earlier laboratory-based results

In a prior publication, XPS and x-ray emission spectroscopy (XES) were used to probe the nature of the uranium tetrafluoride sample.<sup>2,14</sup> Some of these results are shown in Fig. 5. Here, the XES is performed utilizing an electron beam to generate core holes, the decay of which gives rise to

the observed XES lines. The F K (1s) XES spectrum is shown as an inset, in the right side of the Fig. 5. The F K emission energy roughly corresponds to the to the F1s binding energy, because the decay process involves valence electrons dropping down into the core hole, consistent with the illustration in Fig. 2. While the F1s XES emission is strong and sharp, a strong F1s XPS feature is absent in the XPS spectrum.

In the XPS spectrum, there are strong but broadened features for the U4d and U4f levels, as well as clearly obvious O1s and C1s peaks. This suggests multiple U sites with significant chemical inhomogeneity. The oxygen and carbon

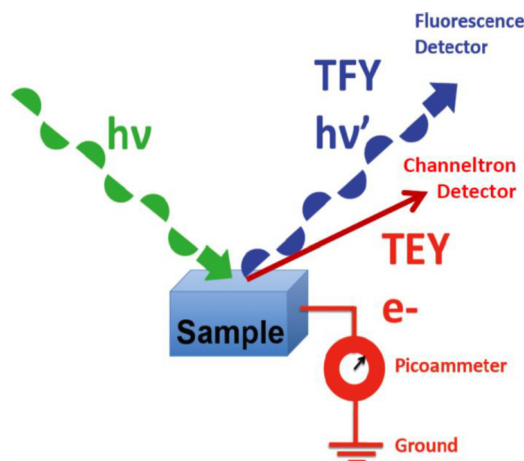


FIG. 3. (Color online) Diagram, which summarizes the excitation and modes of detection for x-ray absorption spectroscopy.

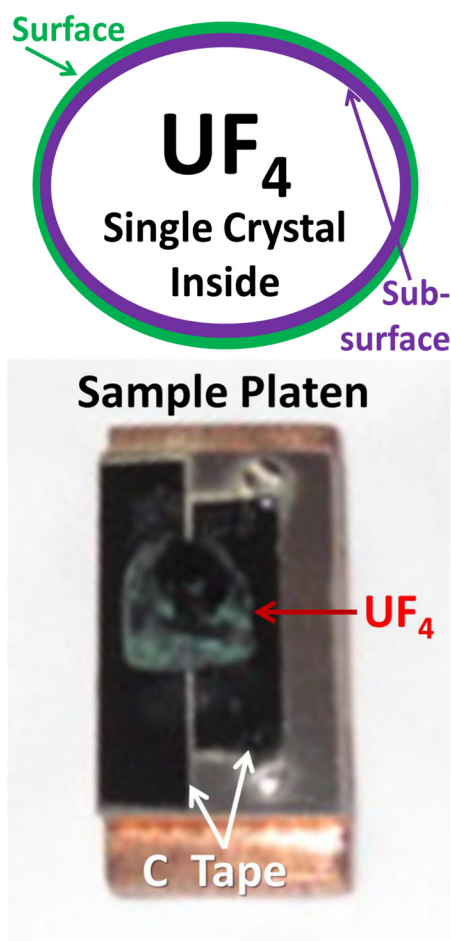


FIG. 4. (Color online) Top panel: A diagram illustrating the simple model for the  $\text{UF}_4$  sample. Bottom panel: A photograph of the  $\text{UF}_4$ , mounted on the sample platen with carbon tape.

features are a sure indication of surface degradation. Furthermore, the absence of a strong F1s feature argues for the absence of any significant amount of fluorine on the surface. There is one, or maybe are two, weak XPS features in

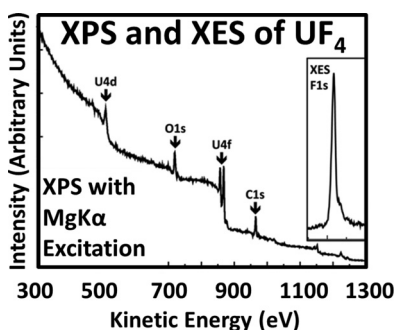


FIG. 5. XPS and XES of  $\text{UF}_4$ . Note the presence of multiple contaminant peaks in the XPS (e.g., O 1s near KE=720 eV and the C 1s near KE=970 eV) and the relatively poor signal to noise (e.g., the U 4d doublet near KE=500 eV and the U 4f near KE=870 eV). The F 1s XPS peak, which should be near KE=550 eV, is not easily observable. Alternatively, the F 1s XES peak shown in the rightmost inset over a 30 eV range is sharp and exhibits good signal to noise. All of these measurements were performed in-house at LLNL, using an electron beam for core-hole generation in XES and an x-ray tube for excitation in the XPS measurements. Similar to Yu and Tobin, JESRP 2013 (Ref. 2).

the vicinity of where the F1s should be, but these are barely above the noise.

From these results and based upon the far greater surface sensitivity of XPS versus XES, it seems likely that while the interior of the sample is  $\text{UF}_4$ , the surface is not. Moreover, the surface is dominated by uranium-oxygen and -carbon species, the exact natures of which are unknown. This simplistic picture of the Uranium Fluoride sample is illustrated in the top panel of Fig. 4. However, as will be shown below, there is also evidence for a subsurface layer, with a different chemical nature.

## B. Synchrotron radiation results

As part of the studies at the ALS, F K (1s) XAS was performed, the results of which are shown in Fig. 6. Here, both total fluorescence (TFY) and TEY were utilized for detection. Once again, it is expected that the TEY will be far more surface sensitive than the TFY. This expectation is borne out in the data. While the TEY is almost featureless with a poor signal-to-noise ratio, the TFY shows sharp, well defined peaks with strong signal-to-noise. Furthermore, it has been demonstrated that the broad features in the middle range of the spectrum are F1s EXAFS, consistent with the U  $L_3$  EXAFS of  $\text{UF}_4$ , which has been measured separately at much higher energies and clearly originates with the bulk.<sup>4,6</sup> This F1s EXAFS strongly suggests that the bulk is an intact  $\text{UF}_4$  structure, consistent with a  $\text{UF}_4$  single crystal. Finally, the sharp features near threshold have been analyzed spectroscopically and are clearly associated with the F2pU5f and F2pU6d unoccupied density of states. So, once again, it is clear that there is significant surface degradation but an intact  $\text{UF}_4$  underneath, in the bulk.<sup>6</sup>

Bearing all of this in mind, it was decided to look at the corrupted surface species using O1s XAS, as can be seen in Figs. 1 and 7. Again, both TEY and TFY were used. Interestingly, the  $\text{UF}_4$  TEY O K (1s) XAS spectrum is fairly similar to those of the carbon tape. (One might expect that the carbon tape spectra would be representative of chaotic surface oxidation. Consistent with that notion, both the TFY and TEY of the carbon tape are qualitatively the same, as can be observed in Fig. 1.) However, the  $\text{UF}_4$  TFY O K (1s) spectrum has some additional spectral structure. In some

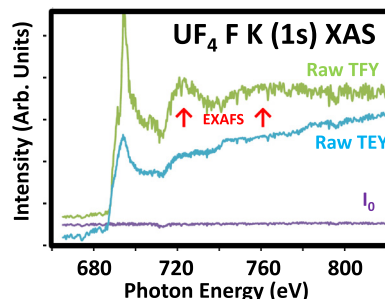


FIG. 6. (Color online) F K (1s) XAS of  $\text{UF}_4$  is displayed here. See text for details. TFY is total fluorescent yield. TEY is total electron yield.  $I_0$  is the incoming photon flux measurement. For the TFY and TEY, the raw data is shown, scaled but uncorrected for  $I_0$ , without smoothing. Note the Fe feature near 710 eV in the  $I_0$  measurement. Similar to Tobin *et al.*, PRB 2015 (Ref. 6).

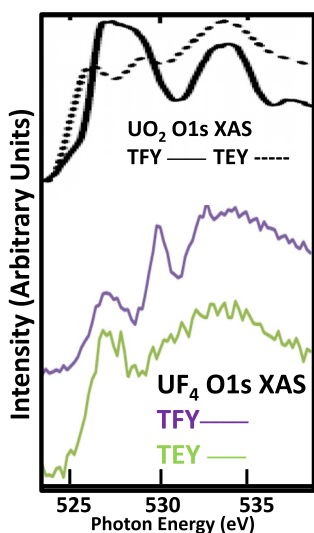


FIG. 7. (Color online) Here are plotted a series of O K (1 s) XAS spectra, using TFY and TEY, for  $\text{UO}_2$  and  $\text{UF}_4$ . The  $\text{UF}_4$  spectra have been shifted to maximize alignment with the  $\text{UO}_2$  spectra. The  $\text{UO}_2$  spectral energies were cross calibrated using the O K (1 s) XAS in first, second, and third orders. The  $\text{UO}_2$  spectra are taken from Ref. 9.

ways, this makes sense: the more surface sensitive detection (TEY) shows more pervasive and complete corruption than the less surface sensitive detection (TFY). At first thought, it might be possible that the species formed could be uranium dioxide, but that is clearly not the case. As shown in Fig. 7, the  $\text{UO}_2$  TFY O K (1s) has a very different spectral structure than the  $\text{UF}_4$  TFY O K (1s). [An extensive study of  $\text{UO}_2$  clearly demonstrated that the  $\text{UO}_2$  TFY O K (1s) spectrum is correct and representative of bulk  $\text{UO}_2$ .<sup>9</sup>] Intriguingly, the TEY spectra are similar, for both  $\text{UO}_2$  and  $\text{UF}_4$ , indicative of related surface corruption in both cases.

This leaves the situation as follows. (1) From XES, TFY XAS, and EXAFS, it is clear that the bulk is intact  $\text{UF}_4$ ,

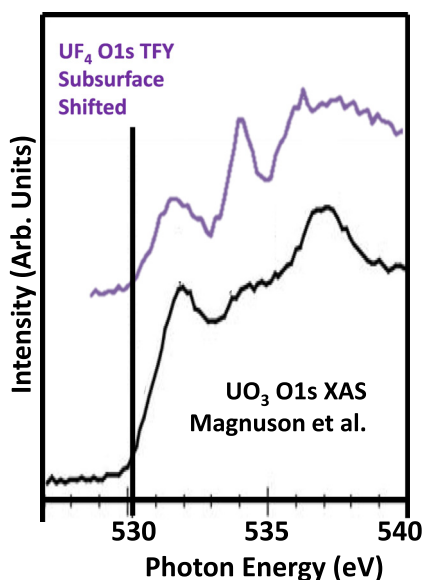


FIG. 8. (Color online) Comparison between the O K (1 s) of  $\text{UF}_4$  vs that of  $\text{UO}_3$  from Magnuson *et al.* (Ref. 15). The topmost spectrum has been shifted to align with the Magnusson energy calibration.

TABLE I. Comparison of peak positions and separations.

Peak Material	References	Positions (eV)			Separations (eV)	
		E(P1)	E(P2)	E(P3)	E(P1)-E(P2)	E(P2)-E(P3)
$\text{UO}_3$	15	532	535	538	3	3
$\text{UO}_2\text{F}_2$	16	531	535	538	4	3
$\text{UO}_2\text{ClOH}$	16	531	534	537	3	3
$(\text{UO}_2\text{Cl}_4)^{2-}$	17	531	534	537	3	3
$(\text{NpO}_2\text{Cl}_4)^{2-}$	17	531	534	537	3	3
$(\text{PuO}_2\text{Cl}_4)^{2-}$	17	531	534	537	3	3
$\text{UF}_4$		524	527	530	3	3

consistent with the single crystalline nature of the sample. (2) From XPS and TEY XAS, it is similarly clear that the surface region is corrupted, with no single clearly defined F species. (3) The O1s TFY XAS suggests the dominance of a single oxygen-related species in a subsurface but nonbulk environment, which is neither  $\text{UF}_4$  nor  $\text{UO}_2$ , consistent with the model of Fig. 4. The goal of the remainder of this paper is to identify the species in (3).

Figure 8 shows a comparison between the  $\text{UF}_4$  O K (1s) TFY XAS and the earlier results for  $\text{UO}_3$ , uranyl oxide, from Magnuson *et al.*<sup>15</sup> Magnuson's spectrum clearly shows a three peak structure that is in substantial agreement with the  $\text{UF}_4$  TFY spectrum. Additionally, in Table I, peak energies and peak separations are compared for a series of samples. The uranyl fluoride and uranyl chloride, from Spectrochimica Acta and an online publication of Duffin *et al.*,<sup>16</sup> have a distinct three peak spectral structure. Clark *et al.* of Los Alamos National Lab have also published online a similar three peak spectral structure for a series of uranyl moieties  $(\text{AnO}_2\text{Cl}_4)^{2-}$ , with An = U, Np, and Pu.<sup>17</sup>

The peak structures for the mixed moieties, particularly those of Duffin *et al.*,<sup>16</sup> are sharper than those reported for the pure uranyl oxide,  $\text{UO}_3$ , but have similar peak positions and energy separations. These comparisons strongly suggest

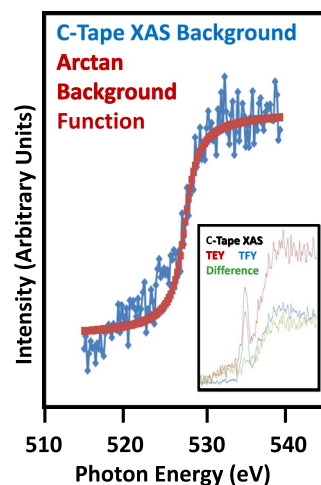


FIG. 9. (Color online) Main figure: Comparison of the arctan function and the experimentally determined background, i.e., the difference curve from the inset. Inset: Carbon Tape TEY, TFY, and difference, removing prepeak. In this figure, the raw XAS data were used, without a correction for  $I_0$  or smoothing.



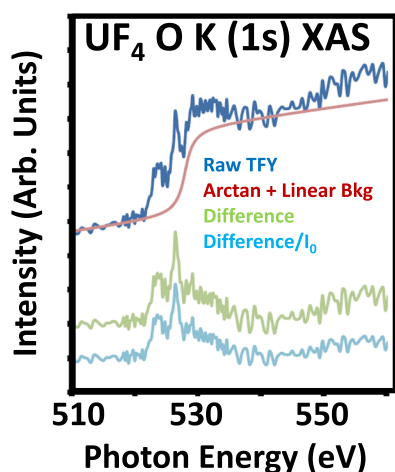


Fig. 10. (Color online) Impact of a simple background subtraction upon the O K (1 s) of  $\text{UF}_4$  spectrum. The spectra shown here are the original raw  $\text{UF}_4$  TFY data, the arctan + linear background, the difference curve and the difference divided by the  $I_0$ . There does not appear to be any significant variation between the last two curves.

the possibility of a uranyl nature to the subsurface species. This includes the possibility of  $\text{UO}_3$ , but  $\text{UO}_2\text{F}_2$  seems more likely, in part because of the observation of the F K (1s) XAS TEY peak in Fig. 6.

A consideration of the spectra in Fig. 8 and Refs. 16 and 17 suggests that the comparison may be improved by a background subtraction. It is possible that the subsurface species is occluded by the background emission associated with the very strongly corrupted surface. As can be seen on Fig. 1, the carbon tape spectra clearly exhibit this steplike background. One way to get a measure of this background would be to normalize the TFY and TEY spectra to each other using the peak near 525 eV and then subtract. The result of this operation can be seen in the inset in Fig. 9. Furthermore, Fig. 9 illustrates the utility of approximating this steplike background with an arctan function. It is this arctan function, coupled to a linear term, which has then been used to approximate the background as shown in Fig. 10. Although imperfect, this does provide a way to remove the step like background. The result of the subtraction of the arctan + linear background from the  $\text{UF}_4$  O K (1s) TFY data is plotted in Fig. 10. Qualitatively, this improves the match with the  $\text{UO}_2\text{F}_2$  spectrum of Duffin *et al.*<sup>16</sup> (not shown).

#### IV. SUMMARY AND CONCLUSIONS

While the bulk of the single crystal sample remains intact  $\text{UF}_4$  and can be successfully interrogated with bulk-sensitive probes, the surface and subsurface regions are corrupted. The surface of the  $\text{UF}_4$  sample is so severely corrupted as to be essentially unrecognizable as originating from  $\text{UF}_4$ . However, the subsurface seems to have a uranyl species, probably  $\text{UO}_2\text{F}_2$ , which may be a precursor on the path to the more total corruption of the surface region.

Finally, it is useful to attempt to quantify the depth sensitivity of these measurements. To do so, one needs to consider the issue of mean free paths (MFP). The concept of mean free paths can be traced back to the kinetic theory of gases.<sup>18</sup> For electrons in solids, the values will depend not only on the energies but also on the materials.<sup>19</sup> As might be expected, the escape depths or penetration depths for electrons tend to be substantially less than those for photons.<sup>20</sup> In the case of total electron yield measurements in XAS, which is dominated by low energy electrons, previous experimental results indicate a MFP of 22 Å or 2.2 nm.<sup>21</sup> A consideration of the results in Ref. 19 confirms that estimate, if one assumes an electron energy of about 10 eV. For the energies associated with the XPS measurements, a MFP of about 10 Å seems reasonable, again based on the results of Ref. 19. Thus, the sampling depth of the XPS and XAS measurements should be on the same scale of about 10–20 Å, with the XAS being perhaps a factor of two greater. This last detail may explain the observation of a F1s XAS peak with TEY but the absence of a significant F1s peak in XPS. One can expect that the photon measurements will penetrate far deeper, on the scale of micrometers (10 000 Å or 1000 nm).<sup>20</sup> The qualitative nature of these estimates must be emphasized. Nevertheless, it is clear that the electrons are probing the near surface regime of nanometers and that the electrons are sampling far deeper into the bulk.

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