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X-Ray Absorption Spectroscopy of Uranium Dioxide

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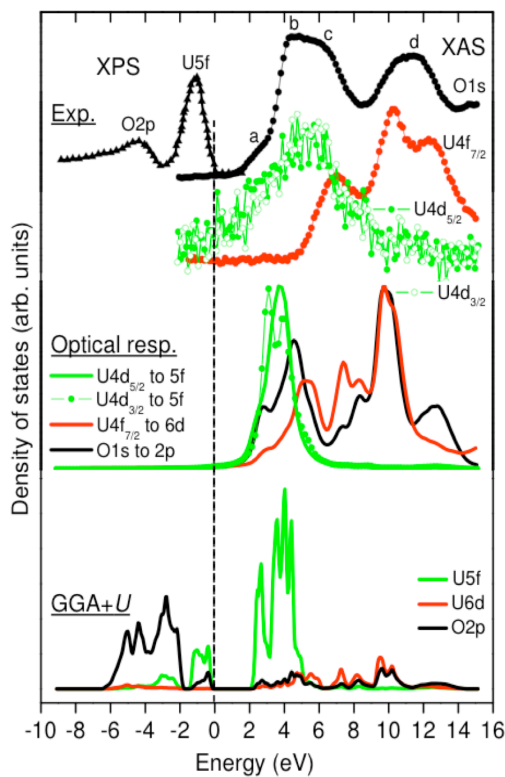
X-ray Absorption Spectroscopy of Uranium Dioxide

Based upon LLNL-JRNL-454674

Motivation of Analysis

After the CMMD Seminar by Sung Woo Yu on the subject of the x-ray spectroscopy of UO₂, there arose some questions concerning the XAS of UO₂. These questions can be distilled down to three issues.

1. The validity of the data.
2. The monochromator energy calibration.
3. The validity of XAS component of the figure shown below.



Results of Analysis

The following will be shown.

1. The data is valid.
2. It is possible to calibrate the monochromator.
3. The XAS component of the above picture is correct.

The remainder of this document is in three sections, corresponding to the three issues. This begins on the next page.

X-ray Absorption Spectroscopy of Uranium Dioxide

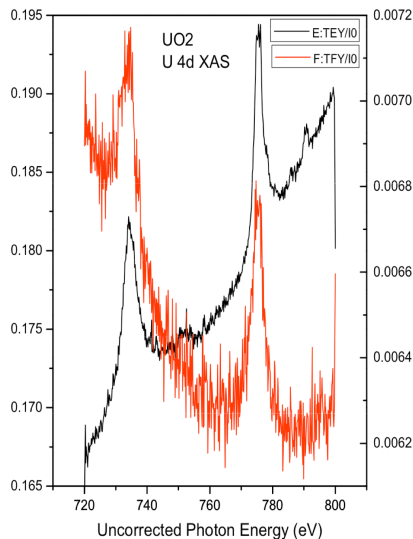
Based upon LLNL-JRNL-454674

Section 1. Validity of Data

There were six data ranges probed. They correspond to the U 4d ($h\nu = 720 - 800$ eV), O 1s ($h\nu = 530$ eV - 580 eV), the U 4f ($h\nu = 380$ eV - 410 eV), the U5p1/2 ($h\nu = 256 - 280$), the U5p3/2 ($h\nu = 174 - 186$ eV), the U 5d ($h\nu = 90 - 140$ eV). The U4d was collected using the high-energy grating and the others were all collected using the middle-energy grating. These are shown below, reordered for ease of comparison.

High Energy Grating U4d Region

TEY = Total electron Yield
TFY = Total Fluorescence Yield



materials such as the sample holder and sample supports. Thus, what you see above is reasonable.

Kalkowski and Kaindl et al, PRB 35, 2667 (1987).

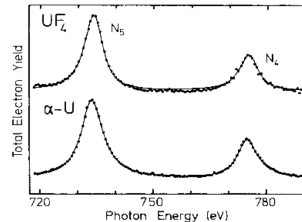


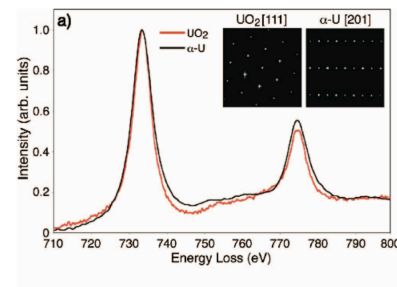
FIG. 7. Total-electron-yield spectra of α -U metal and UF₄ at the N₅ thresholds. The solid lines represent fit results.

Kalkowski and Kaindl 's paper is considered the gold standard for XAS of U. As you can see, our U4d's for UO₂ fall in the same energy range as theirs for U metal and UF₄.

Moore et al, PRB 73, 033109 (2006)

There really isn't any doubt about the validity of the data above. This looks pretty much like the U4d's should. Of course, there is always the issue of backgrounds. Given the constraints placed upon the experimentalists by the ALS, that only a very small sample (1 mm x 1 mm surface area) could be used, background variations and low signal rates are not unexpected. The x-ray beam was larger than the sample and any misalignment could cause contributions from other

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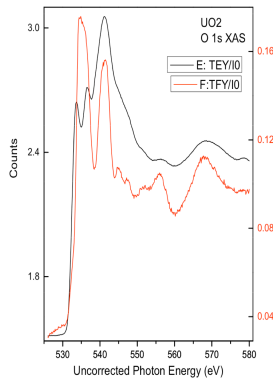
For the sake of completeness, a comparison with UO₂ High Energy EELS is included here. Again, our U 4d XAS is consistent with the EELS result.

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Middle Energy Grating O1s Region-O1s First Order

O1s, Jollet et al, JPCM 9, 9393 (1997)



Electronic structure of UO_2

9395

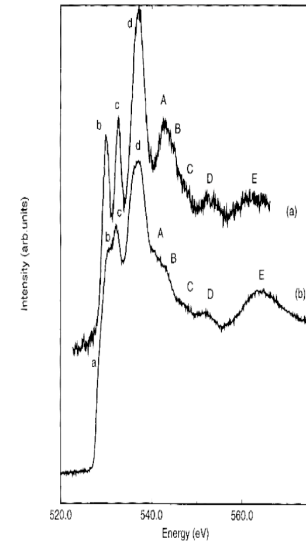
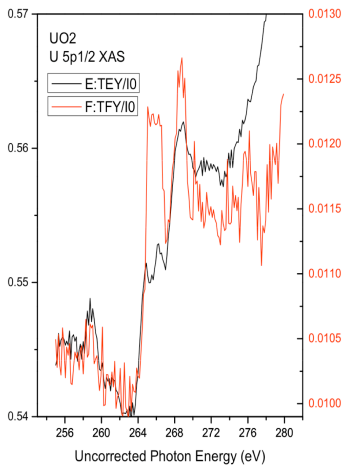


Figure 1. XAS oxygen K edge of CeO_2 (a) and UO_2 (b).

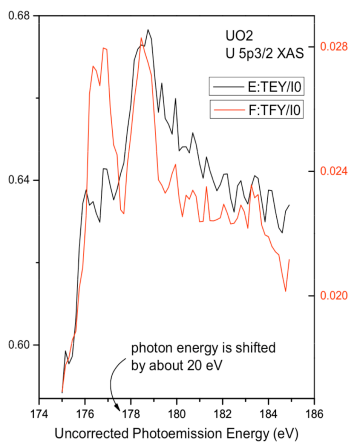
Table 1. Energies of the structures of the O K XAS spectrum for CeO_2 and UO_2 .

	a	b	c	d	A	B	C	D	E
CeO_2 (eV)	—	530.9	533.5	537.9	543.6	545.7	548.7	553.9	563.4
UO_2 (eV)	528.55	530.65	532.2	537.0	540.9	543.1	546.85	551.85	564.05

U5p1/2 Region-O1s Second Order



U5p3/2 Region-O1s Third Order

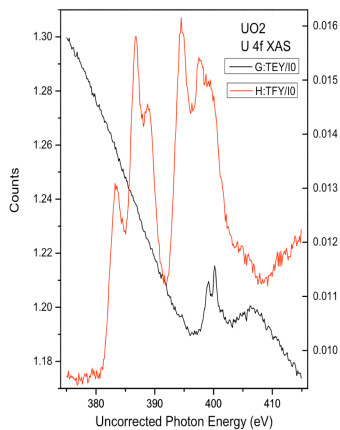


The bad news: the U5p's are overwhelmed by the O1s in 2nd and 3rd order. The good news: this will allow us to calibrate the middle grating perfectly. The other good news, all of our TFY's, 1st, 2nd and 3rd order, are consistent with each other and all of our TEY's, 1st, 2nd and 3rd order, are consistent with each other. The TFY's are a better measure of the bulk electronic structure, with TEY's more sensitive to surface modification. However, our TEY's are consistent with the TEY of Jollet et al. The work by Magnuson et al, [Magnuson, Butorin, Werme, Nordgren, Ivanov, Guo, and Shuh, Applied Surface Science 252, 5615 (2006)] for UO_2 etc is more problematic, possibly representing surface effects in their TEY's. **Our TFY's should be a reliable measure of the bulk electronic structure.**

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Middle Energy Grating U 4f Region



Thorium 4f EELS, Moser, Delley, Schneider and Baer, PRB 29, 2947 (1984)

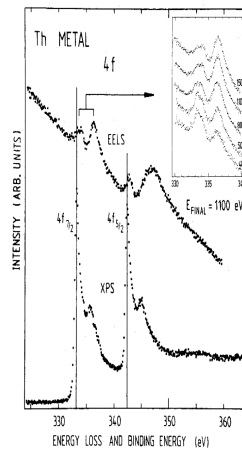


FIG. 2. EELS and XPS $4f$ core-excitation spectra of Th metal on a common energy scale. The inset shows the excitation energy dependence of the low-energy-loss structure. The common onset of the EELS and XPS edges is indicated by two parallel lines drawn through the maxima of the spin-orbit-split $4f_{7/2}$ and $4f_{5/2}$ XPS components.

Uranium 4f EELS, Moser, Delley, Schneider and Baer, PRB 29, 2947 (1984)

Moore et al, PRB 69, 193104 (2004)

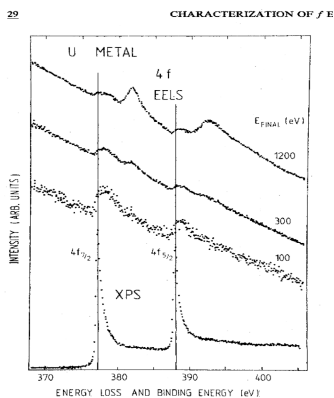


FIG. 3. EELS spectra, taken at the indicated final-state energies, and XPS $4f$ core-excitation spectra of U metal. The common onset of the EELS and XPS emission is indicated by the two parallel lines drawn through the maxima of the spin-orbit-split XPS components.

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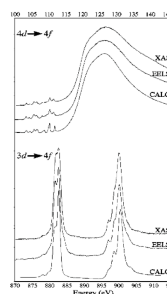
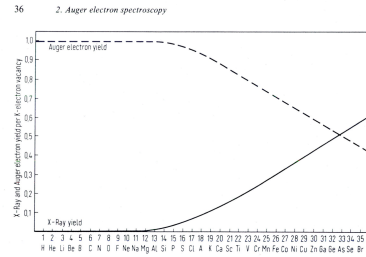
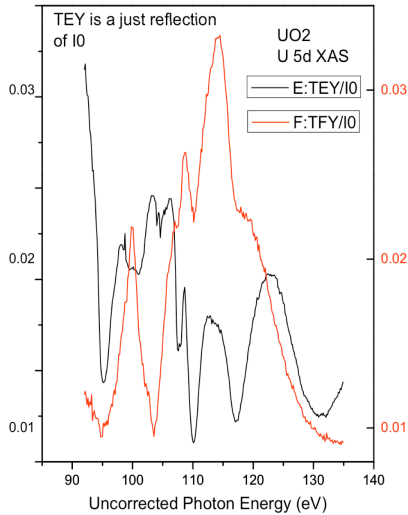


FIG. 4. A series of spectra showing both the N_{4s} ($4d \rightarrow 4f$) and M_{4s} ($3d \rightarrow 4f$) transitions for cerium. The ability of the multielectronic atomic calculations to replicate the XAS and EELS spectra so closely demonstrates the strongly atomic nature of f electrons in cerium metal. Notice that the spectra from XAS and EELS from a monochromated TEM are essentially identical in both resolution and form. The TEM's ability to form a 2 Å probe means that spectral investigations of highly site-specific regions of a sample, such as interfaces, dislocations, grain boundaries, etc., can be performed with very high energy resolution. The additional capability to record images and diffraction patterns is of great importance for lanthanide and actinide metals where a mixture of multiple crystallographic phases is common.

We've searched the literature and so far CANNOT find any U4f XAS. (We'll keep looking...) However, we have found U4f EELS and Th4f EELS, as shown above. From other experiments, we know that XAS and EELS can give the same answer, if the excitation energy is high enough in EELS. (See the example with Ce above.) The Th 4f EELS shows that they are converging to the high energy limit above 1000 eV and the U 4f EELS was taken at 1200 eV, so it seems likely that this U 4f EELS should be the same as U 4f XAS. The U4f XAS TFY looks like it has the same peak structure as the U 4f EELS, if one discounts the region near 400 eV with the Nitrogen contaminant. The fact that the U 4f XAS TFY is so different than the U4f XAS TEY can be explained by stronger surface effects in TEY, which can also be seen in the O1s XAS, shown on the previous page. **So, we think that this is pretty strong evidence that the U4f7/2 XAS TFY is legitimate.**

Middle Energy Grating
U 5d Region



2.5.2. The ionization cross section
The ionization cross section σ_i for excitation by electron impact depends strongly on the energy E_i of the bound electron as well as on the primary energy E_p of the impinging electron beam.

Ertl and Kueppers, "Low Energy Electrons and Surface Chemistry," Verlag Chemie, D-694 Weinheim, 1964, after K. Seigbahn et al, "ESCA Applied to Free Molecules," North Holland, Amsterdam, 1969

U 5d, van Kampen et al, PRA 61, 062706 (2000)

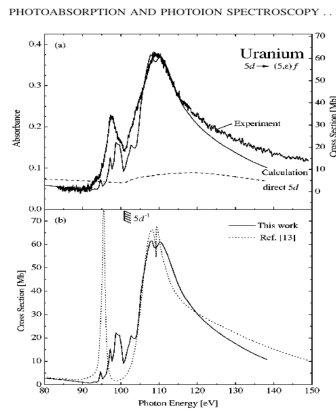


FIG. 3. Experimental and calculated photoabsorption spectra of atomic uranium in the 5d region: (a) experiment, full calculation (solid line) and calculation for direct 5d ionization only (dashed line); (b) comparison of the present calculation and that of Ref. [13]. The arced lines denote the lowest 5d¹ threshold. The calculated cross section is displayed in such a way that the 0-Mb level coincides with the experimental spectrum at the onset of 5d ionization to compensate for the omission of direct photoionization from lower-lying subshells.

The above result is for an atomic U.

The issue of the weakness of the signal in TEY relative to TFY for the U4f and U5d may not be merely a sample size (signal vs background) or surface effect. (TEY is more surface sensitive.) It may also reflect the different fundamental efficiencies of TFY vs TEY. As shown in the figure above, TFY gains relative to Auger as Z increases, at least for the K edges shown. Of course, there can be edge specific effects: e.g., the U4d has a fairly strong TEY, the U4f and U5f don't. Nevertheless, Auger Emission drives TEY and X-ray emission is the source of TFY. The z dependence helps explain why the O1s has both TEY and TFY and the U seems to be losing the TEY but not the TFY.

Once again, we see that our TFY compares well with the literature and that the TEY has some sort of problem. **Again, this indicates that the TFY is legitimate.**

Conclusion: The TFY spectra are legitimate measures of the bulk electronic structure.

Section 2. Monochromator Energy Calibration

High Energy Grating

From the data on page 2 for the U4d region, it appears that the grating calibration is essentially dead on. This is not surprising, since the 3d transition metal L edges are in this range and many people want to work at those edges. Thus, the ALS is fairly highly motivated to keep those calibrations up to date.

Middle Energy Grating

From the O1s data on page 3, for the edges seen with 1st, 2nd and 3rd order light, it is clear that this grating needs to be calibrated. This is where the advantage of having three measurements of the same edge with first, second and third order light becomes so valuable.

Most grating errors, particularly for an SGM, which is just a high-energy Seya-Namioka, are caused by a misalignment of the grating zero, i.e. driven by a single $\Delta\lambda$. If this is true, then the errors should scale with E-squared.

$$E = hv = hc/\lambda \quad \text{with } v\lambda = c$$

$$dE = -hc(d\lambda) / \lambda^2 = - E^2(d\lambda)/hc$$

$$\Delta E = - E^2(\Delta\lambda)/hc \quad \text{with } hc = 12400 \text{ eV-Angstroms}$$

Order	Uncorrected Energy(eV) E	Unknown Value(eV) E0	Energy Correction (eV) - E ² ($\Delta\lambda$)/hc
1 st	534.5	E0	-23.04 $\Delta\lambda$
2 nd	265..5	(1/2) E0	-5.68 $\Delta\lambda$
X2	531	E0	-11.36 $\Delta\lambda$
3 rd	176.5	(1/3) E0	-2.51 $\Delta\lambda$
X3	529.5	E0	-7.53 $\Delta\lambda$

Using the relations in red, there are three equations and two unknowns. We can back out the unknowns, E0 and $\Delta\lambda$, by a linear regression using y = E and x = E²/hc. Then the slope of the line, m, and the intercept, b, give us the following.

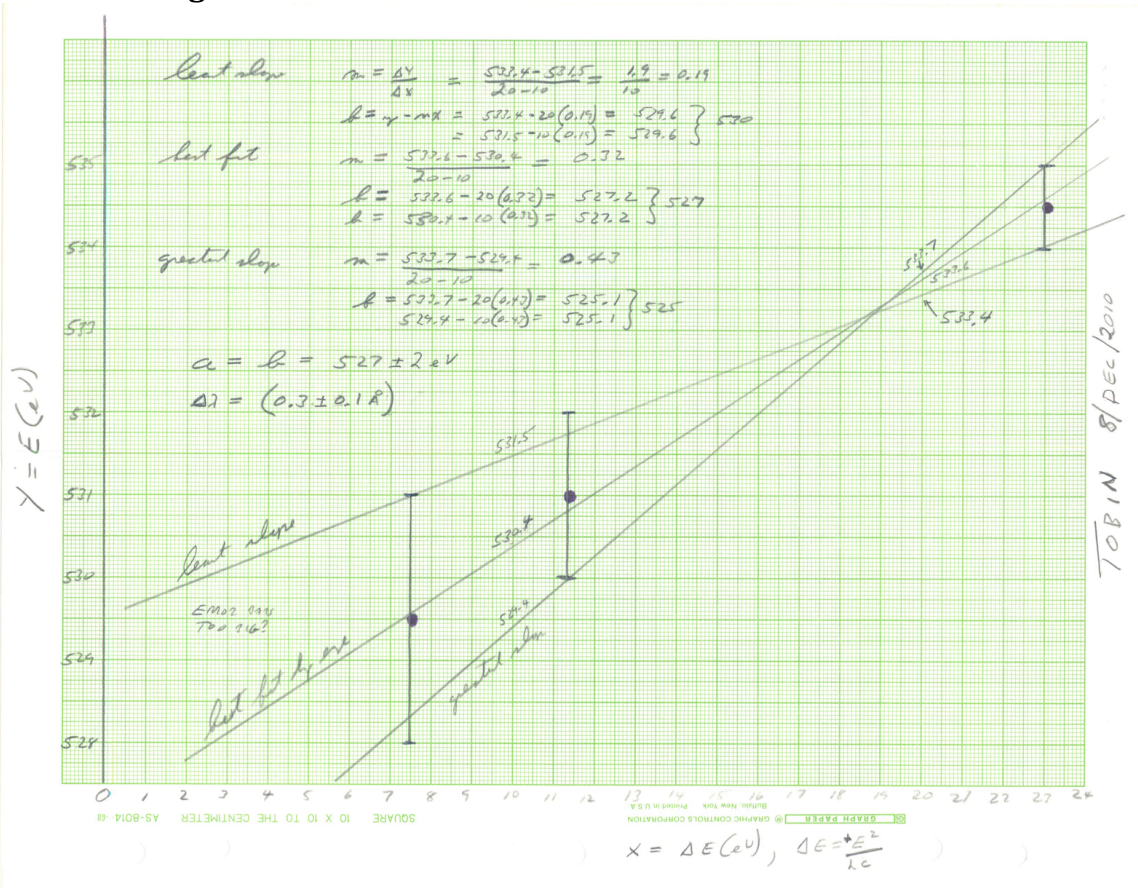
$$m = - \Delta\lambda \quad \text{and} \quad b = E0$$

From our analysis, E0 = 527 eV and $\Delta\lambda = 0.3$ angstroms, as shown on the following page.

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Middle Grating Calibration



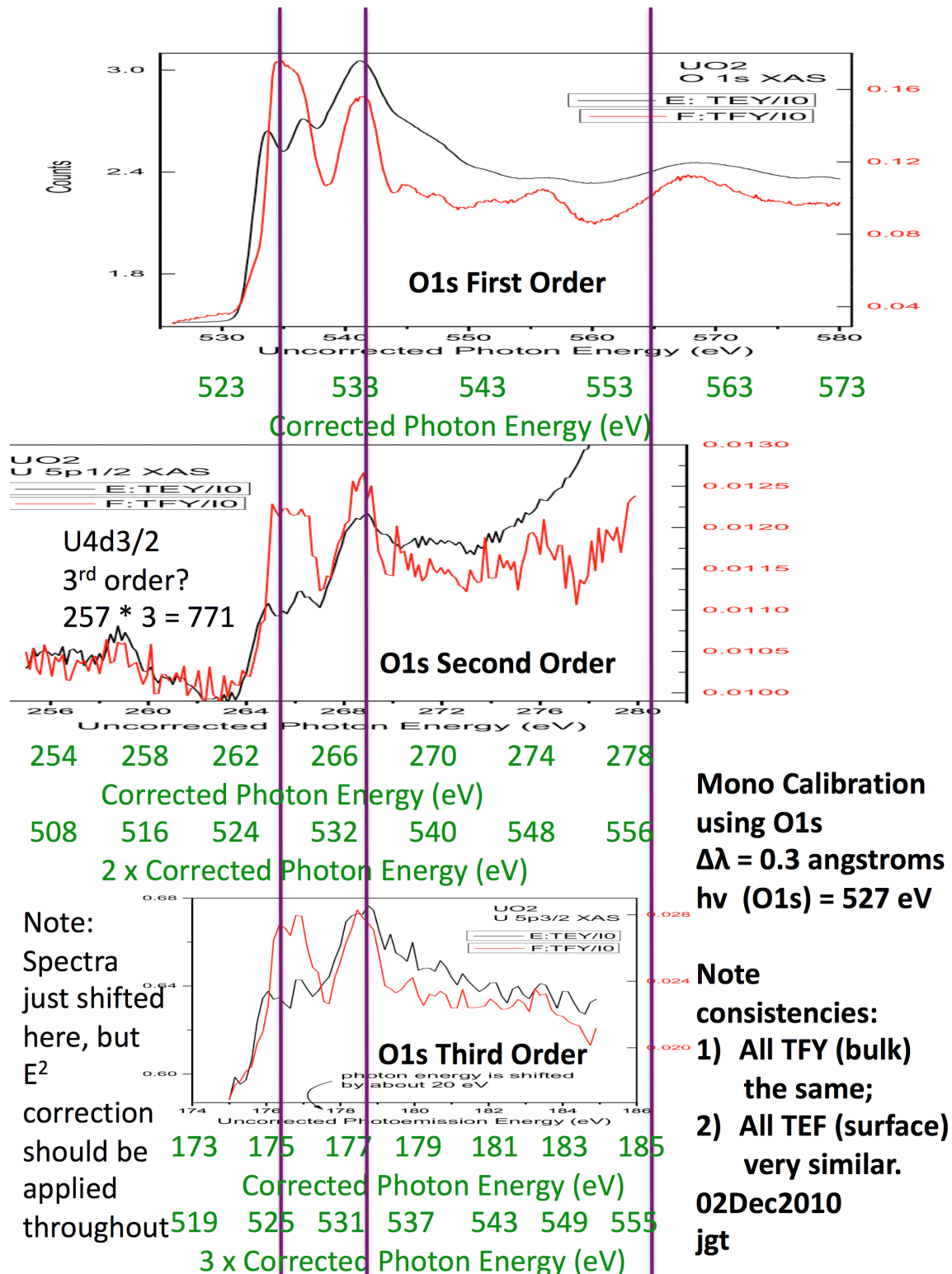
The error bars arise from the assumption of +/- 0.5 eV error in the determination of the photon energies. This is probably too big. For the second and third order cases, because we double and triple the energies, respectively, the error also gets doubled or tripled. There should also be an error for x, from propagating the energy error through the multiplication, but the y error is probably enough to give us a good significant figure estimate.

This is low tech, but it works.

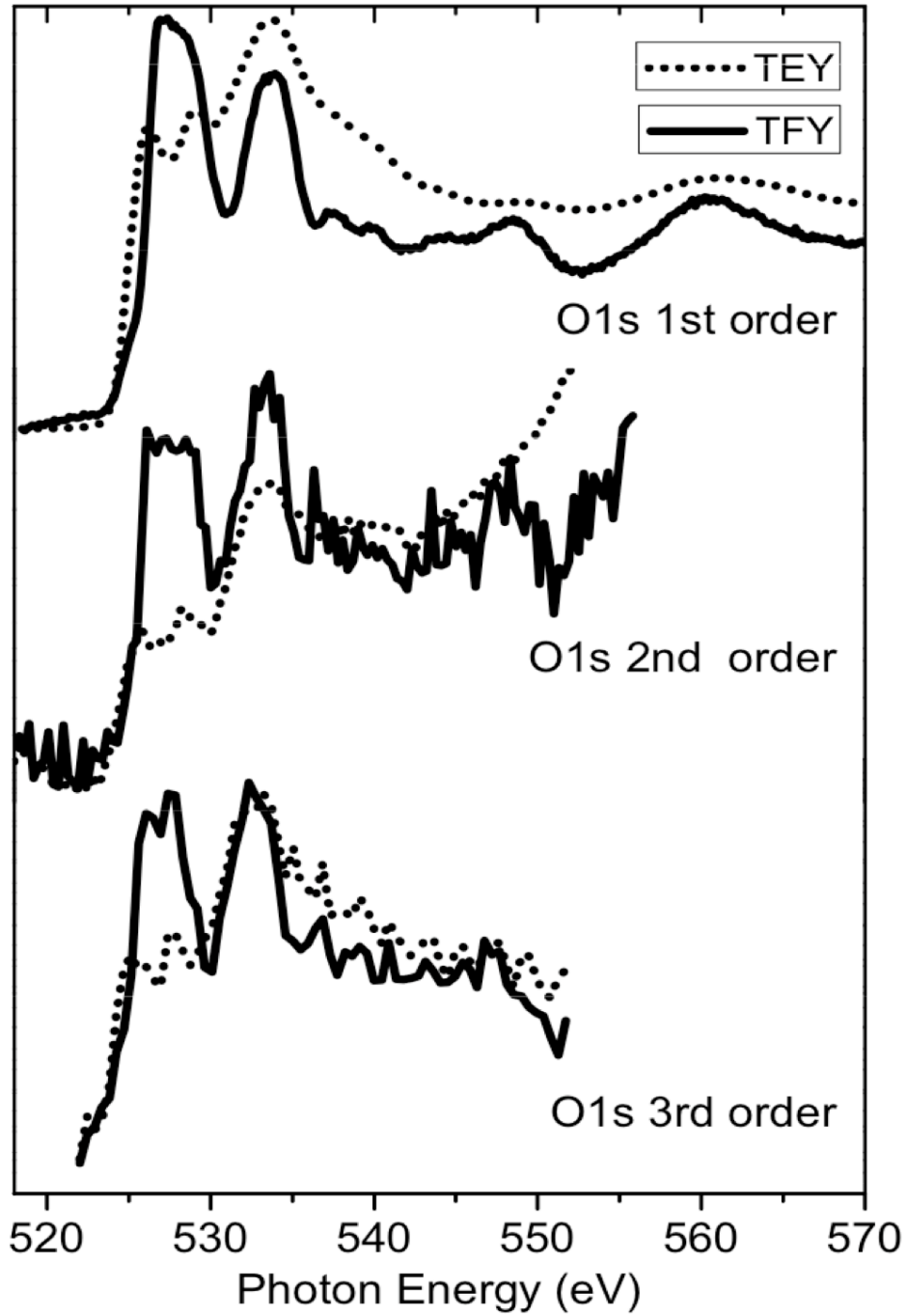
When we shift the spectra, we get the result on the next page.

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Of course, we can re-plot all of this to make it look nice, as shown on the next page.



We find this quite convincing and hope that you do as well.

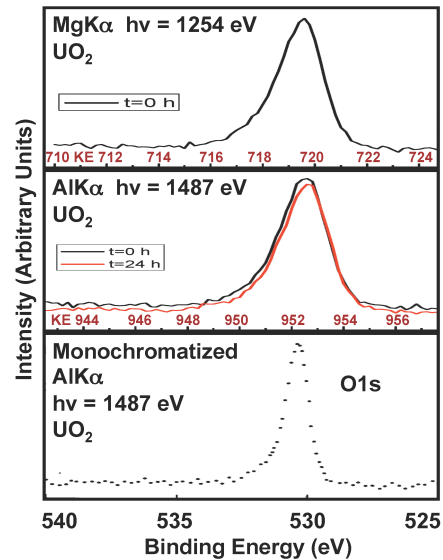
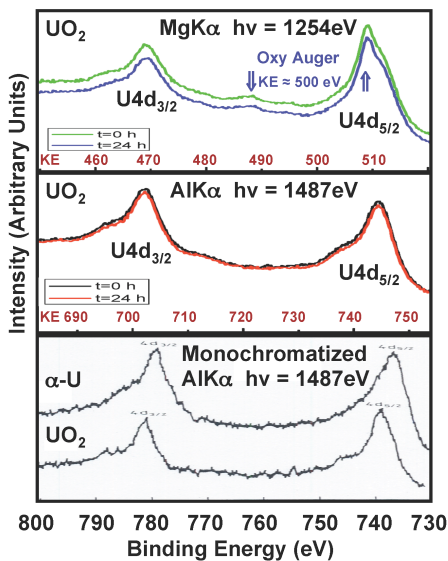
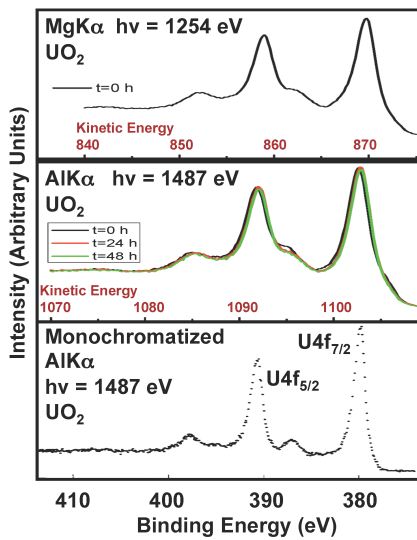
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Section 3. Comparison of Spectra

Having a correct energy calibration for both the high and middle energy grating will then allow us to test the method that Sung Woo proposed in his talk. Note that while the U4d spectrum has the correct hv already, the U4f will need to be shifted by the same relation as on page 6, $\Delta E = -E^2(\Delta\lambda)/hc = -(380)(0.3)/12400 = -3.5$. Then, the binding energies for each core level are subtracted, using our XPS spectra for UO₂, which agree with the literature for UO₂. Below are our spectra, with those from the literature. (All of these are in our MRS Proceedings, a copy of which is attached separately.)

Here are our XPS spectra, with the comparison to the literature values.



The article is JG Tobin, S-W Yu, BW Chung and GD Waddill, Mater. Res. Soc. Symp. Proc. **1264**, 1264-Z11-06 (2010).

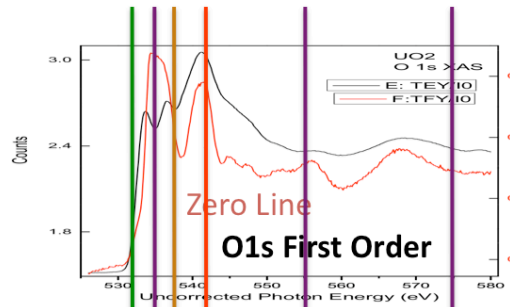
For UO₂, From Baer and Schones, Solid State Commun.
BE (O1s) = 530.5 eV (from plot)
BE (U4d7/2) = 380 eV (from plot)

For UO₂, From G.C. Allen et al, Phil. Mag. 1981
BE (U4d7/2) = 380.25 eV (average)
BE (U4d5/2) = 738.5 eV (average)

The result of the comparison is shown on the next two pages. The second page is a blow-up of the first.

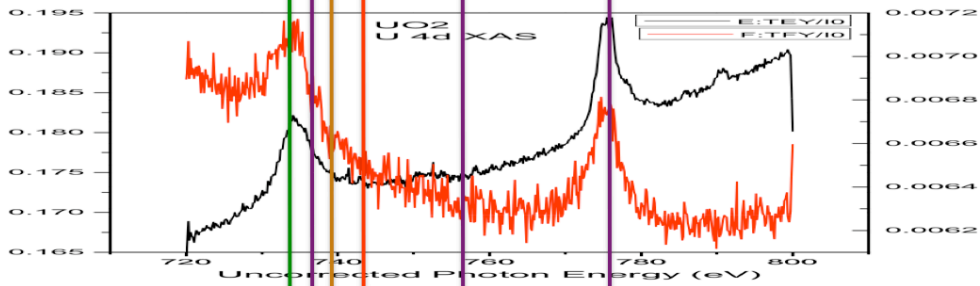
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523 533 543 553 563 573
 Corrected Photon Energy (eV)
 -7.5 2.5 12.5 22.5 32.5 42.5
 Corrected $h\nu - BE(O1s) = \text{Corrected } h\nu - 530.5 \text{ (eV)}$

Comparison of O1s, U4d 5/2 & U4f7/2
 $X = h\nu - \text{Binding Energies}$
 Using corrected $h\nu$ for O1s (middle grating)
 Using uncorrected $h\nu$ for U4d's (high energy grating)
 Based upon comparison of our results and Kalkowski and Kaindl (PRB 1987), our uncorrected $h\nu$'s for the U4d's looked good.
 Using corrected $h\nu$ for U4f7/2
 This is the middle grating, bracketed by the O1s in 1st, 2nd and 3rd order. The U4f spectrum was shifted by -3.5 eV



-19 1 21 41 61
 $h\nu - BE(U4d5/2) = h\nu - 739 \text{ (eV)}$

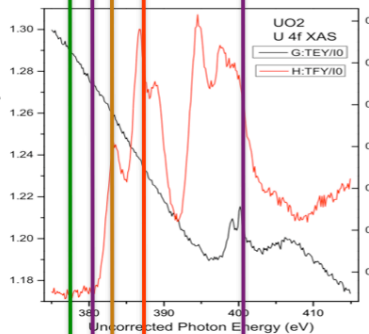
The purple lines are separated by 20 eV and are used for scaling.

The Orange line is the zero, which I used to align the spectra. It has no other special significance.

The green line is for the U4d.

The red line is for the U4f.

All of this needs to be rechecked carefully.



375.5 386.5 396.5 406.5
 Corrected Photon Energy (eV) = $h\nu - 3.5\text{eV}$
 -3.5 6.5 16.5 26.5
 Corrected $h\nu - BE(O1s) = \text{Corrected } h\nu - 380 \text{ (eV)}$

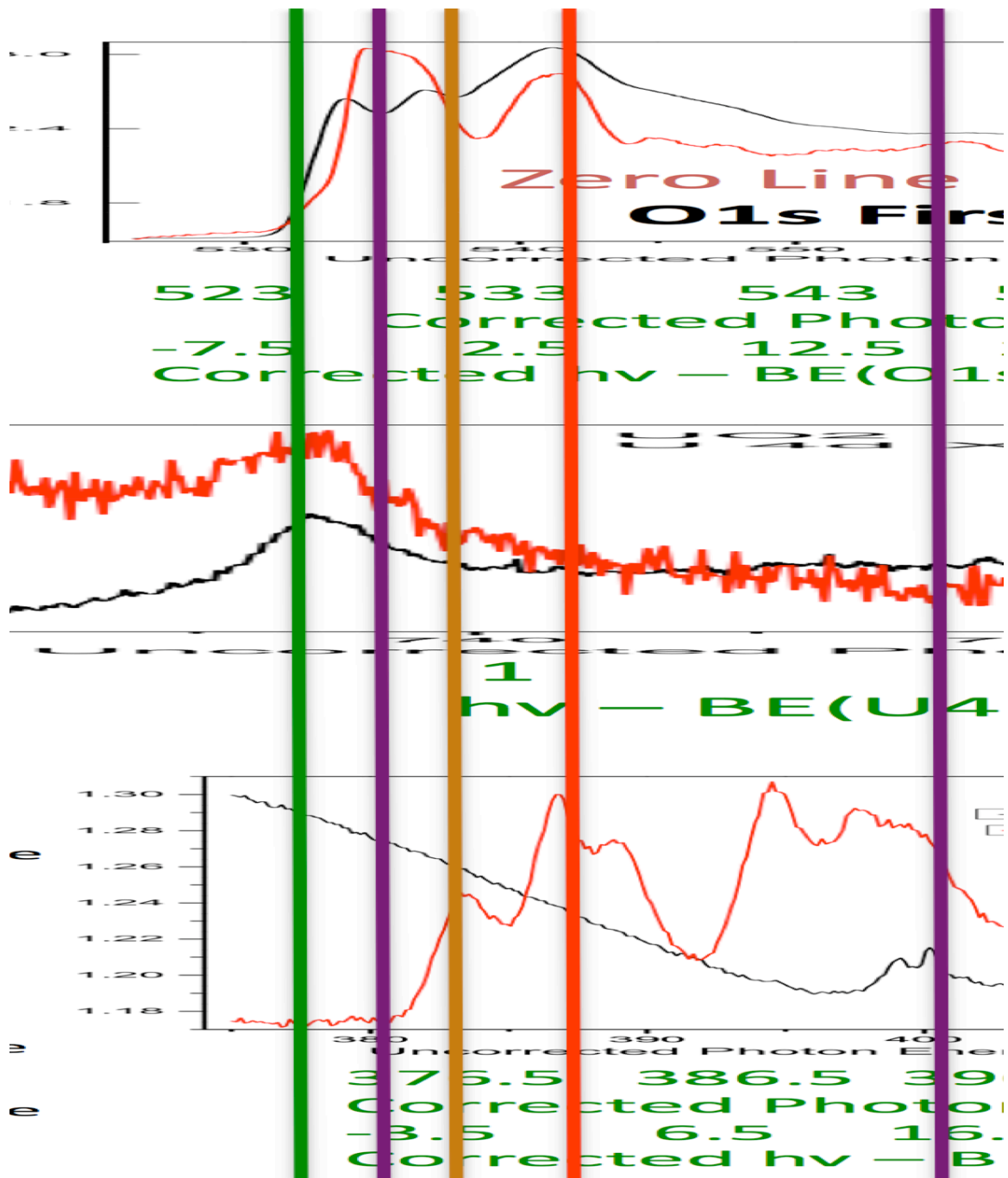
Our binding energies come from our XPS measurements, which are in agreement with the literature.

Please see the attached pages from our MRS Proceedings 2010.

A big question with the U4f is whether it comes from a contaminant. We'll need to resolve that issue.

It might be best to plot everything versus O1s $h\nu$, shifting the U4d and U4f by the difference between their BE and the O1s BE.

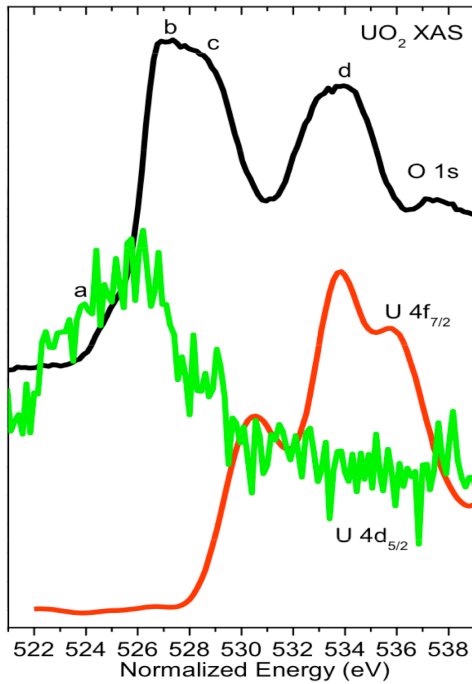
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 jgt



As you can see, we are back to something very close to what the figure on page 1 showed earlier. However, this is probably better. The U4d's have a huge lifetime broadening, giving rise to a Lorentzian, almost triangular, peak shape. The threshold may well be in the center of the white line peak, consistent with the alignment above. On the next page, we re-plot all of this.

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Here, we use “Normalized Energy,” which is essentially the O1s photon energy.

Normalized Energy = NE

$$NE = h\nu - [BE - BE(O1s)]$$

with

$h\nu$ = Photon Energy

and

BE = Binding Energy from XPS

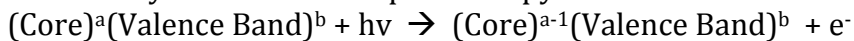
$$O1s \quad NE = h\nu (O1s)$$

$$U4f \quad NE = h\nu (U4f) - [BE(U4f) - BE (O1s)]$$

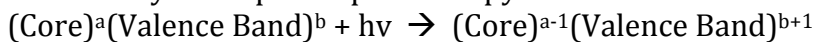
$$U4d \quad NE = h\nu (U4d) - [BE(U4d) - BE (O1s)]$$

There was some concern voiced about subtracting binding energies (from XPS) from photon energies (from XAS), because of the different final states and concomitant effects such as screening, shielding, relaxation etc. (See below.)

XPS = X-ray Photoelectron Spectroscopy



XAS = X-ray Absorption Spectroscopy

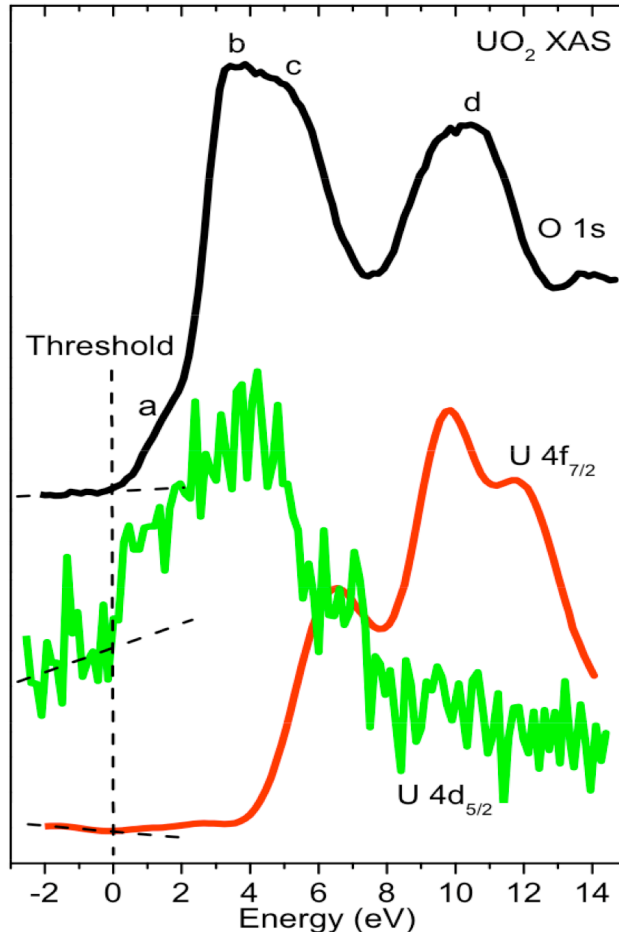


As the plot on the previous page suggests, all of these effects appear to cancel out. We can make that cancellation more obvious by using the Normalized Energy and subtracting a difference of XPS BE's, which will remove any question of reference points in the measurements.

An Alternative Approach: Threshold Analysis

While we are quite confident of the result derived from using photon energies and binding energies, there is a completely independent approach that will give almost exactly the same result. In the U4d spectra, there is a very strong lifetime broadening, which gives rise to a Lorentzian or triangular peak shape. The threshold is probably directly under the centroid of the peak. However, if one were to take a contrarian viewpoint, one could define the threshold as the beginning of the peaks spectral intensity. Then one could align all of the spectra based upon the thresholds, arguing that this represents the Conduction Band Minimum (CBM). If one follows through on this analysis, the result below is obtained, which is almost identical to the result on the previous page.

Either way, one ends up with something that looks very much like the XAS result on page 1.



At this point, we see no show-stopping problems and propose that we continue with re-submission of the article, modifying it first to respond to the referee reports from PRL.