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Oxidant K Edge XES of UF$_4$ and UO$_2$

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The K-Edge (1s) X-ray Emission Spectroscopy of Uranium Tetrafluoride and Uranium Dioxide were compared to each other and to the results of a pair of earlier cluster calculations by Ryzhkov. Using a very simplified approach, it is possible to qualitatively reconstruct the three main features of the XES spectra from the cluster calculation state energies and 2p percentages.

INTRODUCTION

Uranium Dioxide (UO_2) and Uranium Tetrafluoride (UF_4) are isoelectronic [1,2] in the limit of

complete ionozation (U^{4+}, $[Rn]5f^2$) and have essentially the same nearest neighbor distances. [3]

However, their roles in today's highly technological society are vastly different. Uranium dioxide is

the most commonly used nuclear fuel for the generation of electricity, making it of great intrinsic

importance. [1, 2, 4] UO_2 also exhibits a number of scientifically interesting traits, including the

presence of covalent behavior in the U5f states. [4, 5] On the other hand, its cousin uranium

tetrafluoride is, in some respects, much simpler, with behavior more along the lines of the ionic limit.

[1,2] Here, we will compare the experimental results for the O1s and F1s X-ray Emission Spectroscopy

(XES) of these two compounds to each other and to simulated spectra derived from the cluster

calculations of Ryzhkov et al. [6,7]

EXPERIMENTAL

The experiments were carried out at the Advanced Light Source, Lawrence Berkeley National

Laboratory, Berkeley, CA and at Lawrence Livermore National Laboratory, Livermore, CA. XES of

the uranium dioxide was performed at LLNL [8], using a spectrometer described in detail elsewhere.

[9] The XES of the uranium tetrafluoride was done at the ALS [1, 2, 10], using a spectrometer that is

part of Beamline 8. [11] Both samples have been extensively characterized [12 – 14] and the efficacy

of the LLNL spectrometer has been demonstrated with non-actinide samples. [8, 15]

XES AND XPS EXPERIMENTAL COMPARISON

To begin, consider the results shown in Figures 1 and 2 below. In each case, for uranium tetrafluoride

and uranium dioxide, there is a direct comparison of the XES results with the X-ray Photoelectron

Spectroscopy (XPS) and the histogram Occupied Density of States (ODOS) derived from the

calculationsof Ryzhkov. [6, 7] Note that while the energy steps are identical, each of the x-axes can be
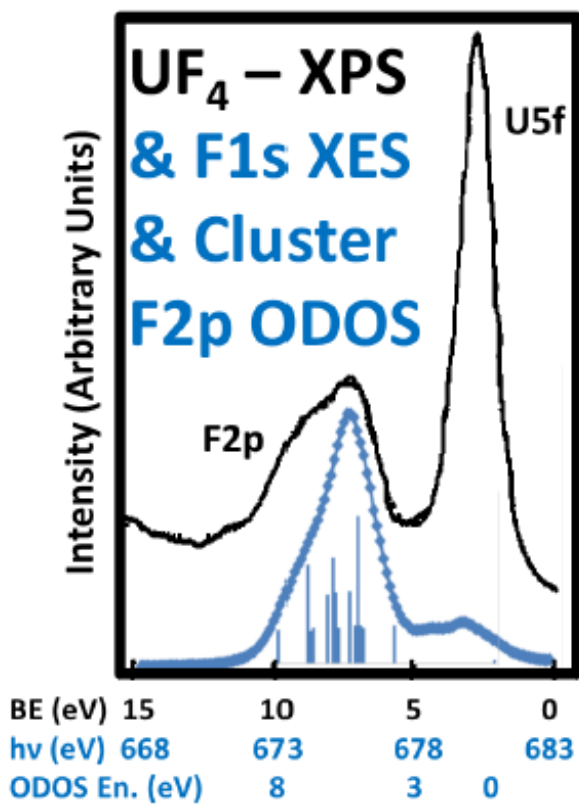
shifted relative to the others.

Figure 1   Comparison of the XES results for UF$_4$ with the X-ray Photoelectron Spectroscopy (XPS) of UF$_4$ from Thibaut et al. [16] and the ODOS derived from the calculations of Ryzhkov [6], for a (UF$_8$)$^{4-}$ cluster. The XES peak is at hv = 675 eV. The XPS measurements of Teterin et al. [6] confirm the Thibaut result.
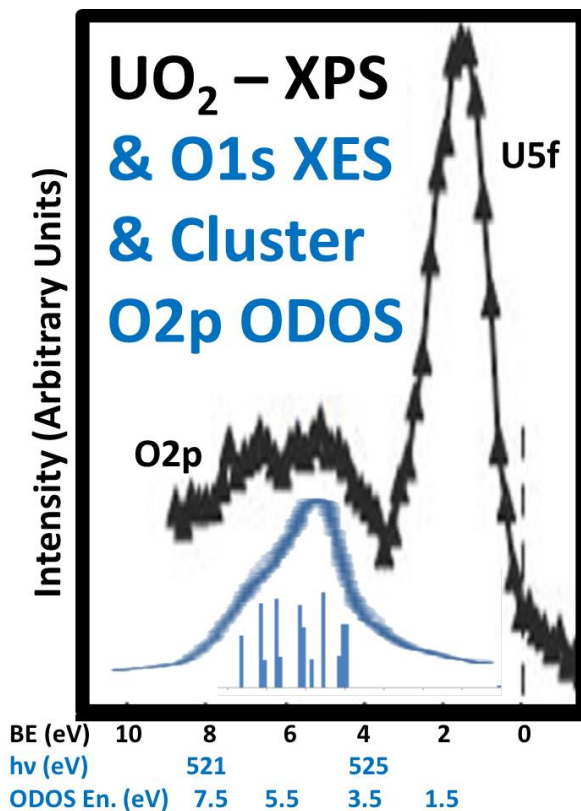
Figure 2   Similarly to Figure 1, this is a comparison of the XES, XPS [5] and cluster results for UO$_2$. The calculations of Ryzhkov [7] are based upon a (UO$_8$)$^{12-}$ cluster. The XPS Spectrum was taken from Ref. 5.

It is of interest to note that there is good agreement between the XPS and XES, with the suggestion that

each XES spectrum is composed of three main features: a strong central peak with a distinct shoulder

on the left side (lower XES energies) and a less distinct shoulder on the right side (higher XES

energies). Clearly, the ODOS histograms from the cluster calculations fall within the manifolds

defined by the XPS and XES spectra. (The weak peak near hv = 680 eV is from a UO_2F_2 surface

contaminant, as described in Ref. 10 and 13.) However, the question remains: are these histograms

consistent with the three feature nature of the XES measurements? That issue will be addressed next.

CONCEPTUALIZATION OF XES SPECTRUM

The K (1s) Edge XES spectrum is the result of a transition of an electron from an occupied 2p state into

a 1s core-hole, as shown schematically in Figure 3. These transitions are electric dipole in nature, with

$\Delta l = \pm 1$. Generally speaking, for each state in the manifold with 2p character, there should be a

corresponding peak in the XES spectrum, with a finite width caused by a variety of factors, including

lifetime broadening and instrumental resolution limitations. This is also shown schematically in Figure

3. Our approach is to take each occupied state in the Ryzhkov cluster calculation with non-zero 2p

character and generate an XES component peak for it, scaling the intensity to the 2p percentage, and

then sum all of the component peaks to get an overall spectrum. For the sake of simplicity and

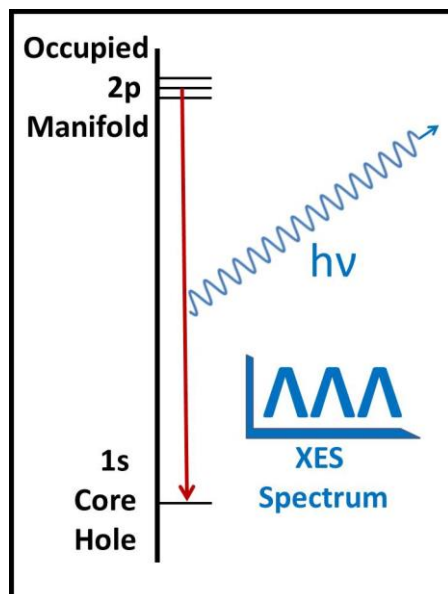transparency, we will begin by utilizing the ubiquitous Gaussian function for our component line-

shape.

Figure 3   The XES process and resultant spectrum.

SPECTRAL SIMULATION BASED UPON THE HISTOGRAM ODOS

In this analysis, we have made a pair of simplifying assumptions. (1) The cross sections are all equal. (2) The component widths and shapes are all the same. To begin, a gaussian lineshape was utilized and the FWHM was varied systematically, as shown in Figure 4 below, for the F2p ODOS, with the intensity scaling from the histograms in Figure 1. The plots in Figure 3 show the summation of the contributions from each component. As can be seen in Figure 4, the best match corresponds to FWHM near 1 eV.
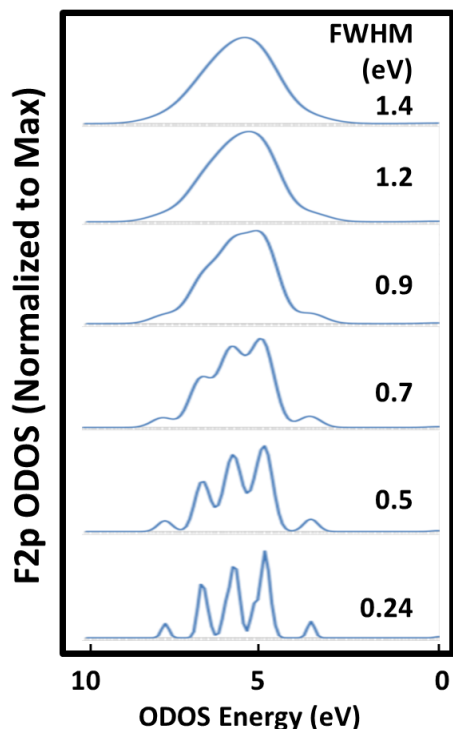

Figure 4   Simulated XES Spectra from the F2p ODOS histograms, utilizing a guassian lineshape and specified Full Width at Half Maximum (FWHM) for each component, For a guassian function, FWHM = 2(2ln2)$^{1/2}$ Sigma = 2.355 Sigma
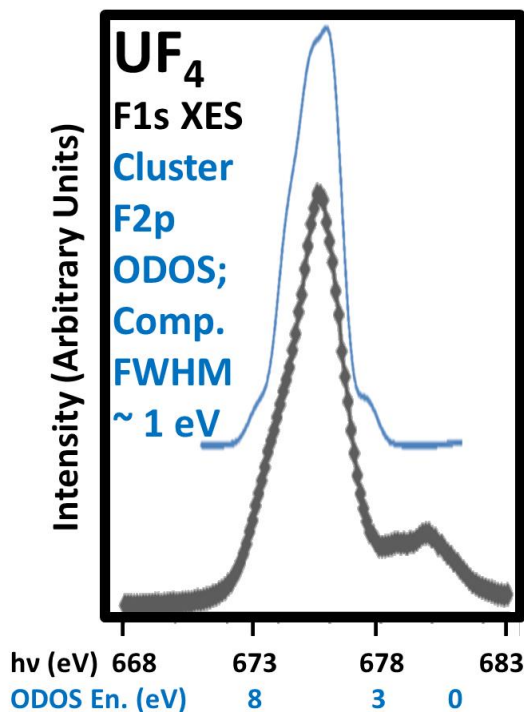

Figure 5 Here is a comparison of the XES spectrum of UF$_4$ and the simulated spectrum with FWHM = 0.9 eV.

Even with this very simple spectral simulation, it is possible to achieve a fairly good match, as shown in Figure 5. Note that the three features are obtained in the simulated spectrum, although the shoulder on the right side (higher XES energy) is stronger than that observed experimentally. There are also two weaker shoulders, one on each side, that are not resolved experimentally, but are consistent with the overall peak width near the base of the 2p envelope peak. We will return to a consideration of these shoulders later.

A similar analysis has been carried out for the O2p manifold in UO_2, as shown in Figures 6 and 7 below. Once again, the best visual match is near FWHM = 1 eV and a three feature spectrum is obtained, with similar limitations as those described above for UF_4.
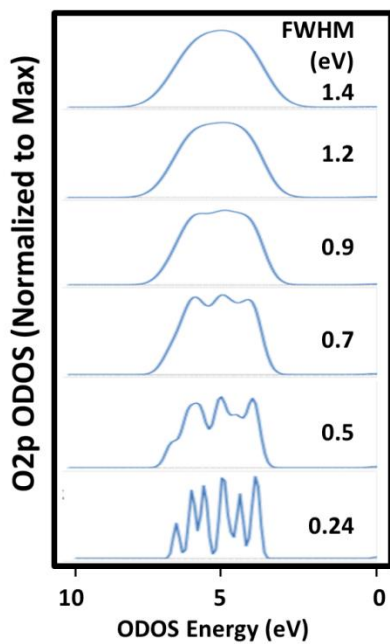

Figure 6 Here are shown the simulated XES Spectra from the F2p ODOS histograms, utilizing a guassian lineshape and specified Full Width at Half Maximum (FWHM) for each component.
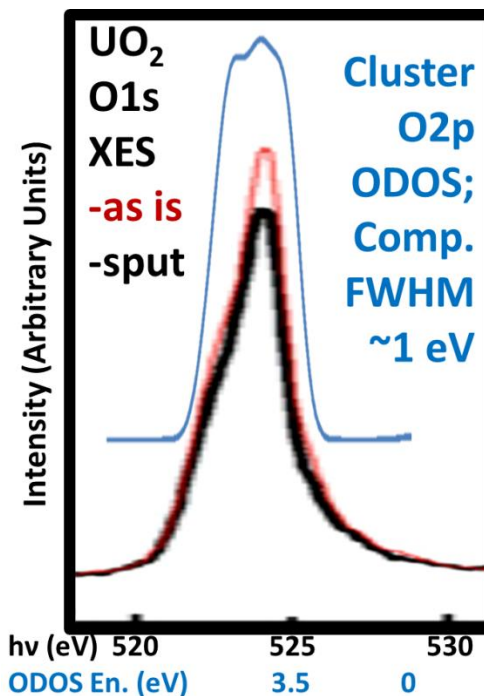

Figure 7 Comparison of the XES spectra of UO_2 and the simulated spectrum with FWHM = 0.9 eV.

However, in this case, it has even more discrepancies at the peak base. Here the gaussian line-shape fails to give the proper width and tailing. This problem can be fixed, by substituting a lorentzian line-shape, as shown in Figure 8. Although there is a slight sharpening of peak tops with the lorentzian, to a large extent, the central part of the line-shape remains much the same for the gaussian and lorentzian cases: only the tailing and the base, with its concomitant broadening, is strongly affected. This result suggests that lifetime broadening is the dominant effect here.
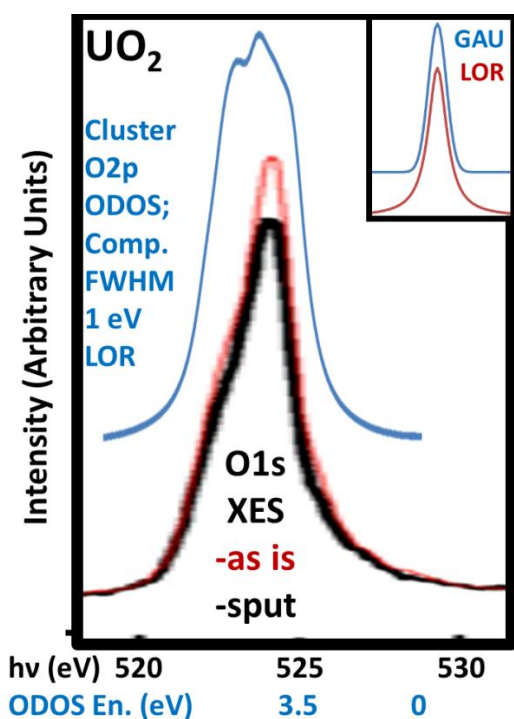

Figure 8 Comparison of the O1s XES spectra with a composite spectrum utilizing a lorentzian line-shape for the component peaks. The inset shows a direct comparison of gaussian and lorentzian line-shapes for equivalent FHHM values. The overall FWHM of the O1s peak was about 2 eV and the projected instrumental broadening was 1.2 eV. [8]

SUMMARY AND CONCLUSIONS

It has been shown, that even with the simplifying assumptions of constant cross sections and component line-widths and shapes, it is possible to construct simulated spectra from the histogram ODOS of the Ryzhkov clusters that agree fairly well with the experimental oxidant K Edge spectra of UO_2 and UF_4.

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