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Separate Measurement of the $5f_{5/2}$ and $5f_{7/2}$ Unoccupied Density of States of UO_2

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Abstract

Coupling High Energy Resolution Fluorescence Detection (HERFD) with electric dipole selection rules, the uranium $5f_{5/2}$ and $5f_{7/2}$ Unoccupied Densities of States (UDOS) have been determined in UF_4, UO_2 and UCd_{11}. Striking changes were observed between UF_4 ($5f^2$) to UCd_{11} ($5f^3$), consistent with the Intermediate Coupling Model. Results for UO_2 were confirmed by Bremstrahlung Isochromat Spectroscopy (BIS). This new approach can be a powerful tool for shedding light on the hidden mysteries of Actinides 5f-electrons properties.

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I.   Introduction

The 5f series of elements known as the actinides have vast technological and scientific

importance in today's world, notably in energy technologies,[1] weapons production and

associated environmental remediation,[2] and medicine. [3] In particular, understanding the

environmental impacts of certain actinides has become a major concern due to the buildup of

nuclear waste. [4]Despite their technological importance, the chemistry and physics of the

actinides remain the least understood of the long-lived elements in the periodic table. Some of

the lack of understanding of the bonding properties of the actinides is due to their relative

unavailability, but the primary issue is actually the complexity of the bonding properties of the

5f orbital [5]. At the heart of this complexity is the importance of spin-orbit coupling and

relativity in determining electron distributions. [6] From a practical standpoint, unlike 4f

orbitals, the 5f orbital can be delocalized, especially for the actinides lighter than Am [7]. On the

other hand, the 5f's can also be localized, but even in these cases, covalent bonds can still exist

[8]. Moreover, most of the actinides can exist in multiple oxidation states (5f occupancies), with

Pu known to exist in many states from, at least, Pu (III) to Pu (VII) [9]. This interplay between

orbital occupancy and delocalization affects not only the chemical structures of the actinides

and their compounds, but also all their electronic and magnetic properties.[10] Despite the

importance of determining the 5f orbital density of states, occupancy and degree of

delocalization, such measurements of these properties have proved elusive. Photoemission

spectroscopies are sometimes successful, but suffer from experimental difficulties and surface

sensitivity. [11] Conventional X-Ray Absorption Spectroscopy and a related technique, Electron

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Energy Loss Spectroscopy (EELS), especially when coupled to branching ratio analysis [12], are likewise useful but suffer from the limitations imposed by the lifetime broadenings on the scale of multiple eV. [13] Actinide L_3-edge spectroscopies can be very useful when configuration splittings are (rarely) observed in the final state [14], but are otherwise limited to measuring peak shifts and intensities that can be due to either delocalization or occupancy changes, potentially even due to non-f-orbitals [14- 16]. The new, higher resolution variants of M-edge spectroscopies can also be successful probes of bonding [17- 19], but are generally still reliant on edge shifts and fingerprinting techniques. In this article, we describe how a coupled use of M_4 and M_5 spectra collected in the high-energy-resolution fluorescence detection (HERFD) mode and properly normalized, can be used to separately determine the $5f_{5/2}$ and $5f_{7/2}$ unoccupied density of states (UDOS), providing a measure of the total 5f UDOS with higher resolution than previously possible.

Utilizing both the M_4 ($3d_{3/2}$) and M_5 ($3d_{5/2}$) edges, outlined below is a method of normalizing M_4/M_5 HERFD spectra that allows for the isolation of the $5f_{5/2}$ and $5f_{7/2}$ UDOS. This approach is based upon the strong electric dipole selection rules and cross section analysis that drive the success of the Branching Ratio Analyses of X-ray Absorption Spectroscopy (XAS) [7, 12, 20-22]. An extensive analysis was performed, using the control samples of UF_4 (localized, two 5f electrons) and UCd_{11} (localized, three 5f electrons) and comparing the measurements to the predictions of the Intermediate Coupling Model. [7,12] From the improved understanding garnered from the control experiment, and confirmed by comparison with the measurement of the UDOS provided by Bremstrahlung Isochromat Spectroscopy, [23-25] a form of high-energy

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Inverse Photoemission, the UDOS's of U $5f_{5/2}$ and U $5f_{7/2}$ of UO_2 have been separately determined for the first time.

In this manuscript, the focus will be upon three 5f localized cases: UF_4, UCd_{11}, and UO_2. For now, delocalized systems such as U metal will not be addressed.

II.   Experiment

The experiments were performed on Beamline 6-2a at the Stanford Synchrotron Radiation Lightsource, using a Si(111) monochromator and a high-resolution Johansson-type spectrometer [26] operating in the tender x-ray regime (1.5 - 4.5 keV). The total energy resolution of this HERFD experiment is ~0.8 eV, sharpening the U M_4/M_5 spectroscopic features almost an order of magnitude when compared to conventional x-ray absorption spectroscopy (i.e., total fluorescence yield or transmission mode XAS). The samples used were the same as those used in earlier RXES and XAS studies. [22] Despite the conventional wisdom that tender x-ray experiments should in general have lessened surface sensitivity, more like hard x-rays than soft x-rays, the impact of surface oxidation for samples stored in air was immediately apparent, as also observed by Kvashnina et al. [19,27]. This sensitivity is due to the very intense x-ray absorption cross sections for U M-edges (for instance, the x-ray probing depth across the intense M_4/M_5 white lines can be less than 100 nm) and the propensity for uranium to react with oxygen. [28, 29] However, by carefully measuring the U $M_{4,5}$ Extended X-ray Absorption Fine Structure (EXAFS) beyond the main (whiteline) absorption features, it was possible to monitor the oxidation levels. Ultimately, by employing freshly cleaved sample surfaces and

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keeping the samples isolated in an Ar atmosphere, this problem was eliminated in the present measurements. In fact, although similar, the EXAFS of the isoelectronic compounds, UF_4 and UO_2, are easily differentiated, consistent with earlier studies. [22] The efficacy and importance of the EXAFS will be discussed further below. The experimental data have been corrected for self-absorption effects, two examples of which are shown in Figure 1 [30].

III.   Results and Discussion

To put the M_4 and M_5 spectra on the same energy and intensity scales, the procedure suggested by Rogalev was followed. [31,32] Here, the first step is to match the EXAFS across a wide energy regime, for each pair of spectra (M_4 and M_5) for a given sample. This normalization is shown for the UF_4 and UCd_{11} spectra in the upper panels of Figures 2. This process produces two white-line peaks that overlap and are separated by about 1 eV. The second step is to scale the M_4 and M_5 EXAFS regimes by their initial state densities: $2/3(M_4$, $3d_{3/2})$ to $1(M_5$, $3d_{5/2})$. An enlargement of the results of this procedure can be seen in Figure 1.

To quantify the changes observed in Figure 1 between UF_4 and UCd_{11}, peak fits were performed. (Lower panels, Figure2) Two asymmetric functions were used, each being a Gaussian with an exponential tail. Note that in Peak0, the tail extended to higher energy deals with the leading edge, and in Peak1, the tail pointed in the reverse direction captures the long trailing tail of the experimental spectrum. The results of the fit are shown in the lower panel of Figure 2, including the experimental Peak Ratio, PR. (PR = Area(Peak0)/Area(Peak1))

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Before going any further, it is necessary to discuss selection rules and cross sections. The strength of the selection rules has been demonstrated by the quantitative agreement in the Branching Ratio approach used in the conventional X-ray Absorption Spectroscopy (XAS) and Intermediate Coupling Model. [7,12,20-22] In the $N_{4,5}$ conventional XAS, the lifetime broadening washes out any fine structure, leaving the cross section measurements as the only viable process. [13] However, within localized systems such as UF_4 and Pu, the jj-skewed Intermediate Coupling Model provides quantitative agreement with the experimental measurements. The jj-skewed Intermediate Coupling Model is based upon the selection rule that transitions between the $4d_{3/2}$ and $5f_{7/2}$ states are forbidden. [33] This selection rule is manifested in the M_4 notation in Figure 1, which shows that the $3d_{3/2}$ electrons can only go into $5f_{5/2}$ unoccupied states. Thus, ignoring any quadrupole transitions that are much reduced in intensity, the M_4 HERFD experiment is probing directly the $5f_{5/2}$ Unoccupied Density of States or UDOS. For the M_5 case, it is slightly more complicated, but the process will be dominated by transitions from the $3d_{5/2}$ into the $5f_{7/2}$, since the relative cross section into an empty 5f manifold for a $3d_{5/2} \rightarrow 5f_{5/2}$ transition is only 5% that of a $3d_{5/2} \rightarrow 5f_{7/2}$ transition. With n =2 and preferential filling of the $5f_{5/2}$ states, that ratio will drop to 3%. Thus, within a 3% error, it is possible to say that the M_5 experiment provides a measurement of only the $5f_{7/2}$ UDOS. (The small $5f_{5/2}$ contribution also helps explain why the M_5 is broader than the M_4.) In support of the contention that the M_4 intensity represents the $5f_{5/2}$ UDOS and the M_5 intensity represents the $5f_{7/2}$ UDOS, it is interesting to note the similarity of the spectra in Figure 1 to the calculations of $5f_{5/2}$ UDOS and $5f_{7/2}$ UDOS of U by Kutepov [7] and the success of Kutepov's calculations in

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recapturing the essence of the UDOS measurements of U using Bremstrahlung Isochromat

Spectroscopy. [7, 23, 34]

The dominant result shown in Figure 1 is the large reduction in the main peak in the M_4

spectrum going from UF_4 to UCd_{11}. The first step to understanding this reduction is to consider

the nominal spin-orbit split degeneracy, 6 for the $5f_{5/2}$ and 8 for the $5f_{7/2}$. In the case of n=2, the

$5f_{5/2}$ is 67% empty, while for n=3, it is 50% empty, which is only a 25% reduction. The observed

reduction is closer to 50%, and this could be explained if these nominally degenerated 6 states

are further split into a series of doubly degenerate states. One possibility for this split

transition could be the Crystal Field Splitting in UF_4 and UCd_{11}. [22, 29, 35, 36] The lower

symmetry of these crystals would not support degeneracies above two-fold. A cartoon

depicting this situation is shown in the inset of Figure 2. It should be noted that the dominant

effect in actinide 5f states is total angular momentum coupling in an Intermediate Coupling

Model, which is skewed towards a jj-limit. (Among other things, the success of the Branching

Ratio (BR) analysis of experimental results from localized systems such as UF_4 and Pu supports

this contention [7, 12, 20-22]). Thus, a crystal field splitting of these states would result, in a

first order perturbation, to split states but not mixed states. [22] In this picture, the lowest

doublet is filled for both UF_4 and UCd_{11} allowing no intensity for the $3d_{3/2}$ → $5f_{5/2}$ transition.

The second lowest doublet is either empty (UF_4, n = 2, N =12) or ½ filled (UCd_{11}, n = 3, N =11),

where n + N =14 , with n = number of 5f elections and N = number of 5f holes. The beauty of

this picture is that the prior results for localized systems within the Intermediate Coupling

Model can then be used to predict the expected Peak Ratios. [7] In such a model for n =2 : $N_{5/2}$

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$= 6 - n_{5/2} = 6 - 1.96 = 4.04$ and for n = 3, $N_{5/2} = 6 - n_{5/2} = 6 - 2.79 = 3.21$, using $n_{5/2} + N_{5/2} = 6$, with

5/2 designating the $5f_{5/2}$ manifold. The transition from n = 2 to n = 3 would then generate a

change in the number of 5/2 holes: $\Delta N_{5/2} = 4.04 - 3.21 = 0.83$. It is reasonable to assume that for

Peak0, $\Delta N_{5/2}$ is ½ of the initial number of holes in that level, 2*0.83 = 1.66. (Again, the n, $n_{5/2}$

and $n_{7/2}$ values are taken directly from the tables containing the Intermediate Model results in

Ref 7 and it is physically logical to assume that the filling process of going from n = 2 to n= 3

would change the number of holes in the states associated with Peak0 by a factor of 1/2.) Then,

for n = 2, PR = 1.66/(4.04-1.66) = 0.70 and for n = 3, PR = 0.83/(4.04-1.66) = 0.35. These

theoretical results agree nicely with the experimental results, as shown in the tabular insets in

the lower panels of Figure 2.

Above, it was briefly alluded that Bremstrahlung Isochromat Spectroscopy, BIS, can

provide a measure of the 5f UDOS, albeit with the loss of separate resolution of the 5/2 and 7/2

components and with poorer overall energy resolution. [7, 23, 24, 25, 34] BIS is the high energy

variant of Inverse Photoelectron Spectroscopy. Just as X-ray Photoelectron Spectroscopy can

provide a measure of the occupied density of states (ODOS), BIS can provide a measure of the

UDOS. Next, a comparison will be made of a state-of-the-art BIS measurement with the HERFD

results for UO_2, [24,25] as a final test of our model and contention that these HERFD

measurements are an effective measure of the 5f UDOS.

For the sake of convenience and appearance, the EXAFS scaling between the M_4 and M_5

was set to 2/3 above, consistent with the initial state occupation ratios. However, a better

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quantitative scaling would be to use the ratio from the BR measurements. For UO_2, BR = 0.68

[14] and the M_4/M_5 EXAFS ratio would then be (1/BR) - 1 = 0 .47, less than the value of 0.67

used earlier.

The result of such as scaling is shown in Figure 3, along with the wide scan EXAFS

matching for UO_2. As shown, there is a remarkable match between the M_4+M_5 Sum and the BIS

spectrum. At each change in slope in the BES spectrum, there is a corresponding change in

slope of the M_4+M_5 spectrum, as denoted by the vertical orange lines. The HERFD sum is

narrower, evidencing better energy resolution than the BIS, but exhibiting all the same fine

structure. To test the effect of worsening the HERFD resolution, the HERFD data were

convolved with a Gaussian function of 3eV Full Width at Half Max. (The value of 3eV was

extracted from the 10%-90% width of the leading edge of the BIS spectrum and is roughly

consistent with earlier resolution measurements of this BIS spectrometer. [37]) The result is a

loss of fine structure but an overall peak that matches the BIS spectrum closely. (Not shown.)

Thus it is clear: the HERFD measurements provide a high resolution probe of the total 5f UDOS

and a separation of the $5f_{5/2}$ and $5f_{7/2}$ UDOS of UO_2.

At this point, it is useful to put our results in context. Strictly speaking, HERFD, as being

a cut of RIXS map, does not give a direct 1-to-1 measurement of the true unoccupied

DOS. Rather, the full RIXS plane provides a detailed measure of the density of states convolved

with the transition matrix elements via the Kramers-Heisenberg equation [38]. Making a cut

through a RIXS spectrum using a constant emission energy, as is done to produce a HERFD

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spectrum, mimics something that is linearly related to the UDOS for these samples, as we have demonstrated. However, for samples with a more complex electronic structure than the model compounds measured here (e.g. a mixed valence compound), it may be necessary to measure a full RIXS map.   In any case, due to a combination of the choice of emission energy and self-absorption effects, there is a need to carefully determine the scattering geometry and thus use reasonably flat samples. Regarding the measurement of the DOS, there have been parallel discussions for XPS and BIS, over the decades. Strictly speaking, photoemission and inverse photoemission are measures of the joint density of states (initial and final) connected and moderated by electric dipole selection rules. [39] On that basis, one might argue that those factors in XPS and/or BIS cannot be deconvolved to directly provide the DOS. Nevertheless, there is an immense amount of data that supports the argument that, under many circumstances, XPS provides a very useful measure of the occupied density of states (ODOS). [40, 41] (The basis of this observation is probably a significant amount of angular and energy averaging, taking out directional effects and smoothing over cross-section variations.) This capability is one of the reasons for the popularity of XPS as an analysis platform. More recent results for U metal, comparing the BIS of Baer and Lang with the calculations of Kutepov, demonstrate a similar success for BIS. [7,23,34]

IV.   Conclusions and Projections

We have shown that the HERFD/RIXS experiment performed at M4/M5 edges is a powerful approach that is consistent with earlier traditional XAS BR investigations, the

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Intermediate Coupling Model and their underlying selection rules and provides an effective, high resolution measurement of the $5f_{5/2}$, $5f_{7/2}$ and 5f total UDOS states in Uranium compounds. This approach can be applied broadly for Actinide elements to directly reveal their 5f-electrons properties.

While the nature of the additional splitting remains unknown at this point, one strong possibility is crystal field splitting. Conventional XAS Branching Ratio measurements have been shown to have negligible dependence upon crystal field splitting. [22] Nevertheless, the improved resolution of the HERFD measurements has revealed the previously unavailable detail underlying the broadened spectra of conventional XAS. In a recently published article [42], the interplay of crystal field splitting, spin-orbit splitting and total angular momentum coupling is addressed. Because the coulombic repulsion can cause energy differences between different total angular momentum states on the scale of 20eV, it is conceivable that crystal field splittings could be on the scale of 1 to 2eV and still remain in the perturbative regime relative to the larger energy scale. The energy splittings that are observed here, in the M_4 and M_5 spectra, are on the scale of 1 to 2 eV. It is not the ratio of the crystal-field splitting to spin-orbit splitting that is the crucial parameter, but rather the ratio of crystal-field splitting to the energy differences between the total angular momentum states. The differences in energy between the total angular momentum states (~20eV) enforce the dominance of spin-orbit splittings, even though the spin-orbit splittings are on the order of 1 to 2 eV themselves. Finally, because the crystal-field splitting is still only perturbative relative to the energy differences of the total angular momentum states, cross sectional measurements such as conventional XAS Branching

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Ratios will not be sensitive to crystal field splittings. That is because in First Order Perturbation Theory, states are split but not mixed, so the low resolution cross section measurements will sum the same, with or without the crystal-field splitting. [42]

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Figure Captions

Figure 1.   The M$_4$ and M$_5$ HERFD spectra are shown here, for UF$_4$ and UCd$_{11}$. The upper

panels (a & b) have the "raw data" and the lower panels (c & d) display the self-absorption-

corrected spectra. As can be seen, upon normalization, the "raw data" and self-abs-corrected

spectra are essentially the same, with only a slight degradation of feature resolution with the

correction. For the remainder of this work, the "raw data" will be used. These spectra have

been scaled such that the EXAFS regime is 2/3 (M$_4$) to 1(M$_5$), following the initial state densities

of the U3d$_{3/2}$ and U3d$_{5/2}$, respectively. N is the number of 5f holes, while n is the number of 5f

electrons. N + n = 14. The selection rules are discussed in the text below. The effective spin-

orbit splitting is about 1 eV, consistent with earlier results. [7]

Figure 2.   Two top panels (a & b): The1:1 EXAFS matching of UF$_4$ and UCd$_{11}$. The peak

position of the M$_4$ peak is set to 0 and the peak height of the M$_5$ peak is set to unity. Lower

Panels (c & d): The M$_4$ peak fitting for UF$_4$ and UCd$_{11}$. The data is shown in red, the result of the fit

as black +, and the two component peaks as yellow (Peak0) and purple (Peak1). PR is the peak

ratio, equal to the area of Peak0 divided by the area of Peak1. Ex stands for experiment and Th

for theory. The errors in the experimental values are ±0.03 to ±0.06. The insert near the top (e)

is a cartoon that illustrates a simple model based upon crystal field perturbation of the spin-orbit

split states. It shows a proposed origin for Peaks 0 and 1.

Figure 3.   Top panel (a): the 1:1 EXAFS matching. Lower panel (b): the HERFD with a 0.47

scaling of M$_4$: M$_5$ EXAFS, and the BIS spectrum. The vertical orange lines denote regions with

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changes in slope for the HERFD and BIS. The HERFD energy scale was shifted to compare with

the BIS data, and was normalized to the magnitude the BIS scale. The energy of the BIS electron

beam was 736 eV. The BIS spectrum is taken from Ref. 25.

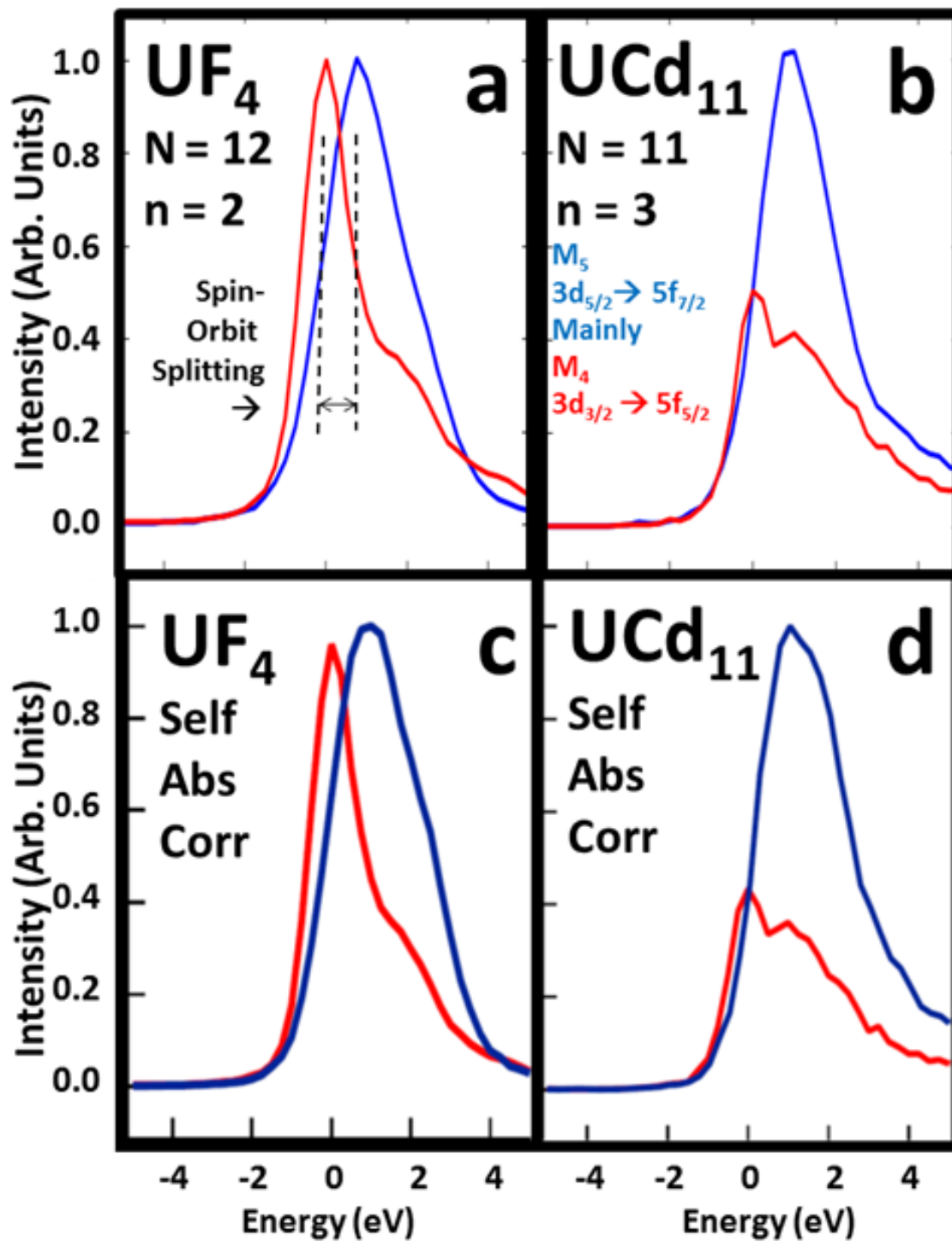# Separate Measurement of the 5f$_{5/2}$ and 5f$_{7/2}$ Unoccupied Density of States of UO$_2$

a UF$_4$ N = 12 n = 2 Spin-Orbit Splitting →

b UCd$_{11}$ N = 11 n = 3 M$_5$ 3d$_{5/2}$ → 5f$_{7/2}$ Mainly M$_4$ 3d$_{3/2}$ → 5f$_{5/2}$

c UF$_4$ Self Abs Corr

d UCd$_{11}$ Self Abs Corr

Intensity (Arb. Units) vs Energy (eV)

Figure 1

Separate Measurement of the $5f_{5/2}$ and $5f_{7/2}$ Unoccupied Density of States of UO_2

Figure 2

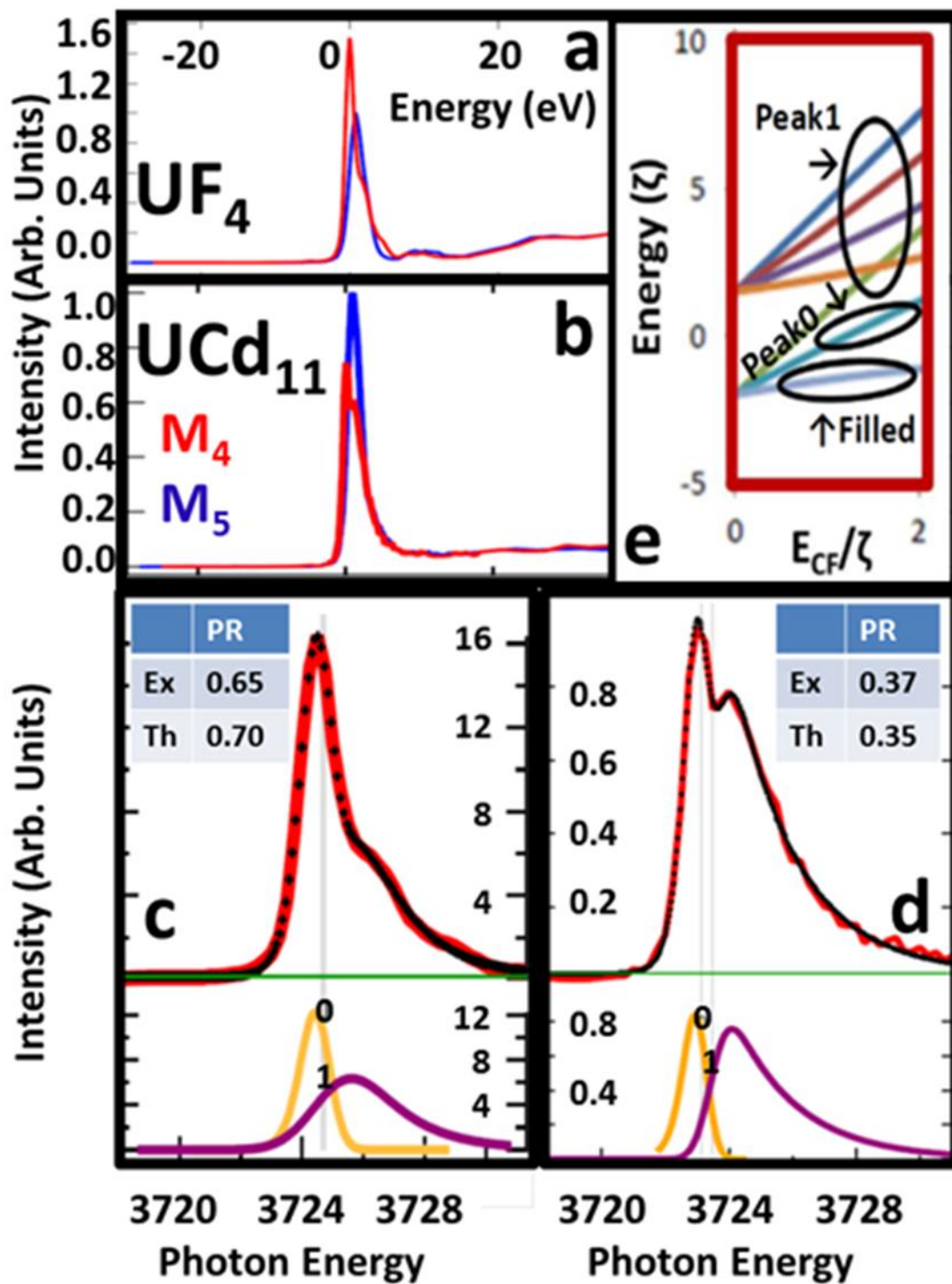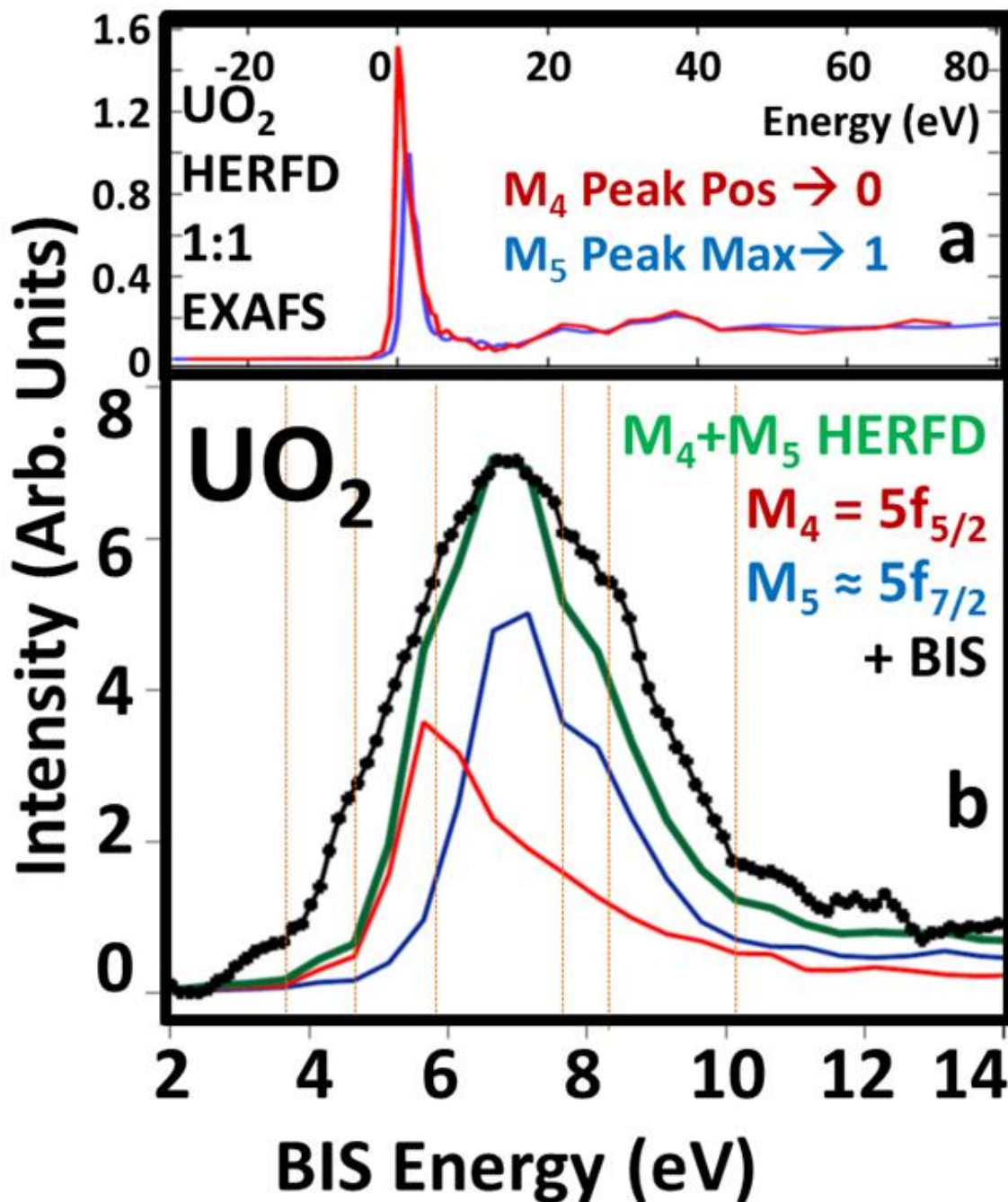# Separate Measurement of the $5f_{5/2}$ and $5f_{7/2}$ Unoccupied Density of States of UO_2

Figure 3