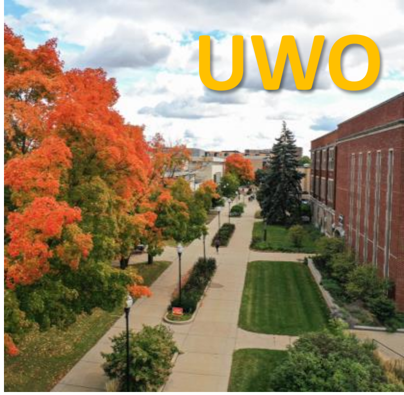
Observation of 5f Intermediate Coupling in Uranium X-ray Emission Spectroscopy*



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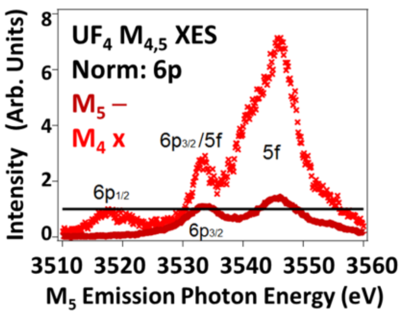

Figure 1 Shown here are the M_4 ($3d_{3/2}$ hole) and M_5 ($3d_{5/2}$ hole) XES spectra of UF_4. The spectra have been normalized to the M_4 $6p_{1/2}$ ($p_{1/2} \rightarrow d_{3/2}$, $\Delta j = 1$) and M_5 $6p_{3/2}$ ($p_{3/2} \rightarrow d_{5/2}$, $\Delta j = 1$) peaks. Note the very large enhancement of the 5f peak in the M_4 spectrum relative to that of the M_5 spectrum. Red X = M_4. Dark red line = M_5. Black line = unity (1) for 6p normalization. The M_4 spectrum has been shifted -181 eV to align the peaks on the M_5 energy scale. $6p_{1/2}$:$6p_{3/2}$ intensity ratio = 0.8, following the lectric dipole cross sections. See text for details.

Nuclear energy is an important component in the provision of electrical power. Regardless of whether one supports the continued use of nuclear power for this purpose, it is essential to have a firm scientific foundation for the understanding of actinide materials, if only to optimize safety, environmental remediation and long-term storage and disposal. The scientific work described here should add to that foundation in a significant way, by opening up high energy variants of various spectroscopic methods that are now limited by radioactive contamination containment issues.

Prior to this present work, the Intermediate Coupling Model developed by van der Laan and Thole [1] had been experimentally confirmed [2] and utilized to explain 5f filling across the light actinides. These prior measurements used X-ray Absorption Spectroscopy and probed the Unoccupied 5f states. Here, we demonstrate for the first time that similar cross sectional and angular momentum coupling effects can be seen in the Occupied 5f states. However, the cross calibration of intensities is a bit more complicated and requires a normalization via the 6p states. The result is the observation of a very large effect which can be quantum mechanically justified. The analysis includes FEFF spectral simulations, QM cross sectional calculations and a detailed peak fitting analysis. These XES measurements were made at the new, high resolution facilities recently developed at SSRL at SLAC.

To summarize: The first observation of Intermediate Coupling effects in the occupied 5f states has been made using X-ray Emission Spectroscopy (XES). In the past, the impact of Intermediate Coupling of the 5f states in actinides has long been observed and quantified, using X-ray Absorption Spectroscopy (XAS) to probe the unoccupied 5f states, providing great insight into the enigma of 5f electronic structure, but no measure of its effects in the occupied states had been reported. Moreover, because the 5f occupied states in UF_4 are almost completely of $5f_{5/2}$ character, the observed effect in XES is twice that in XAS for UF_4.

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References

[1] G. van der Laan and B. T. Thole, Phys. Rev. B 53, 14458 (1996).
[2] J. G. Tobin, K. T. Moore, B. W. Chung, M. A. Wall, A. J. Schwartz, G. van der Laan, and A. L. Kutepov, Phys. Rev. B 72, 085109 (2005).

Table 1

		$6p_{1/2}$ Full	$6p_{3/2}$ Full		$6p_{1/2}$ Full	$6p_{3/2}$ Full
M_5	$3d_{5/2}$ Empty	0	12/5	$3d_{5/2}$ 1 Hole	0	2/5
M_4	$3d_{3/2}$ Empty	4/3	4/15	$3d_{3/2}$ 1 Hole	1/3	1/15

$I^{M4}_{6p1/2}$ --------- = $I^{M5}_{6p3/2}$ (1/3)/(2/5) = 0.833

Table 2

		$5f_{5/2}$ Full	$5f_{7/2}$ Full		$5f_{5/2}$ Full	$5f_{7/2}$ Full
M_5	$3d_{5/2}$ Empty	$\frac{4}{15}$	$\frac{16}{3}$	$3d_{5/2}$ 1 Hole	$\frac{4}{90}$	$\frac{16}{18}$
M_4	$3d_{3/2}$ Empty	$\frac{56}{15}$	0	$3d_{3/2}$ 1 Hole	$\frac{56}{60}$	0

$(I^{M4}_{5f}/I^{M5}_{5f})_{Th}$ = (56/60) --------- = 21 4/90

Table 3. Fit results from figure 5.

	Peak0 area	Peak1 area	Peak2 area	Peak3 area	Peak4 area
M4	0.33 ± 0.02	0.37 ± 0.01	1.05 ± 0.07	2.27 ± 0.08	0.13 ± 0.03
M5	7.84 ± 0.08	13.6 ± 0.01	1.3 ± 0.1		

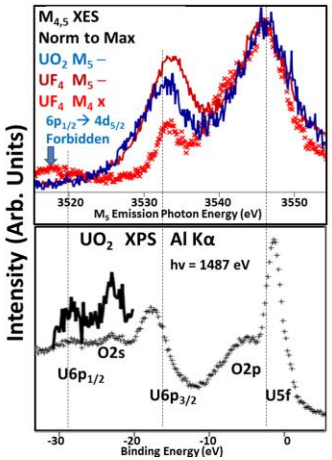

Figure 2 Comparison of XES and XPS. Upper Panel: The $M_{4,5}$ XES is shown here, with normalization to the largest feature, the U 5f peak. Blue Line: UO_2 M_5; Red Line: UF_4 M_5; Red X: UF_4 M_4, shifted -181 eV to be on the same energy scale as the M_5 spectra. Lower panel: UO_2 XPS using AlKα (hν = 1487 eV) as the excitation. Black +: regular spectrum. Black Line: Blowup of the $U6p_{1/2}$ and O2s region. XPS is not element selective, so O2p and O2s features are also present. The O2p and U5f will have significant intermixing. [21] Similar XPS spectra can be found for UF_4.

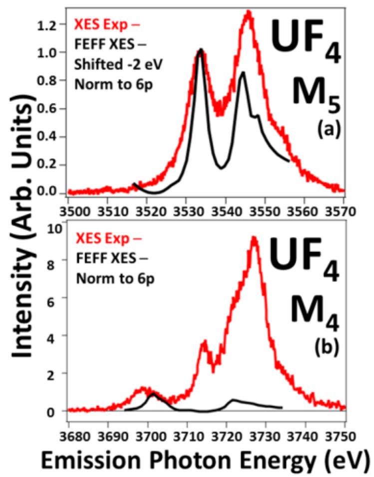

Figure 3 The comparison of the UF_4 $M_{4,5}$ XES spectra with the results of the FEFF simulation are shown here. The spectra have been normalized to unity at the 6p peaks as shown. Red: XES experiment. Black: FEFF XES. In Panel (a), the FEFF spectrum has been shifted – 2 eV to align the 6p peaks. See text for details. The absence of multiplet structures in FEFF may contribute to the narrowness of the FEFF peaks.

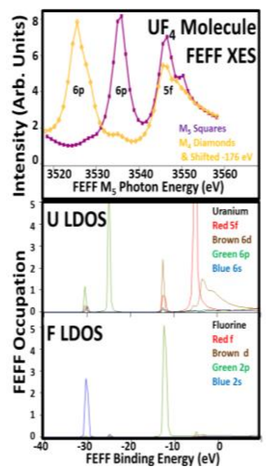

Figure 4 Shown here are the FEFF $M_{4,5}$ XES spectra and the FEFF orbital angular momentum specific density of states (LDOS) for U and F from a UF_4 Molecule model. The FEFF XES were not scaled: the magnitudes were taken directly from the FEFF simulation. The M_4 FEFF spectrum has been shifted -176 eV, to put it in the same energy scale as the M_5 FEFF spectrum.

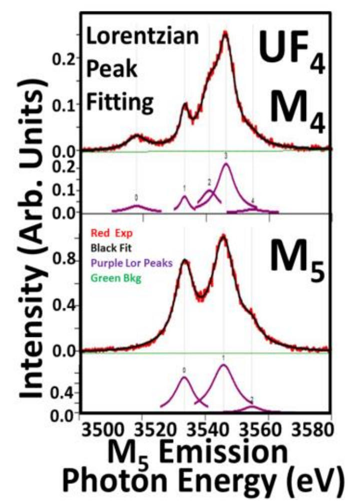

Figure 5 Peak fittings of the UF_4 M_4 and M_5 spectra. Here, lorentzian line-shapes were used, but a full parallel analysis with gaussian line-shapes was also pursued, with similar results. The M4 $6p_{3/2}$ (Peak 1) is too strong to be pure p3/2 without mixing. However, mixing p3/2 and p1/2 to get the required intensity for correct p3/2:p1/2 ratio in Table 1 would require significant mixing. The result of this mixing would be that M_5 $6p_{1/2}$ would no longer be zero or small: It would be easily observable. Similar arguments should also apply to quadrupole transitions. Thus it appears likely that the M_4 $6p_{3/2}$ feature (Peak 1) probably has 5f contributions, similar to other 5f structure in the M_4 spectrum. See Table 3 for a summary of the results.

the M_4 and M_5 spectra are shown in figure 5, producing the results below.

$$RR = \frac{\frac{I^{M4}_{5f}}{I^{M4}_{6p1|2}}}{\frac{I^{M5}_{5f}}{I^{M5}_{6p3|2}}} = 5.5 \pm 0.7 \text{ and}$$

$$\left(\frac{I^{M4}_{5f}}{I^{M5}_{5f}}\right)_{EXP} = RR * \left(\frac{I^{M4}_{6p1|2}}{I^{M5}_{6p3|2}}\right) = 5.5 \pm 0.7 * 0.833 = 4.6 \pm 0.6$$

$$(I^{M4}_{5f}/I^{M5}_{5f})_{Th} = 21 \text{ from Table 2}$$

For the first time, the effect of Intermediate Coupling is reported for the 5f Occupied Density of States (ODOS), using X-Ray Emission Spectroscopy. In fact, because of the high purity of the 5f ODOS (predominantly $5f_{5/2}$) the M_4:M_5 intensity ratio, i.e. $I_{d3/2}/I_{d5/2}$, is very large, on the scale of a factor of 5. This over twice the value of the N_5:N_4 peak ratio (~2) that underlies the reported XAS Branching Ratio of UF_4 of 0.68. The value of 21 predicted for a pure $5f_{5/2}$ occupancy, with a purely spherical symmetric potential and perfect electric dipole transitions, is shown to be unrealistic and the value of 5 is consistent with a more realistic appraisal of the systems under consideration.