Investigation of the Unoccupied Electronic Structure of UO2 with Bermstrahlung Isochromat Spectroscopy and X-Ray Absorption Spectroscopy


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Investigation of the Unoccupied Electronic Structure of UO$_2$ with Bremstrahlung Isochromat Spectroscopy and X-ray Absorption Spectroscopy

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Overview of talk

- Motivation
- Description of instrumentation and data collection
- XAS, XPS, BIS: The whole is greater than the sum of the parts!
  - Occupied Density of States: XPS
  - XAS: O1s - old and new
  - XAS: U4f - new data vs previous EELS
  - XAS: U4d and U5d – old and new
  - Monochromator calibration → Unoccupied DOS
  - Confirmation with BIS
  - Confirmation with Theory
- Summary, conclusions and prospects
Motivation and Instrumentation

- $^{235}\text{UO}_2$ is an important nuclear fuel for electrical power generation.
- Global goal: Actinides ($5f$ electron systems) exhibit fascinating physical and chemical properties, due to $5f$ electron correlation, including the highly radioactive systems such as $^{239}\text{Pu}$.
- Onsite Instrumentation: A spectroscopic system containing spin resolved photoelectron spectroscopy (SRPES) and bremsstrahlung isochromat spectroscopy (BIS) has been built and commissioned at LLNL.
- ALS Instrumentation: The XAS was done on Beamline 8. Both Total Electron Yield (TEY) and Total Fluorescence Yield (TFY) were used. TFY is less surface sensitive than TEY.
Experimental setup at LLNL for actinides research

**BIS and RIPES:**
XES 350 (VG Scienta)

**Photoelectron Spectroscopy**, with spin and without spin (multichannel)

**SRPES:**
Phoibos 150 with Mott detection (Specs)

**Fano Spectroscopy** with the chirally configured He UPS sources

**XPS** with the X-ray tube, AlKα and MgKα

Sample handling system for actinides
Comparison of Processes: BIS, XPS and XAS

<table>
<thead>
<tr>
<th>BIS/IPES</th>
<th>XPS VB</th>
<th>XPS core</th>
<th>XAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incoming e⁻</td>
<td>Out-going e⁻</td>
<td>Outgoing e⁻</td>
<td></td>
</tr>
<tr>
<td>hv</td>
<td></td>
<td></td>
<td>hv ≈ BE (core)</td>
</tr>
<tr>
<td>CB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gap</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VB</td>
<td></td>
<td></td>
<td>hv ≈ KE, KE ≈ hv, KE ≈ hv- BE (core)</td>
</tr>
</tbody>
</table>

Photon absorption and emission:

- **electric dipole transitions with \( \Delta l = +/- 1 \)**

- **XPS samples the occupied DOS or Valence Band (VB)**
- **BIS and XAS sample the unoccupied DOS or Conduction Band (CB)**
X-ray Photoelectron Spectroscopy (XPS) gives us the Occupied Density of States

The assignments here go back to Veal and Lam (1974) and are supported by other workers as well.


For the complete UPS and XPS study, see Yu and Tobin, JVSTA 29, 021008 (2011).
Our data in 1st, 2nd and 3rd Order

- Our TEY looks just like that from Jollet et al.

- However, TFY gives a better measure of the bulk electronic structure, that will be used instead.

- The three orders permit a quantitative calibration of the hv scale on the middle energy grating.

- All three orders agree...

Jollet et al, JPCM 9, 9393 (1997)

Electronic structure of UO₂

Table 1. Energies of the structures of the O K XAS spectrum for CoO and UO₂.

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO (eV)</td>
<td>510.9</td>
<td>531.5</td>
<td>537.9</td>
<td>541.6</td>
<td>543.7</td>
<td>553.9</td>
<td>561.4</td>
<td></td>
</tr>
<tr>
<td>UO₂ (eV)</td>
<td>528.59</td>
<td>530.65</td>
<td>532.2</td>
<td>533.0</td>
<td>541.5</td>
<td>543.1</td>
<td>548.85</td>
<td>551.85</td>
</tr>
</tbody>
</table>
U4f XAS new data agrees with EELS

U4f XAS → U6d UDOS

• TFY shows a strong signal while TEY only shows the Nitrogen contaminant at 400 eV. This may be driven by surface contamination or cross section effects.

• Our 4f\textsubscript{7/2} XAS looks like the EELS of Moser et al.

• Using middle grating calibration from O1s

EELS from Moser, Delley, Schneider and Baer, PRB 29, 2947 (1984)

They showed convergence to high KE limit: EELS = XAS
Our signal to noise ratio and contamination are worse because of the limitations on sample size at the ALS.

- The U4d\(_{5/2}\) looks just like that of KKBK and the energy calibration of the high energy grating is dead on.

- The TEY and TFY are similar, but the TEY is used because of the better statistics.

- The widths are driven by lifetime broadening.

• Our U5d spectrum looks very much like that of KKBK for UO$_2$.
• The photon energy scale of our data was shifted slightly to align with that of KKBK.
• Unlike all of our other U XAS spectra, our U5d was NOT normalized to I$_0$.
• TEY: problems again
The XAS spectra can be aligned with the mono
calibration and BE correction or by the threshold...

- Colinearity of three points confirms
the monochromator calibration.

- One correction factor: \( \Delta \lambda = 0.3 \text{ Å} \)

Binding Energy Correction

\[
\begin{align*}
NE_{O1s} &= hv(O1s) \\
NE_{U4f} &= hv(U4f) - \{BE(U4f) - BE(O1s)\} \\
NE_{U4d} &= hv(U4d) - \{BE(U4d) - BE(O1s)\}
\end{align*}
\]

U-XAS smoothed slightly.

Either way, the
result is the same!
A confirmation can be obtained from BIS and IPES.

- The BIS spectrum will be dominated by the 5f contribution, because the 5f Cross section is about 10x the 6d Cross section. [Yeh and Lindau, At. Data Nucl. Data Tables 32, 99 (1985).]

- At the lowest energies, a weak 6d state can be seen in the IPES of Chauvet and Baptist, Solid State Commun. 43, 793 (1982).

The Conduction Bands can be separated experimentally into U5f-O2p and U6d-O2p parts!
A final confirmation can be obtained from theory.

- Although there is a shift, the same pattern is present in theory as in the experiment, with the U5f states below the U6p states.
- Note the sharpness of the U5f states. The U4d XAS has lifetime broadening and the BIS is instrumentally broadened.
- The match with theory is strengthened by the calculation of the simulated spectra.
Summary, Conclusions and Prospects

• A combined experimental and theoretical study of Uranium Dioxide has been performed, including XAS, BIS, XPS and spectral simulations.

• The Conduction Bands or Unoccupied Density of States (UDOS) of UO$_2$ are shown to be divided into two parts, the lower region being U$_5$f-O$_2$p and the upper region U$_6$d-O$_2$p. This means that UO$_2$ is an f-f Mott Insulator, electron-correlated system.

• The keys to success with the XAS were the (1) the utilization of both TEY and TFY and (2) the accurate co-location of the uranium and oxygen states, which in turn hinged upon a proper calibration of the gratings of the beamline monochromator.

• The calibration of the gratings was greatly aided by the availability of the O1s XAS from 1$^\text{st}$, 2$^\text{nd}$ and 3$^\text{rd}$ order light.

• The success of this approach to differentiation of the Uranium UDOS into U$_5$f and U$_6$d components is of great importance and bodes well for its application to other actinide systems.

• Our ultimate goal remains Pu and its electron correlation.