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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

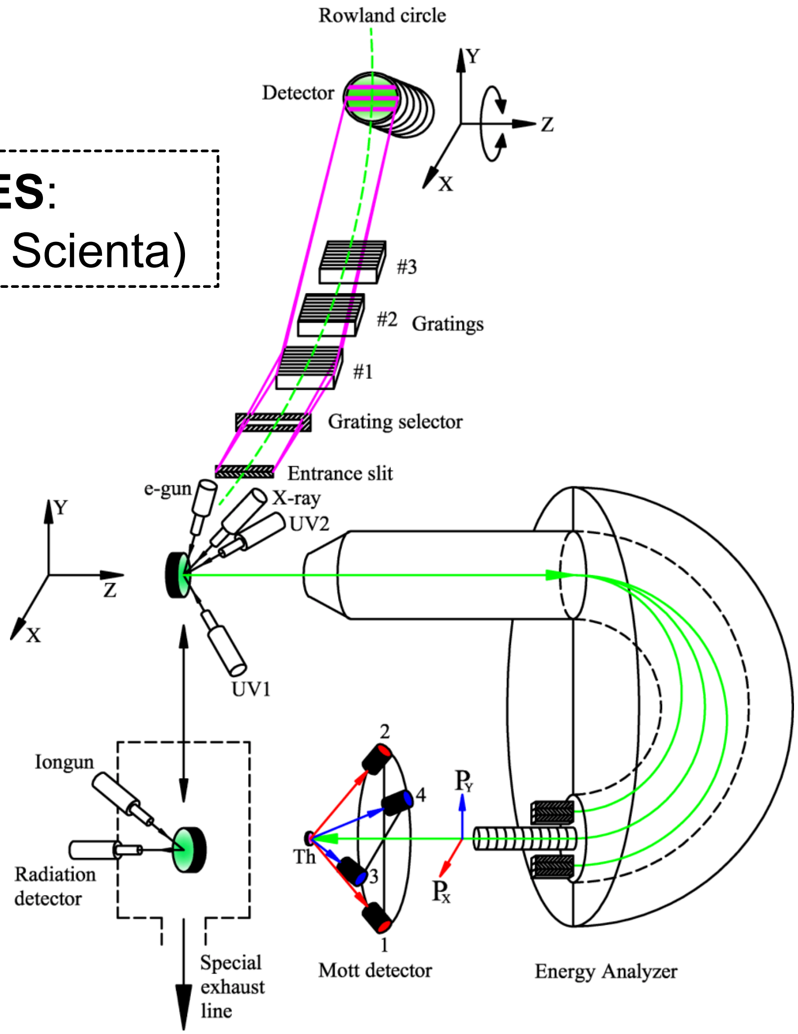
Motivation and Instrumentation

- UO_2 is an important nuclear fuel for electrical power generation.
- Global goal : Actinides (5*f* electron systems) exhibit fascinating physical and chemical properties, due to **5f electron correlation,** including the highly radioactive systems such as 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)

Sample handling system for actinides



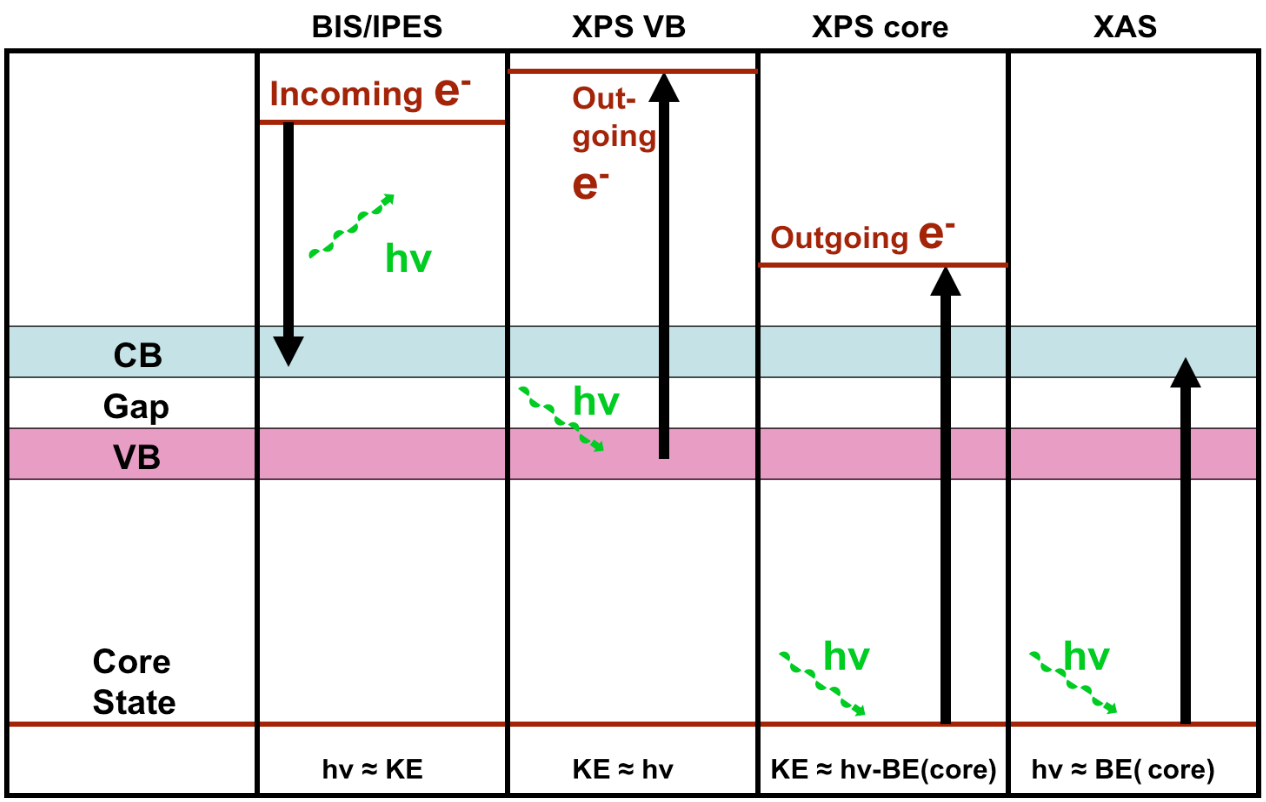
Photoelectron Spectroscopy, with spin and without spin (multichannel)

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

Comparison of Processes: BIS, XPS and XAS



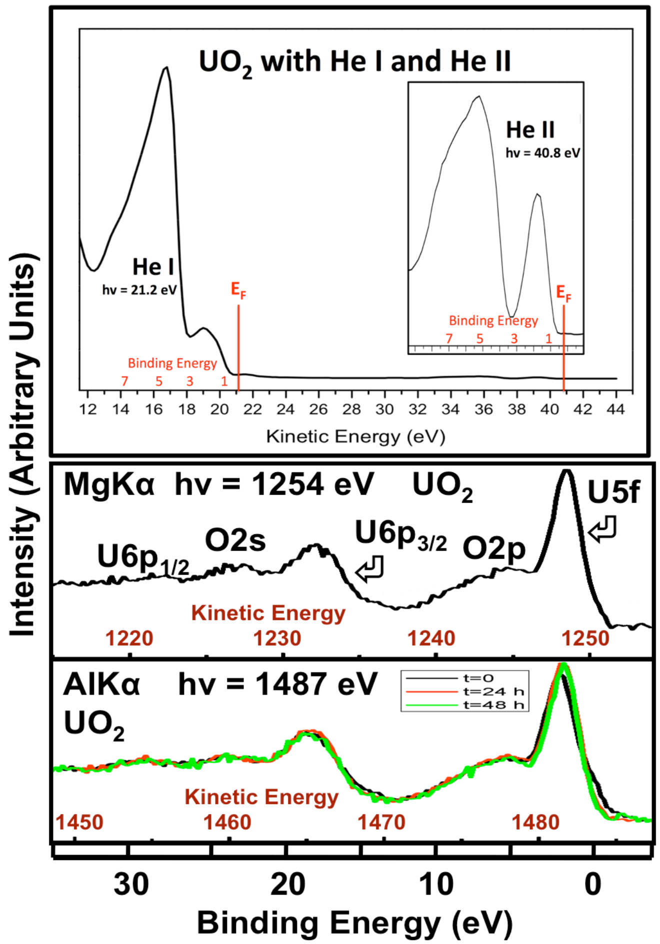
- **XPS samples the occupied DOS or Valence Band (VB)**
- **BIS and XAS sample the unoccupied DOS or Conduction Band (CB)**

Photon absorption and emission:

electric dipole transitions with Δl = +/- 1

X-ray Photoelectron Spectroscopy (XPS) gives us the Occupied Density of States

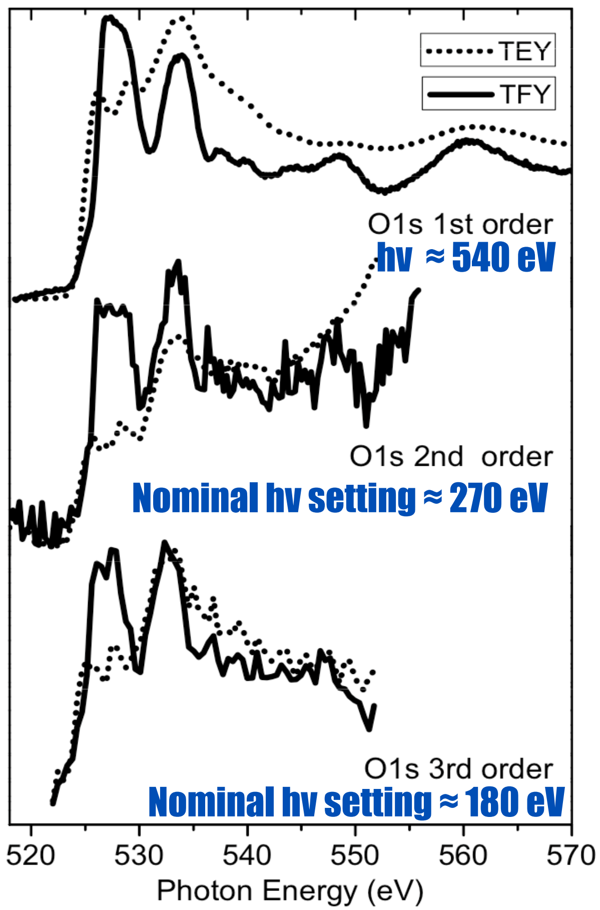
UPS and XPS of UO_2



- **The assignments here go back to Veal and Lam (1974) and are supported by other workers as well.**
- **B.W. Veal and D.J. Lam, Phys. Rev. B 10, 4902 (1974) and Phys. Letters 49A, 466 (1974).**
- **J.R. Naegele, "Actinides and Some of their Alloys and Compounds," Electronic Structure of Solids: Photoemission Spectra and Related Data, Landolt-Bornstein "Numerical Data and Functional Relationships in Science and Technology," ed. A Goldmann, Group III, Volume 23b, Pages 183 – 327 (1994).**
- **For the complete UPS and XPS study, see Yu and Tobin, JVSTA 29, 021008 (2011).**

O1s XAS: old and new → O2p UDOS

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 hν scale on the middle energy grating.
- All three orders agree…

Jollet et al, JPCM 9, 9393 (1997)

Electronic structure of UO_2 9395

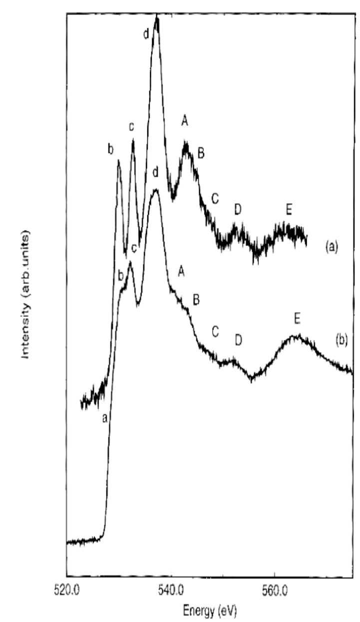
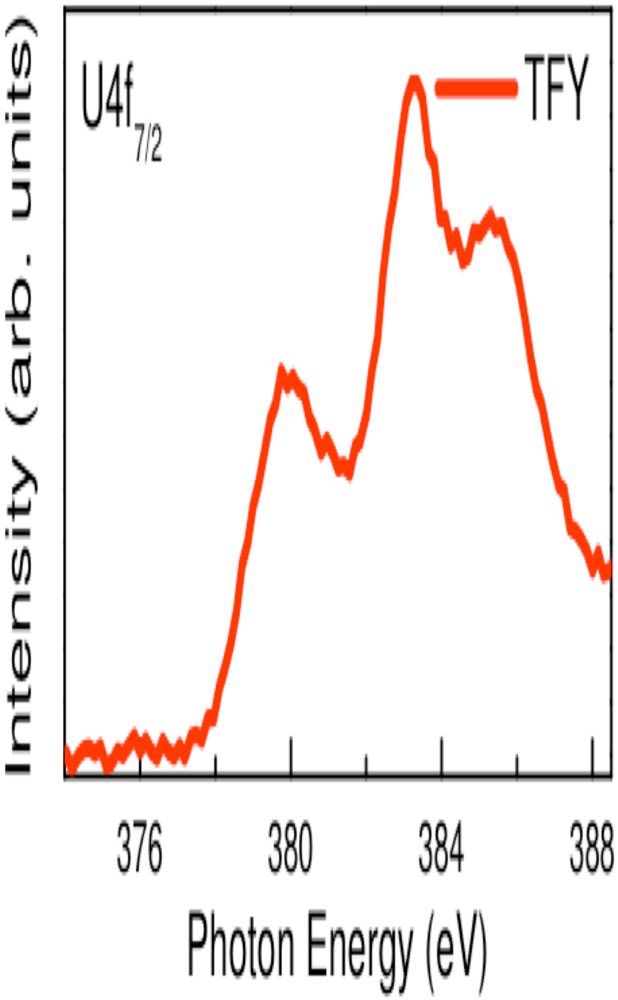


Figure 1. XAS oxygen K edge of CeO_2 (a) and UO_2 (b).

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

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 $4f_{7/2}$ 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

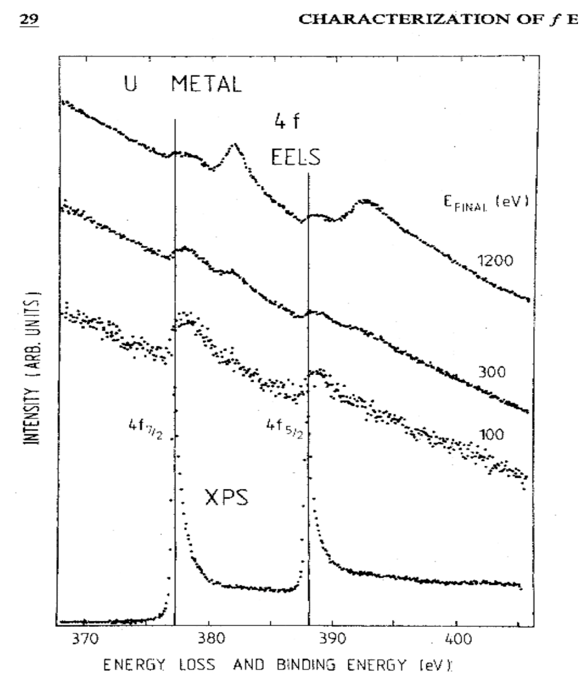
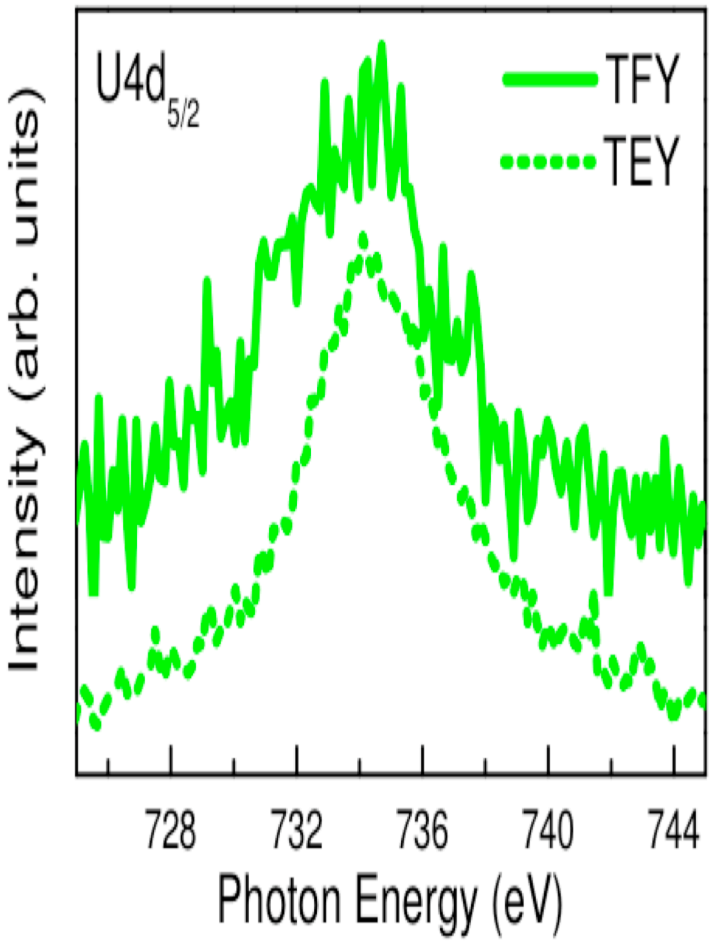


FIG. 3. EELS spectra, taken at the indicated final-state energies, and XPS 4f core-excitation spectra of U metal. The common onset of the EELS and XPS emission is indicated by the two parallel lines drawn through the maxima of the spin-orbit-split XPS components.

U4d XAS: old and new → U5f UDOS



- 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.

Kalkowski, Kaindl, Brewer and Krone, PRB 35, 2667 (1987)

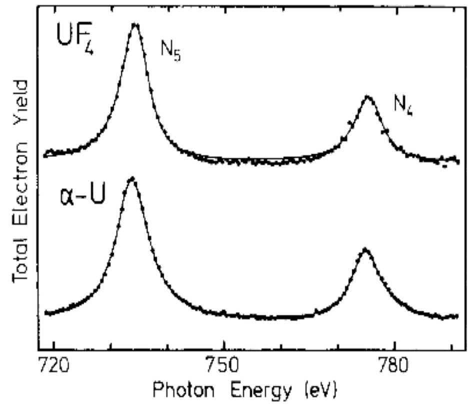
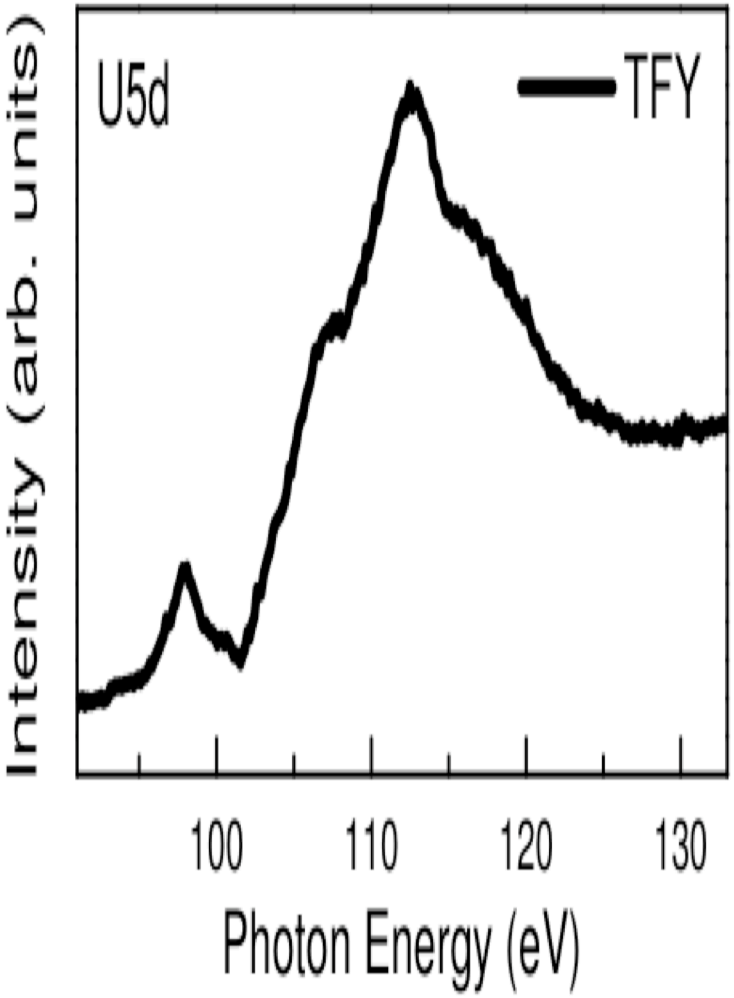


FIG. 7. Total-electron-yield spectra of α-U metal and UF_4 at the $N_{4,5}$ thresholds. The solid lines represent fit results.

Our signal to noise ratio and contamination are worse because of the limitations on sample size at the ALS.

U5d XAS: old and new
Confirmation of Sample Quality



- 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

Kalkowski, Kaindl, Brewer and Krone, PRB 35, 2667 (1987)

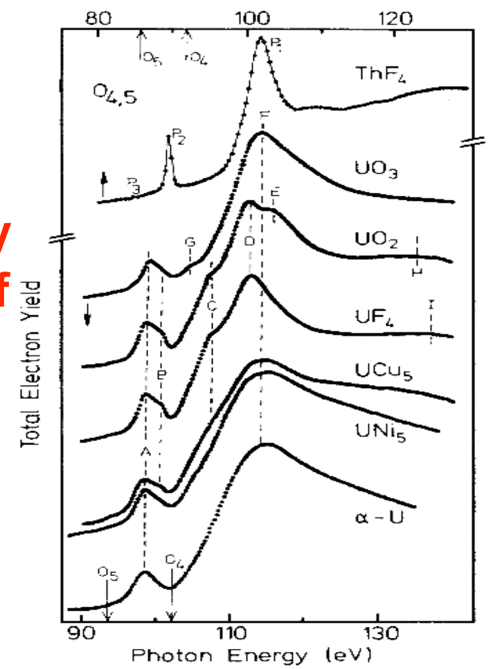
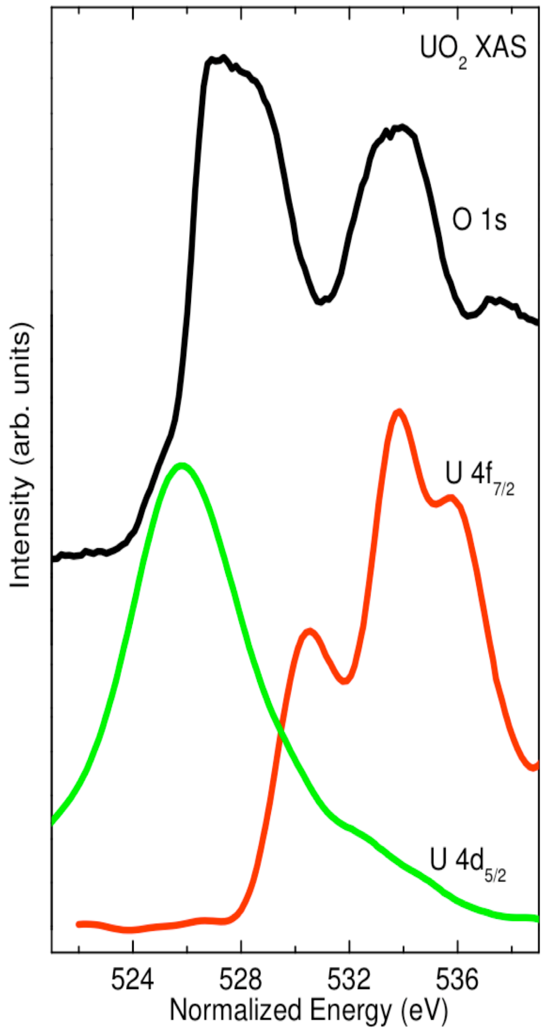
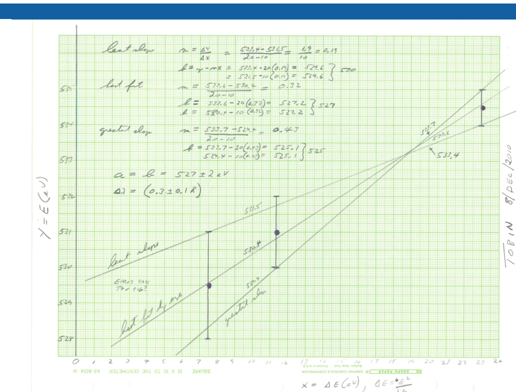


FIG. 8. Total-electron-yield spectra of various U compounds and of ThF_4 at the $O_{4,5}$ thresholds. Note the different energy scales for the Th and U spectra; the arrows specify the O_4 and O_5 thresholds from XPS measurements of Th and α-U metal, respectively (Ref. 46). The various spectral features are explained in the text. The solid lines through the data points serve as guides to the eye.

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: $\Delta \lambda = 0.3$ Å**

Binding Energy Correction

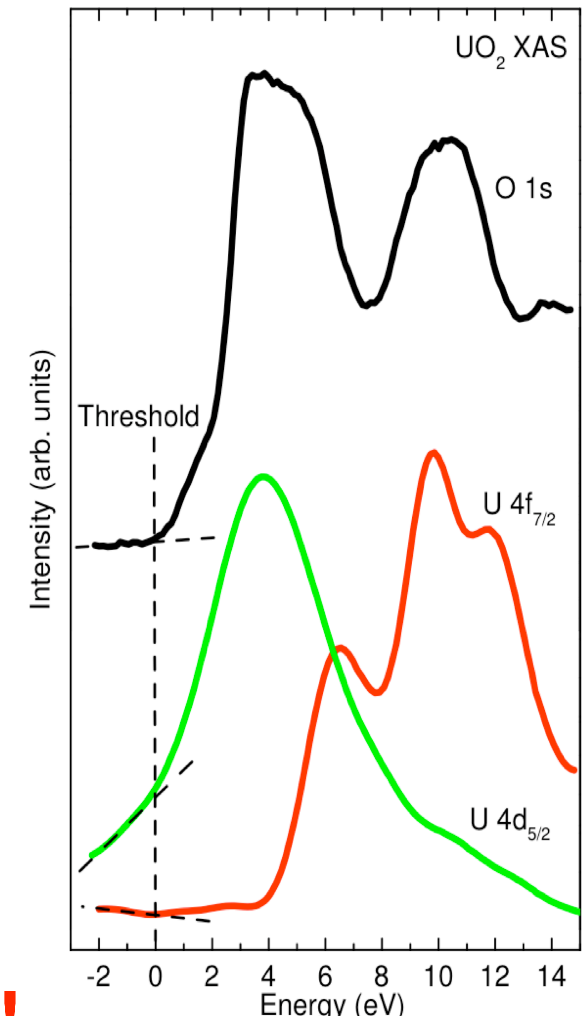
$NE_{O1s} = h\nu(O1s)$

$NE_{U4f} = h\nu(U4f) - [BE(U4f) - BE(O1s)]$

$NE_{U4d} = h\nu(U4d) - [BE(U4d) - BE(O1s)]$

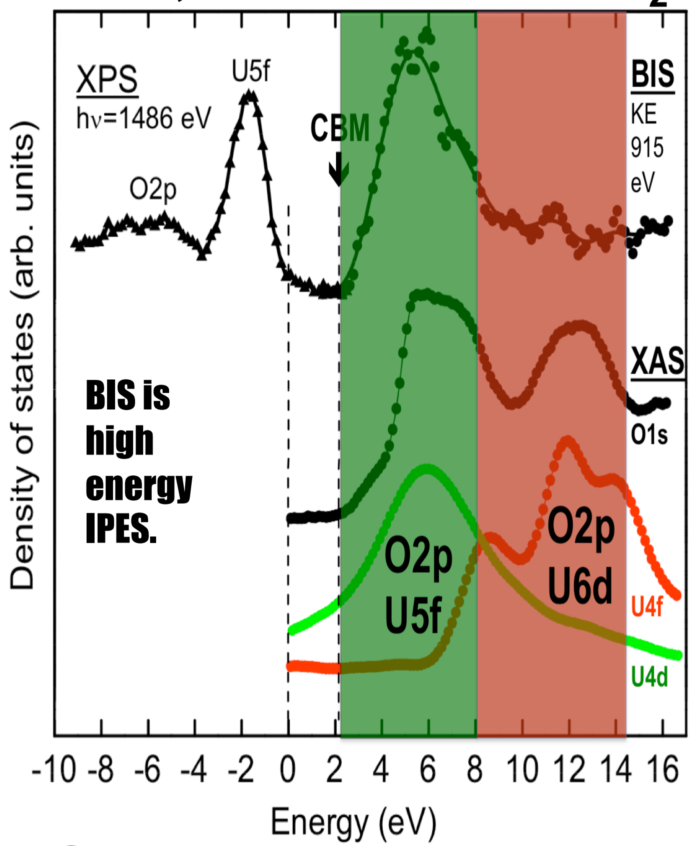
U-XAS smoothed slightly.

Either way, the result is the same!



A confirmation can be obtained from BIS and IPES.

BIS, XAS & XPS of UO_2



The Conduction Bands can be separated experimentally into U5f-O2p and U6d-O2p parts!

- 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).

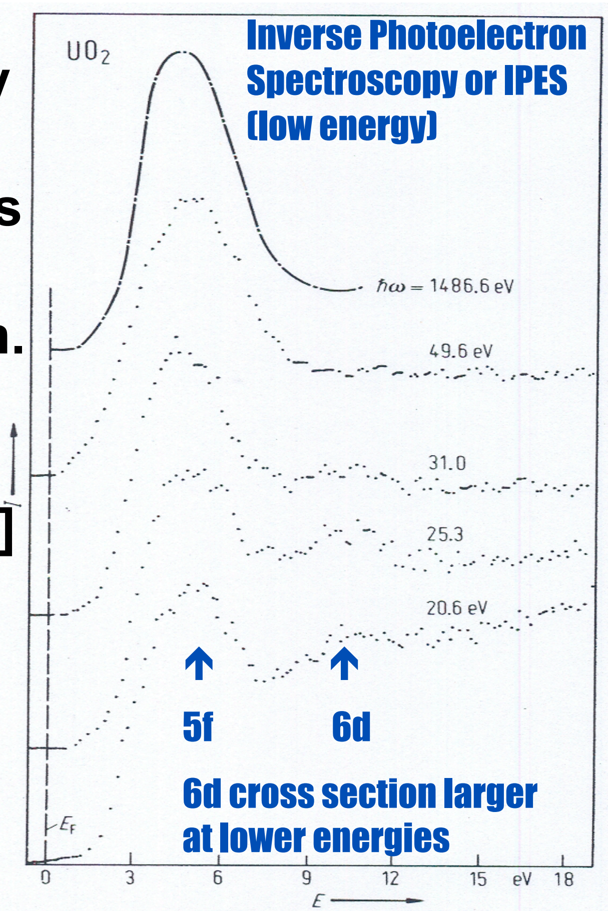
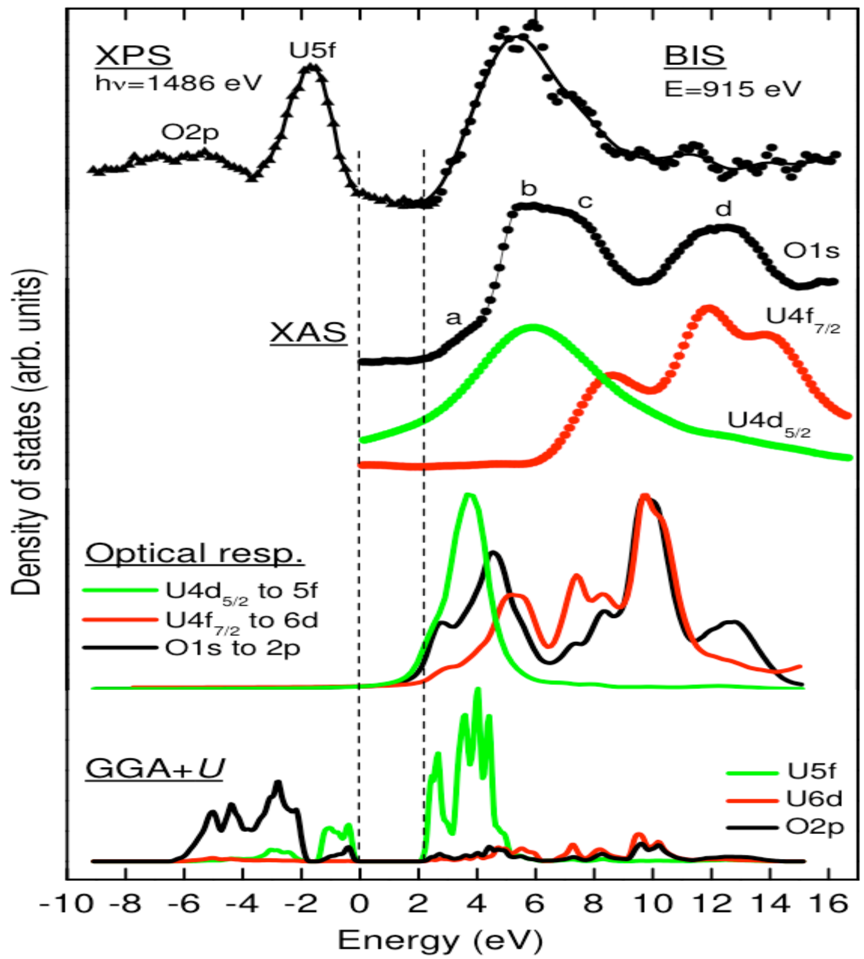


Fig. 117. UO_2. Inverse photoemission (BIS) spectra recorded for different photon energies: $\hbar\omega = 20.6 \cdots 49.6$ eV [82C2] and $\hbar\omega = 1486.6$ eV [80B3].

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 U5f-O2p and the upper region U6d-O2p. 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 availibility of the O1s XAS from 1st, 2nd and 3rd order light.
- The success of this approach to differentiation of the Uranium UDOS into U5f and U6d components is of great importance and bodes well for its application to other actinide systems.
- Our ultimate goal remains Pu and its electron correlation.