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SOFT X-RAY STUDIES OF PU ELECTRONIC STRUCTURE: PAST LESSONS FROM XAS AND FUTURE DIRECTIONS WITH BIS

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Abstract

Synchrotron-radiation-based spectroscopies such as X-ray Absorption Spectroscopy (XAS) have contributed greatly to our improved understanding of Pu electronic structure. However, significant questions remain concerning the nature of Pu electronic structure. Perhaps the missing piece of the puzzle is the direct experimental determination of the unoccupied electronic structure using high energy inverse photoelectron spectroscopy (IPES) or Bremstrahlung Isochromat Spectroscopy (BIS). Past BIS studies of Th and U indicate the feasibility and utility of Pu studies. To this end, a new BIS capability has been developed in our laboratory. Electron stimulated emission of photons has been carried out using the XES-350 monochromator and detector system. Our preliminary results and future plans will be presented.

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Introduction

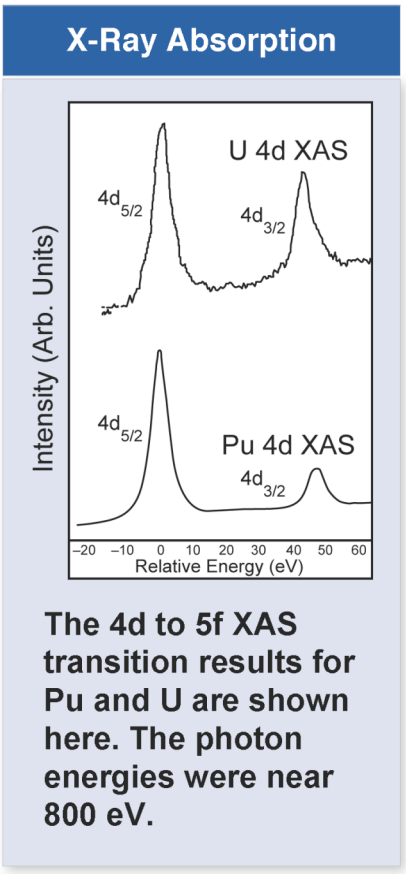
Significant questions remain concerning the nature of Pu electronic structure. [1-5] While chemically toxic and highly radioactive, Pu may be the most scientifically interesting element in the periodic table. It's properties include the following: six different phases, close to each other in energy and sensitive to variations of temperature, pressure and chemistry; the face-centered-cubic phase (delta) is the *least* dense; Pu expands when it solidifies from the melt; and it is clearly the nexus of the actinide binary phase diagram of the actinides. In a sense, it is the boundary between the light (ostensibly delocalized 5f electrons) and heavy (ostensibly localized or correlated 5f electrons) actinide elements, but this is an over-simplification. The localized atomic 5f states are naturally correlated, but important regimes of correlated electron states are conceivable as extended states on the delocalized side of the possible Mott transition. The proximity to this crossover may be the driving force behind all these exotic properties. Pu remains of immense technological importance and the advancement to a firm, scientific understanding of the electronic structure of Pu and its compounds, mixtures, alloys and solutions is a crucial issue.

Photoelectron Spectroscopy [1] and X-ray Absorption Spectroscopy [2-4] have contributed greatly to our improved understanding of Pu electronic structure. From these and related measurements, the following has been determined.

1. The Pu 5f spin-orbit splitting is large.
2. The number of Pu5f electrons is 5.
3. The Pu 5f spin-orbit splitting effect dominates 5f itineracy.

Figure 1

To the right, the X-ray absorption spectra (XAS) of alpha-U and alpha-Pu.



The 4d to 5f XAS transition results for Pu and U are shown here. The photon energies were near 800 eV.

BIS and the UDOS

Perhaps the missing piece of the puzzle is the direct experimental determination of the unoccupied density of states (UDOS) using high energy inverse photoelectron spectroscopy (IPES) or Bremstrahlung Isochromat Spectroscopy (BIS). [5] Past BIS studies of Th and U indicate the feasibility and utility of Pu studies. [6]

To this end, a new BIS capability has been developed in our laboratory. [7] Electron stimulated emission of photons has been carried out using the XES-350 monochromator and detector system. Our preliminary results and future plans will be presented.

Moreover, while there are a number of ongoing experimental efforts directed at determining the occupied (valence band, below the Fermi Energy) electronic structure of Pu, there is essential no experimental data on the unoccupied (conduction band, above the Fermi Energy) electronic structure of Pu.

We have begun an experimental effort to help resolve the controversy regarding the electronic structure of Pu. The objective of this effort is to determine the conduction band (unoccupied) electronic structure of Pu and other actinides, in a phase specific fashion and emphasizing bulk contributions. It can be argued that the conduction band (unoccupied) electronic structure is the missing link in studies of Pu. As illustrated in Figure 2 below, Bremstrahling Isochromat Spectroscopy or BIS is the best way to determine the unoccupied electronic structure of the actinides. While experimental BIS data exists for Th and U, there is no such data for Pu. [6]

The central technique is BIS, or high energy Inverse Photoelectron Spectroscopy. BIS is the high-energy variant of inverse photoelectron spectroscopy (IPES: electron in, photon out), which is essentially the time reversal of photoelectron spectroscopy (photon in, electron out), as illustrated in Figure 2. IPES can be used to follow the dispersion of electronic states in ordered samples. Owing to its low energies, IPES is usually very surface and band sensitive. However, by working at higher energies, we will sample preferentially for the bulk density of states, downgrading the impact of surface and band effects.

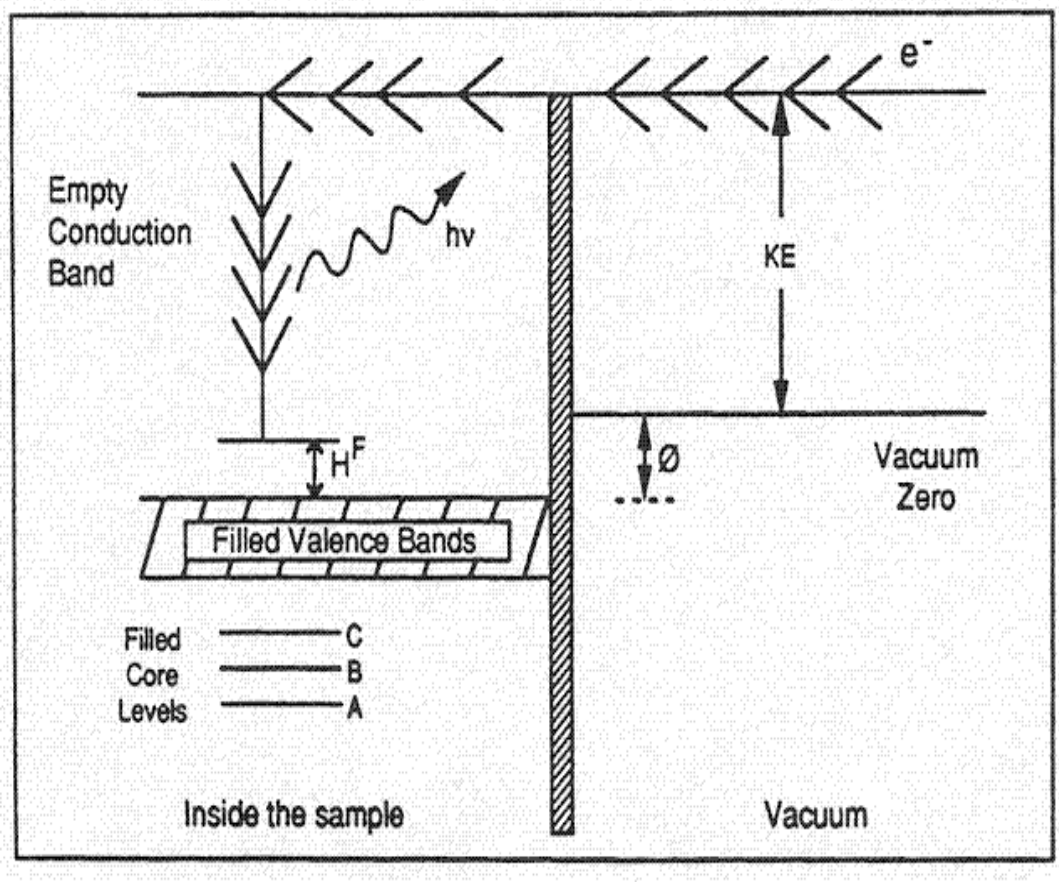


Figure 2

Shown here is a schematic of the inverse photoelectron process. KE is kinetic energy of the incoming electron, θ is the work function, H^F is the energy of the state relative to the Fermi Level, an hv is the energy of the emitted electron. A defining characteristic of IPES/BIS is that hv ≈ KE.

Thus, from BIS, we would argue that we should have a direct measure of the conduction band or unoccupied electronic structure of the bulk Pu. In support of this contention, we present the comparison shown below. Here, experimental BIS data from Baer and Lang [6] is directly compared to a simulated BIS spectrum generated from a calculation of the density-of-states of alpha-U. The match is excellent, strongly supporting the validity of this approach.

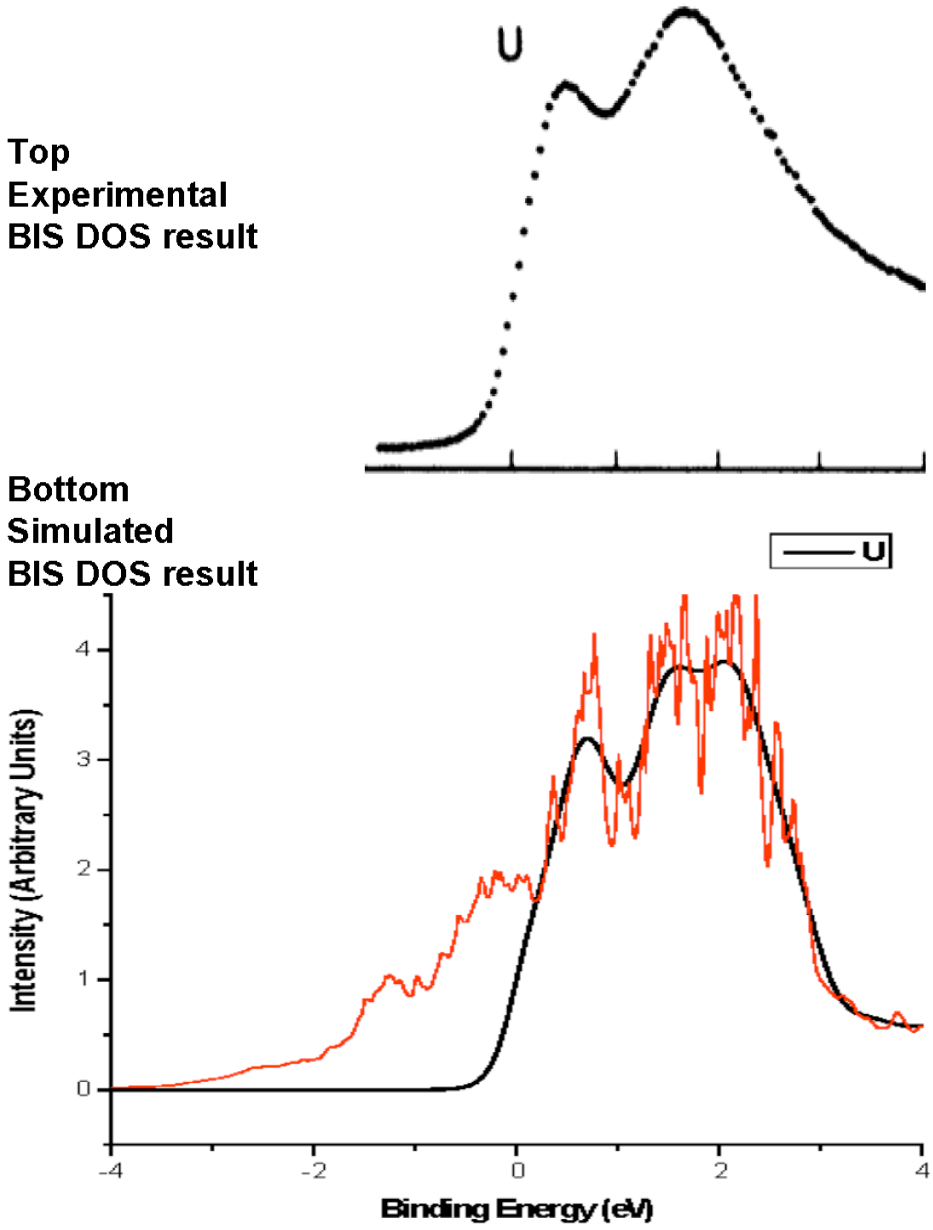


Figure 3
This is a comparison of an earlier BIS measurement by Baer and Lang [6] of Uranium with a simulated Density of States generated by starting with a calculation by Kutepov (in red), [4] which is the truncated at the Fermi Energy (only unoccupied states can contribute to BIS) and then smoothed to reflect broadening from the instrumental band-pass (in black).[8] Top: Experimental BIS result of Baer and Lang,. Bottom: Red: DOS calculations by A.L. Kutepov; Black: DOS calculation times inverse Fermi function, with some instrumental broadening. [8]

Experimental Instrumentation: Fano/Bis Spectrometer
To this end, a new BIS capability has been developed in our laboratory, as shown schematically in Figures 3 and 4 below. [7]

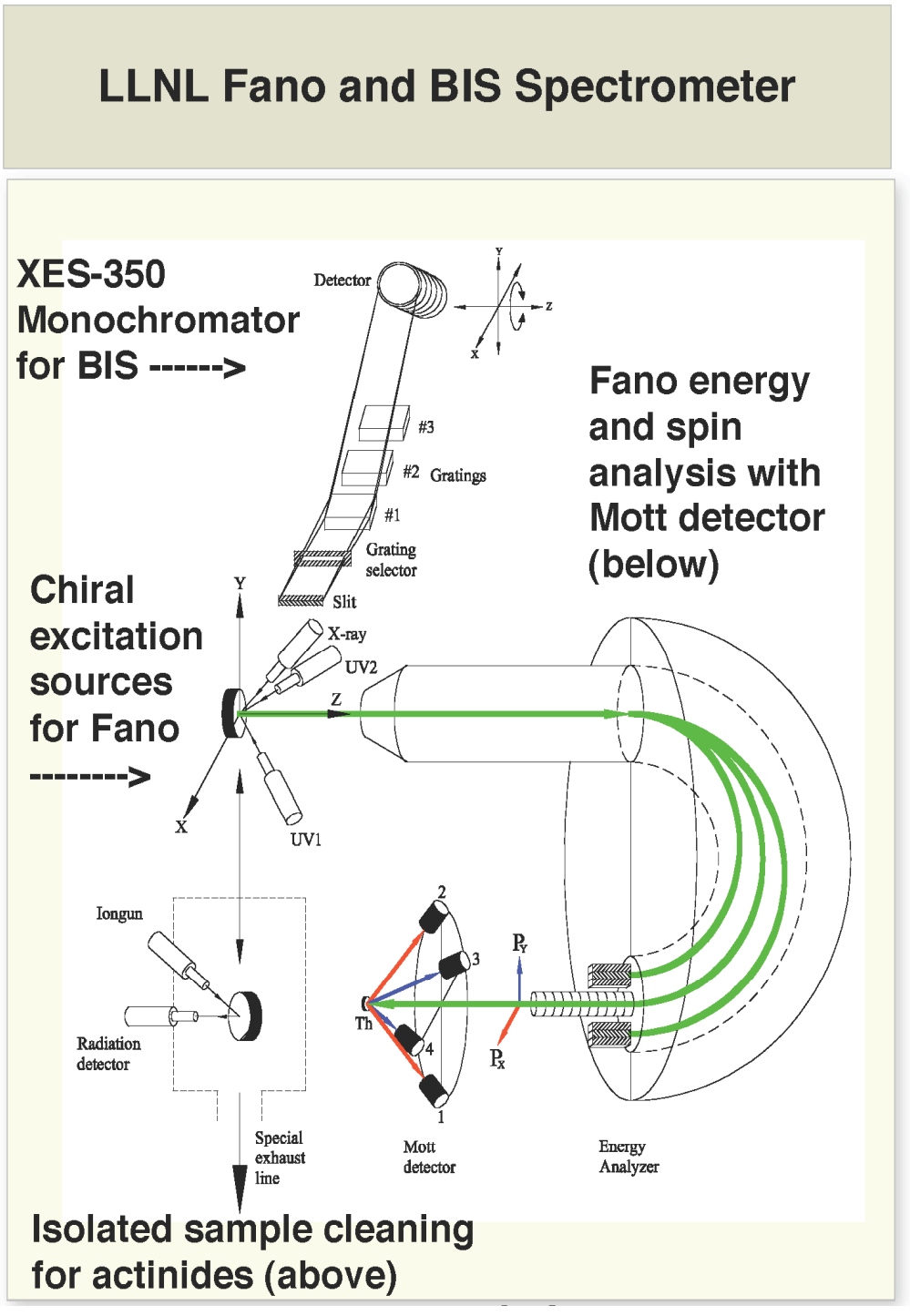


Figure 3

Figure 3 Caption
Sketch for BIS and spin resolved photoelectron spectroscopy (SRPES) experimental setup installed recently at Lawrence Livermore National Lab for the electronic structure study of actinides. For BIS, the detection of the photons is performed with the XES-350 monochromator and multi-channel detector. For SRPES, unpolarized light hits sample at an angle of 45 degrees with respect to the surface normal. The energies and the spins of the normally emitted photoelectrons are analyzed by hemispherical electron energy analyzer and Mott detector which has a thorium target operated at 25 keV with Sherman function of 0.16 $\pm$ 0.04, respectively. Two transversal spin components *PX* and *PY* can be measured in Mott detector simultaneously.

BIS Photon Detection

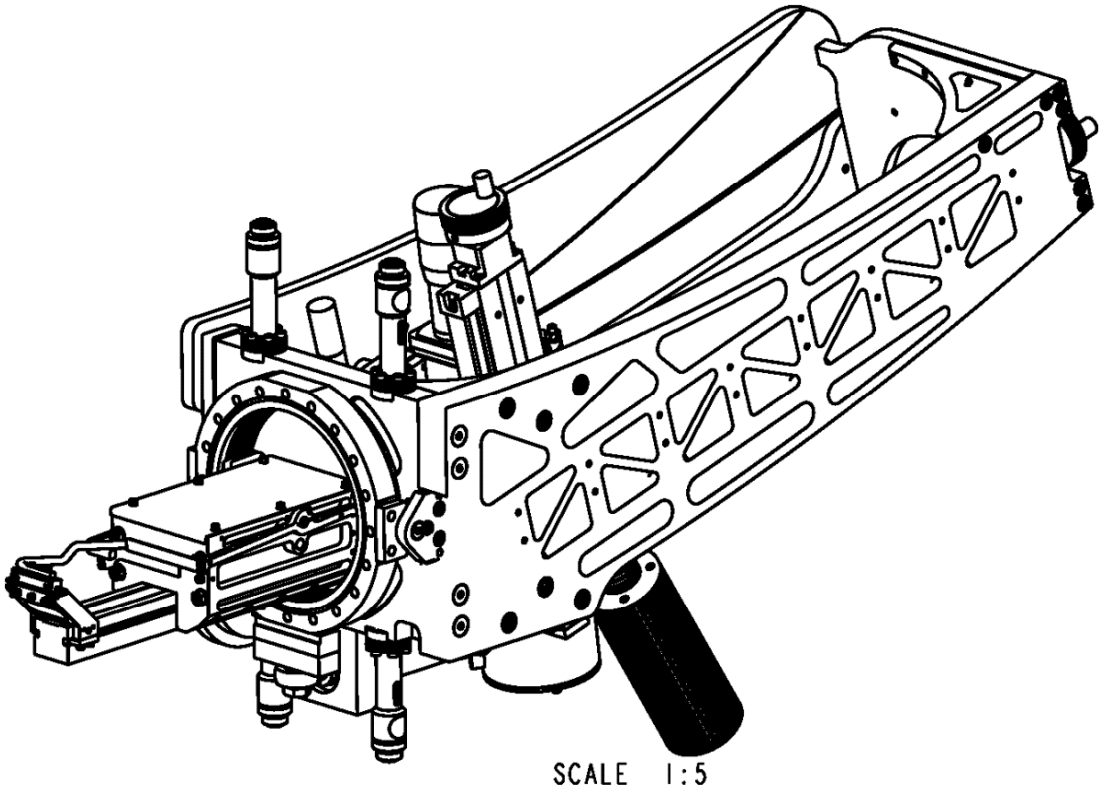


Figure 4
A Schematic of the XES-350 monochromator and detector is shown here. Figure provided by Scienta.

The XES-350 uses three overlapping gratings to cover the energy range from below 100 eV to above 1000 eV. The image of the exit slit of the monochromator then falls upon a multichannel detector, which can be summed in the non-energy direction to provide energy dispersive spectra of the photon emission. In the case of IPES/BIS, the photon energy (hv) and kinetic energy (KE) are approximately equal. This is a demanding experiment, in which the cross sections are relatively low [9]. In some of our initial measurements in the Fano/BIS

spectrometer, a relatively low current electron was used. To aid in data collection in IPES/BIS, we have installed a new high current electron gun and are presently commissioning it. As a preliminary test of the XES-350 system, electron stimulated emission of photons had been carried out using the XES-350 monochromator and detector system. Some of our preliminary results are shown below in Figures 5 and 6, using an electron-excitation-beam-energy of 3000 eV.

X-Ray Emission Spectroscopy

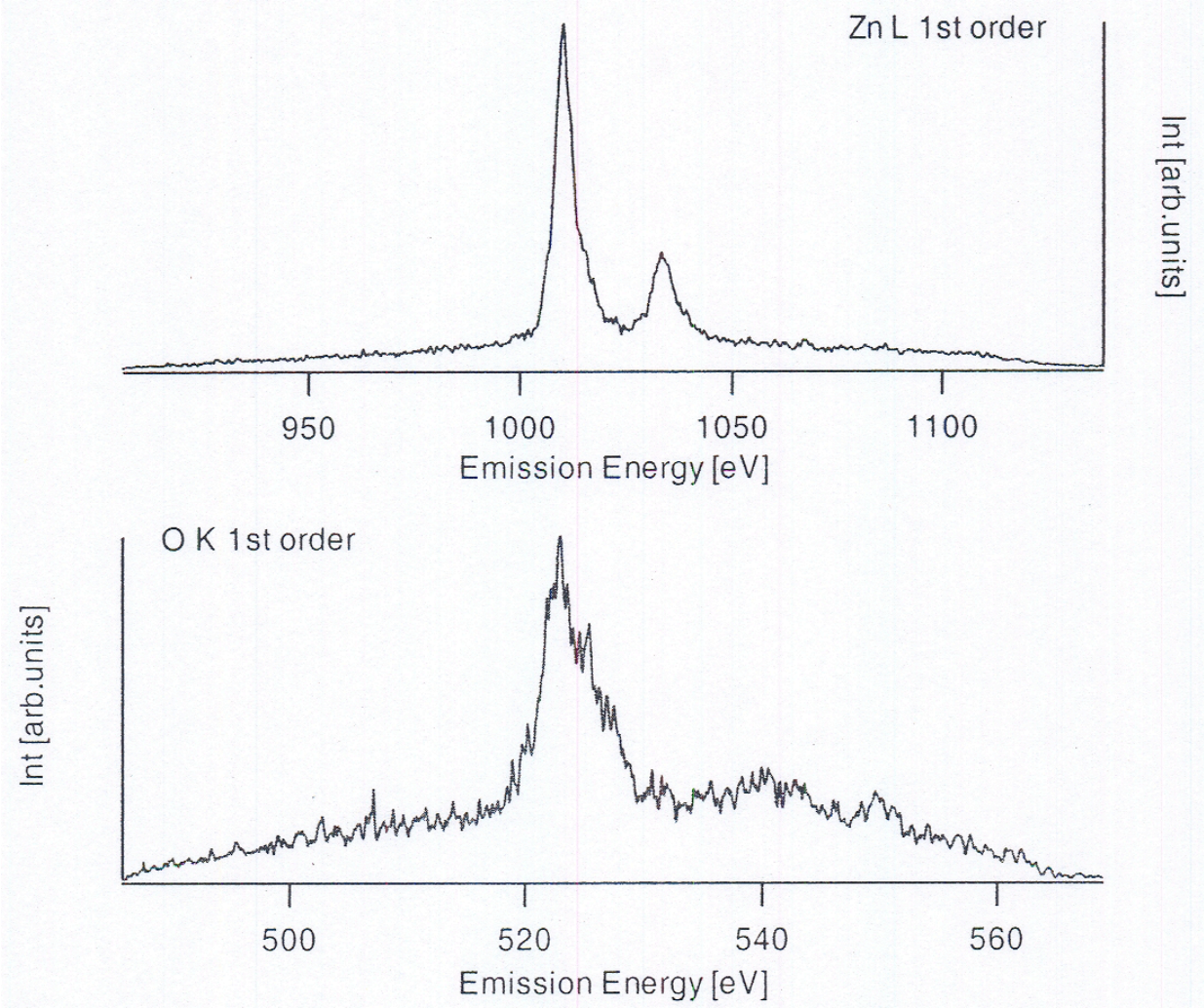


Figure 5
Zn L (2p) and O K (1s) emission in first order, measured at the calculated positions on Grating 1.

X-ray Emission Spectroscopy (XES) is a generic name that includes BIS. However, the spectra shown in Figure 5 and 6 correspond to core level XES. Here, a high-energy electron beam (3000 eV) is used to generate holes in the core levels. This would correspond to the levels A, B and C shown in Figure 2. Subsequently, a decay process can occur, where electrons in less tightly bound levels transition into the core hole. If the extra energy is transferred to an electron,

Auger Spectroscopy is the result. If the extra energy is emitted as an X-ray photon, then XES is the result. If one were to substitute photonic excitation for electronic excitation, then this process would be called fluorescence or phosphorescence.

In the case of Figures 5 and 6, the XES is coming from the core levels of Zinc and Oxygen. For the Zinc, the source is the Zn2p doublet: the Lα1 and Lα2 at 1011.7 eV and the Lβ1 at 1034.7 eV. In the case of the Oxygen, it is the O1s level: Kα1 at 524.9 eV. [10]

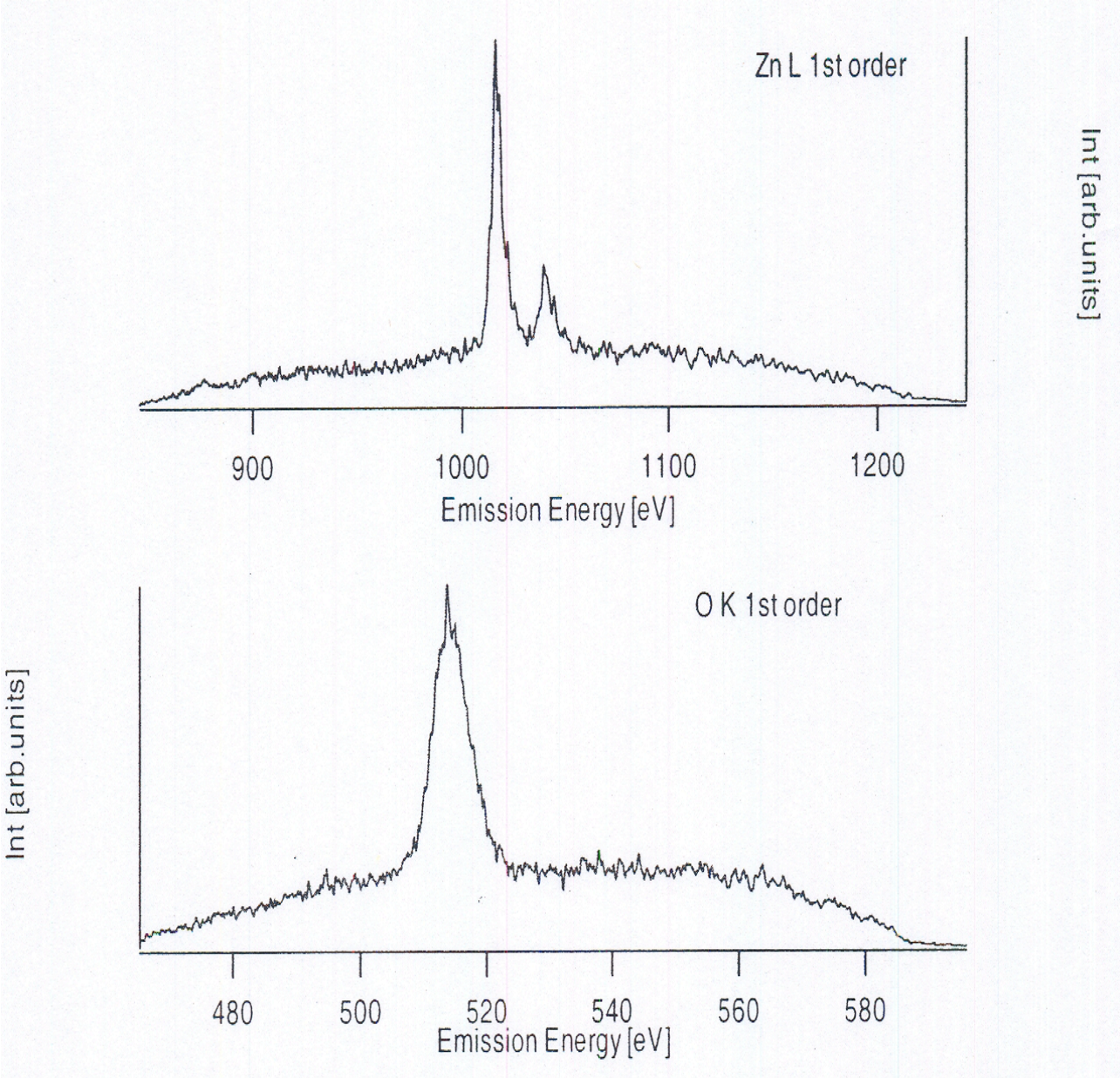


Figure 6
Zn L (2p) and O K (1s) emission in first order, measured at the calculated positions on Grating 2.

Summary

After briefly summarizing our previous results, we have discussed the efficacy of BIS measurements as a means of determining the UDOS of Pu and resolving the Pu electronic structure controversy. Technical details and preliminary test results of the new BIS capability have also been presented.

Acknowledgements

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