



Multi-electronic effects in uranium dioxide from X-ray Emission Spectroscopy



S.-W. Yu, J.G. Tobin*

Lawrence Livermore National Laboratory, Livermore, CA, USA

ARTICLE INFO

Article history:

Received 12 January 2013

Received in revised form 26 February 2013

Accepted 26 February 2013

Available online 18 March 2013

Keywords:

X-ray emission
Uranium dioxide

PACS:

78.70.En

71.20.Gj

71.20.Ps

78.70.Dm

ABSTRACT

X-ray Emission Spectroscopy (XES) and Bremsstrahlung Isochromat Spectroscopy (BIS), two electron-in/photon-out measurements, have been used to probe multi-electronic effects in the important actinide compound, uranium dioxide (UO_2). The new observables in the XES are a distinct satellite, a core-to-core transition, and the lack of a spin-orbit-split satellite peak. New XES data for 4f and 4p derived transitions are presented and discussed. Electron shielding in the $4d_{5/2}$ main and satellite XES peaks is discussed in light of the experimental observations.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Whether loved, hated, feared or merely tolerated, actinides are an important part of modern technological society. They play crucial roles in applications that range from smoke detectors [1] to national defense [2], space exploration [3] to electrical power generation [4]. In fact, an immense amount of electricity is generated, with a fairly small carbon-footprint, using nuclear power. This includes about 20% of the electrical grid of the USA, 40% in Sweden, 55% in Slovakia and 80% in France [5–8]. In nuclear power generation, uranium dioxide (UO_2) is the most commonly used fuel [9].

Uranium dioxide is also a very interesting material scientifically. UO_2 is part of a larger family of uranium oxides, that spans U_4O_9 ($\text{UO}_{2.25}$), U_3O_8 ($\text{UO}_{2.67}$) and UO_3 [10–12], as well as the off-stoichiometric $\text{UO}_{2\pm x}$, with $x \ll 1$ [13]. In terms of formal charge [14], the uranium atom is U^{+4} with a valence configuration of $5f^2$ and the oxygen atoms are each O^{-2} , with $2s^2 2p^6$. In its neutral metallic state, the uranium valence configuration is $5f^3(\text{spd})^3$ [15]. (The spd electrons are associated with the 7s, 7p and 6d orbitals.) While the formal charges in UO_2 suggest a strongly modified electronic structure, it is useful to remember that formal charges are an ionic limit, assuming complete electron transfer to the oxidant.

Reality can be quite a bit different, with partial ionization and significant levels of electron sharing [14,16]. Where uranium dioxide falls still remains a matter of debate, with calculations that suggest both ionicity [17] and covalency [18].

Spectroscopically, UO_2 is also complicated. There are multiple peaks, multiplets and/or satellite structures reported in X-ray Photoelectron Spectroscopy (XPS) [19–22], Inverse Photoelectron Spectroscopy (IPES)/Bremsstrahlung Isochromat Spectroscopy (BIS) [20,23], X-ray Absorption Spectroscopy (XAS) [24–27] and, most recently, Resonant Inverse Photoelectron Spectroscopy (RIPES) and X-ray Emission Spectroscopy (XES) [28]. (See Figs. 1 and 2.) While these processes are related, they are also each significantly different. For example, the photoemission process will leave the system in a +1 charge state, while the inverse photoemission will have a final –1 charge state. Generally, XAS will leave the system excited but charge neutral, however the XES final state can depend upon the nature of the generation of the core hole and whether the process is occurring at or above threshold. There are also differences between valence band to core and core-to-core transitions. This paper extends the work initially reported in Reference [28], including new spectroscopic observations and an analysis of multi-electronic shielding in the XES process and includes results from both the oxygen and uranium core levels, e.g. as shown in Figs. 3 and 4. These spectra will be discussed in more detail below, but first, the experimental details must be described.

The remainder of the paper is organized as follows. In Section 2, the experimental details are reviewed. Section 3 has the

* Corresponding author. Tel.: +1 925 422 7247; fax: +1 925 423 7040.
E-mail address: Tobin1@LLNL.Gov (J.G. Tobin).

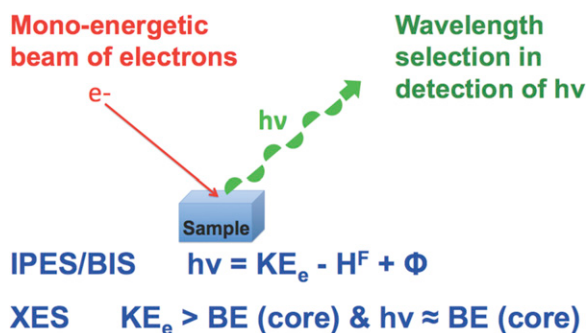


Fig. 1. A diagram of the experiment is shown here. $h\nu$ is photon energy. KE_e is the energy of the excitation, the electron beam. H^F is the energy of the hole above the Fermi Level. Φ is the work function. BE is binding energy. The generalization that BE is approximately equal to the observed photon energy is applicable only to the valence band to core level transitions, such as those associated with the resonances in RIPES. (See Fig. 2.) For core-to-core XES transitions or other more complicated decay paths, this relation will not hold.

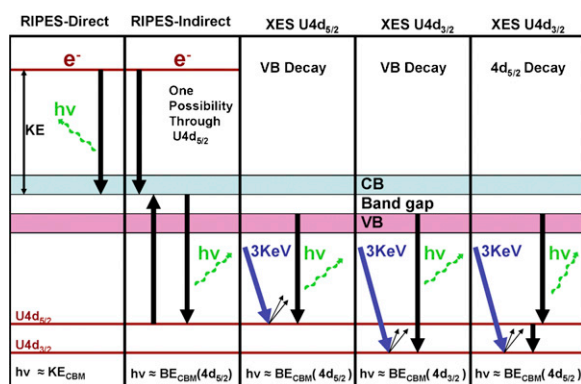


Fig. 2. Energy level diagram and experimental processes, CBM is conduction band minimum. CB is conduction band. VB is valence band.

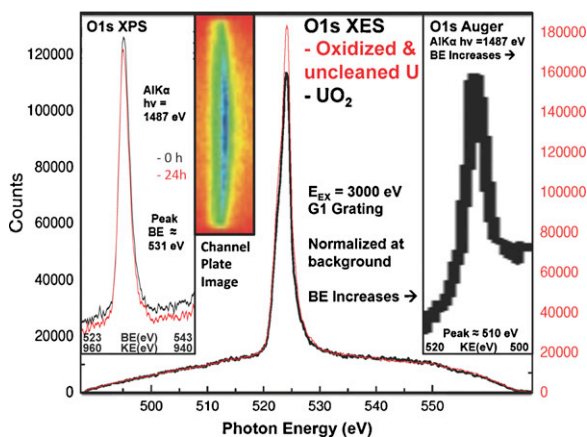


Fig. 3. O 1s spectra: XES (main figure), Auger (right inset), XPS (left inset) and the channel plate image (central inset). See text for detail.

spectral results and discussion, followed by Section 4, concerning the shielding effects in XES. Finally, Section 5 has the summary and conclusions.

2. Experimental

2.1. General experimental considerations

The experiments were performed on site at Lawrence Livermore National Laboratory, using a spectrometer configured to

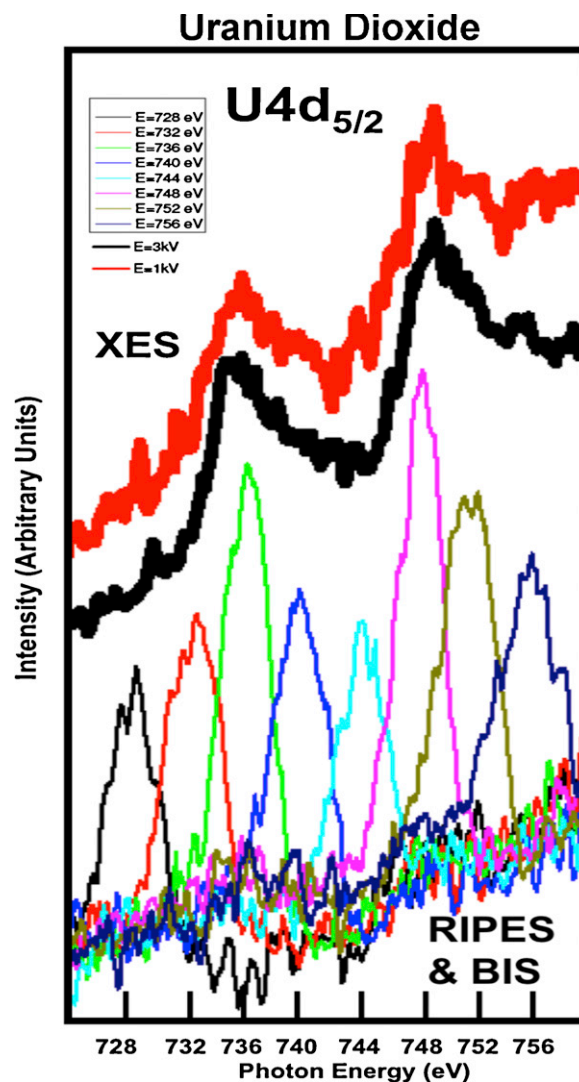


Fig. 4. Previous results from RIPES and XES from Reference [28], without individual background subtraction. See text for detail.

perform Spin Resolved Photoelectron Spectroscopy and Inverse Photoelectron Spectroscopy [27–31]. As illustrated in Figs. 1 and 2, XES/BIS/RIPES are electron-in/photon-out processes, with different constraints in terms of the energetics and different experimental sensitivities. The preparation of the UO₂ sample is described in detail elsewhere, including an exhaustive characterization with XPS and UPS *in situ* [29]. The high quality and pedigree of the underlying uranium substrate has been demonstrated previously [22,29]. The technical specifics of the measurements, such as the previous monochromator calibration and resolution determination, have been discussed earlier [30].

2.2. Experimental confirmation of the G1 monochromator calibration

The photon detection system consisted of a soft X-ray monochromator with three gratings: G1 (high energy, 1200 l/mm, first order of ~ 300 – 1200 eV); G2 (middle energy, 400 l/mm, first order of ~ 100 – 450 eV); and G3 (low energy, 300 l/mm, first order of ~ 20 – 200 eV) [31]. While the original monochromator energy calibration for the G1 grating was quite good, it was necessary to make a final correction using *in situ* experimental data [30]. The most direct way to do this is to use BIS over a wide energy range, away

Download English Version:

<https://daneshyari.com/en/article/5396205>

Download Persian Version:

<https://daneshyari.com/article/5396205>

[Daneshyari.com](https://daneshyari.com)