Inverse photoemission of uranium oxides

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ABSTRACT

Understanding the itinerant-localised bonding role of the 5*f* electrons in the light actinides will afford an insight into their unusual physical and chemical properties. In recent years, the combination of core and valance band electron spectroscopies with theoretic modelling have already made significant progress in this area. However, information of the unoccupied density of states is still scarce. When compared to the forward photoemission techniques, measurements of the unoccupied states suffer from significantly less sensitivity and lower resolution. In this paper, we report on our experimental apparatus, which is designed to measure the inverse photoemission spectra of the light actinides. Inverse photoemission spectra of UO_2 and $UO_{2.2}$ along with the corresponding core and valance electron spectra are presented in this paper. UO_2 has been reported previously, although through its inclusion here it allows us to compare and contrast results from our experimental apparatus to the previous Bremsstrahlung Isochromat Spectroscopy and Inverse Photoemission Spectroscopy investigations.

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1. Introduction

The chemistry and physics of the lanthanide and actinide elements furnish an intriguing area of research, both from an experimental and theoretical perspective. While in the lanthanide elements the 4*f* electrons are essentially localised, the behaviour changes within the light actinides, being localised at thorium and americium, and somewhat delocalised for the elements in-between. This 5*f* electron delocalisation for the elements from protactinium to plutonium affords many aspects of the characteristic behaviour of these elements, for example from low symmetry crystal structures to multiple oxidation states. Much progress in characterising the itinerant-localisation behaviour of the valance electrons has been gained from photoelectron spectroscopy. However, it has been well established that core level X-ray photoelectron spectroscopy (XPS) data can be perturbed by localisation of screening orbitals [1]. The amount of screening depends on the states above Fermi level (E_F) and the degree of localisation of these unoccupied levels. Thus, information of the unoccupied states close to the Fermi level can aid interpretation of core level XPS data.

There are several techniques available to probe the unoccupied states, these include X-ray Absorption Spectroscopy (XAS), Electron Energy Loss Spectroscopy (EELS), Bremsstrahlung Isochromat Spectroscopy (BIS) and Inverse Photoemission Spectroscopy (IPS) [2]. The former two techniques rely on the promotion of core

electrons into unoccupied electronic states, whereas the latter two involve impinging the sample surface with electrons which populate the unoccupied states and subsequently undergo radiative decay into the unoccupied states between the E_F and the vacuum level. The BIS and IPS techniques are more direct methods of measuring the unoccupied density of states and can be considered as a time reversal of the XPS and Ultraviolet Photoelectron Spectroscopy (UPS) experiments, respectively [3]. However, measurements of the unoccupied density of states using BIS and IPS are typically reduced sensitivity $\sim 10^{-3}$ and $\sim 10^{-5}$ times, respectively, when compared to the corresponding photoelectron techniques for measuring the occupied electronic states. Furthermore, the overall resolution in the IPS technique (0.4–1 eV) is somewhat less than the corresponding UPS experiment (<100 meV), whereas the BIS experimental design typically uses an XPS monochromator so comparable resolution is obtained ($\sim$0.5 eV) [4].

Previously, we have employed XPS to investigate the kinetics of plutonium oxidation [5], and intend to employ IPS to complement our existing photoemission measurements and further the understanding of the electronic states, both occupied and unoccupied, observed in plutonium. Described in this paper is the experimental equipment we employ to undertake IPS measurements from actinide surfaces. We also present our first data, acquired on surface grown films of UO_2 and hyper-stoichiometric uranium oxide formed via further exposure to an oxygen atom source. Although BIS and IPS measurements have been reported for UO_2 previously [6,7], the different photon energy used in this study makes an interesting comparison, and reveals the extent to which 5*f* states can be probed using IPS methods.

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2. Experimental

The IPS equipment, which consists of a solid state band pass photon detector and low energy electron gun, were designed and built by PSP Vacuum Technology [8]. The band pass photon detector was based on the design by Schedin et al. [9], and has a centre energy of 9.7 eV. The electron gun is a PSP ELS100 using a BaO filament, with data acquisition undertaken using the SPECTRA® software. The photon detector and electron gun were retro-fitted to a Vacuum Generators ESCALAB MkII photoelectron spectrometer specially modified for plutonium containment. An overall instrumental response function of 1 eV was measured from a National Physics Laboratory silver standard sample cleaned by Ar sputtering, and checked for cleanliness by XPS prior to IPS measurement. The sample current is simultaneously measured using a Keithley Model 6485 Picoammeter and typically resides in the range of 5–10 μA. Data from the photon detector is normalised to the measured sample current providing uniform statistics across the entire energy range of the IPS experiment. The peak energy and full width half maximum (FWHM) of the unoccupied states being probed were determined after removal of a smooth polynomial background function, which represents the Fermi function and secondary electron tail [10]. The binding energy scale was corrected for the photon detector, often referred to as the initial energy, minus the work function of the electron gun.

A polycrystalline sample of alpha uranium was used in this study. After subjecting the sample to multiple sputter-heating cycles to obtain a clean surface as confirmed by XPS measurements of U4f manifold, the sample was exposed to 500 Langmuirs of oxygen at room temperature to afford the characteristic U4f and O1s peak shapes and associated shake up satellites attributed to UO_2 [11]. After IPS data acquisition the same sample was further exposed to 1100 Langmuir of oxygen atoms generated by an Oxford Applied Research TC50 thermal cracker source operating at 50 W. XPS spectra were acquired using non-monochromatic Mg K$_\alpha$ with XPS peak positions quoted in binding energy referenced to Ag3d. XPS data were subjected to mathematical removal of the X-ray induced satellites, Shirley background removal and curve fitting using CASA-XPS® software. Additional characterisation was undertaken using UPS (He^{II}, 40.8 eV) with oxygen gas purity being checked using a mass spectrometer prior to the exposure experiments.

3. Results and discussion

After formation of the UO_2 surface film, analysis of the uranium 4f region (Fig. 1(a)) afforded the corresponding spin-orbit doublet and associated shake up satellites previously reported for UO_2 [11]. No other peaks could be detected and so confirmed complete transformation of the surface to UO_2 to at least the depth probed by the XPS technique. The UPS spectrum is shown in Fig. 2(a) and agrees well with previously reported data [12]. The as collected IPS data (not shown) exhibits a broad peak on a steadily rising background. The steadily rising background occurs from inelastic scattering of incident electrons and is known to increase relative to decreasing initial state energy [13]. This increase in background intensity with decreasing initial energy is well presented for UO_2 in the previous IPS study, where data was collected at initial state energies of 49.6, 31, 25.3 and 20.6 eV [7].

The background subtracted IPS spectra is shown in Fig. 3(a). Initial inspection of the data shows it to be almost identical to the BIS data of Baer and Schoenes [6]. The spectrum displays a broad peak centred at 5.1 eV (FWHM 2.2 eV), which Baer and Schoenes attributed this peak to the 5f^3 final state. They also mentioned the possible existence of a shoulder on the low energy side of the main peak which was not observed in the previous IPS study by Chauvet
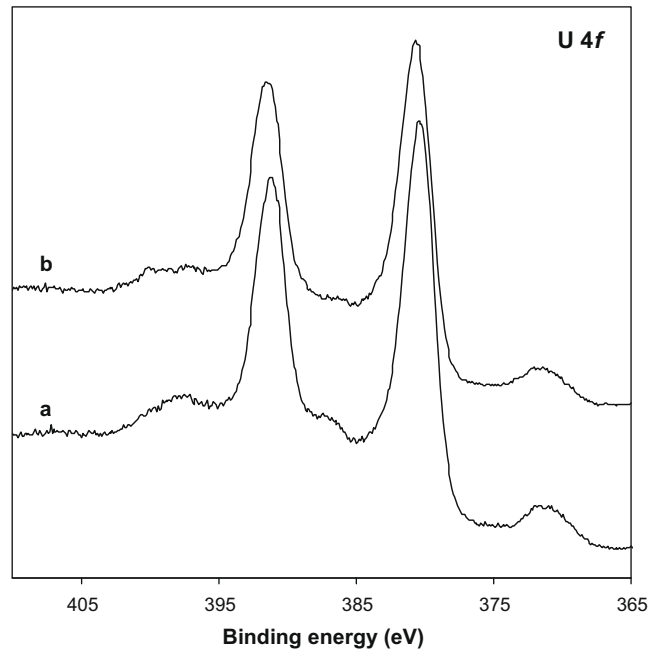

Fig. 1. Uranium 4f XPS spectra of (a) UO_2 and (b) $UO_{2.2}$, captured using non-monochromatic Mg K$_\alpha$ X-ray radiation.
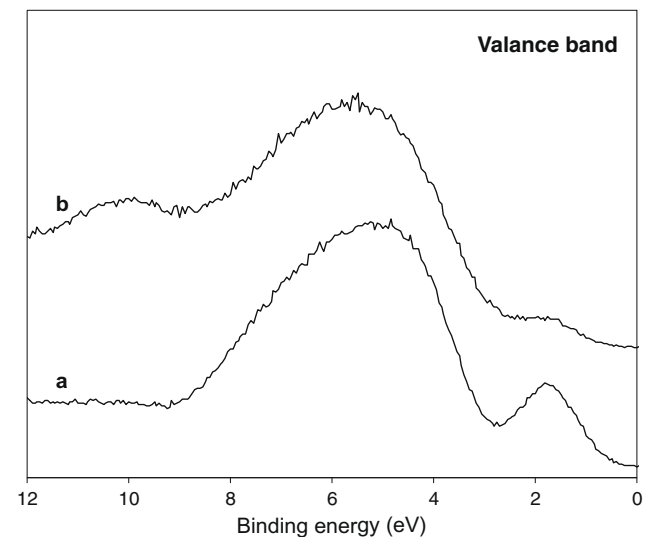

Fig. 2. Valance band UPS spectra of (a) UO_2 and (b) $UO_{2.2}$, captured using He^{II} radiation at 40.8 eV.

and Baptist [7]. Closer examination of the data in Fig. 3(a) shows the possible existence of this peak (indicated by a dashed line), which Baer and Schoenes attributed to 6d states. Chauvet and Baptist believed the reason that they did not observe this pre-peak in their IPS study was due to the fact that initial state energies used in their study were not suited for the detection of the 6d states. They further mention that the ideal initial energy to prove this should be around 9.7 eV, that being used in the work presented here. The energy dependence of cross-sections in IPS measurements has been shown to be similar to that of PES experiments [14]. The calculations of the atomic cross-sections for photo-ionisation by Yeh and Lindau would suggest that the initial energy of 9.7 eV, as used in this work should predominantly detect the 6d over 5f states [15]. The relative intensity of the pre-peak to the
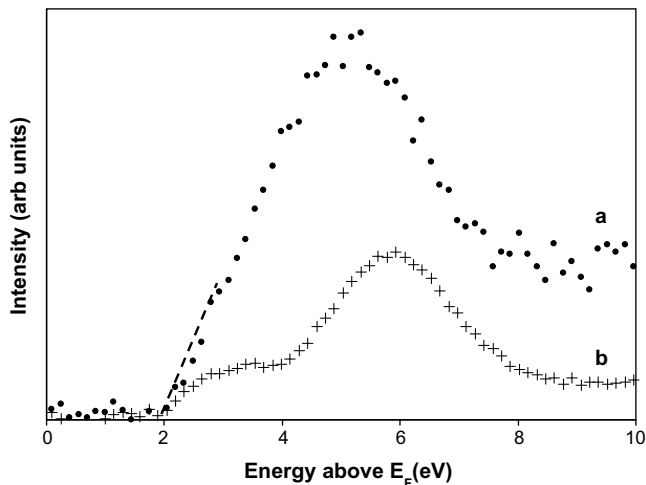
Fig. 3. Background subtracted IPS spectra of (a) UO_2 (dots) and (b) $UO_{2.2}$ (crosses). The dashed line on the UO_2 spectra represents the pre-peak attributed to the $6d$ states by Baer and Schones [6].

main peak in this study is nearly twice that of the reported BIS data, which supports the nature of the pre-peak as being attributable to the $6d^1$ final states. Combining the IPS with the UPS spectrum affords a band gap of ~4.4 eV and would suggest a $5f$-$6d$ transition to be the lowest in energy. This is in contrast to the oxygen K-edge XAS study reported by Jollet et al., who found UO_2 to be an f-f Mott Hubbard insulator [16].

The same sample then underwent subsequent exposure to 1100 Langmuirs of oxygen atoms. The use of oxygen atoms to further oxidise a UO_2 surface film in a surface science spectrometer has been recently reported [17], and the resulting uranium $4f$ XPS spectrum is shown in Fig. 1(b). Compared to the spectrum of UO_2 the peak positions of the $4f$ spin-orbit doublet have increased by 0.3 eV to 380.7 and 391.4 eV for the $4f_{7/2}$ and $4f_{5/2}$, respectively, and these peaks also appear to have broadened slightly and compares well with the spectra for $UO_{2.2}$ reported by Allen et al. [18,19]. Furthermore, curve fitting for U^{4+} U^{5+} and U^{6+} using the peak parameters described by Ilton et al. [20] afford no U^{6+} component and a U^{4+}:U^{5+} ratio of 1.41 consistent with the $UO_{2.2}$ stoichiometry. Though as expected, there is little change to the oxygen $1s$ signal (not shown) with the increased oxidation of the surface. The UPS spectrum of the sample is shown in Fig. 2(b), and when compared to the spectrum for UO_2 there is clearly a reduction of the peak at ~2 eV. This peak is attributable to the uranium $5f$ states, and the reduced intensity is indicative of increased oxidation of the UO_2 sample, but the continued existence of a small peak at ~2 eV means the surface has not completely oxidised to UO_3. The broad peak between 3 and 8 eV is from photoemission of the oxygen $2p$ band. Finally, there is a small feature observed in the background of the UPS spectrum at ~10 eV. A possible explanation for this feature could be surface hydroxyl species being an undesired by-product formed during use of the thermal cracker [21].

The background subtracted IPS spectrum of the $UO_{2.2}$ surface is presented in Fig. 3(b), and shows two broad peaks situated at 3.3 eV (FWHM ~2.3 eV) and 5.9 eV (FWHM ~2.3 eV). The peak at 3.3 eV is a third the intensity of the peak observed at 5.9 eV. By a comparison of the overall $UO_{2.2}$ data to that of UO_2, one can see that the $UO_{2.2}$ intensity is just less than half that of UO_2. Determination of the exact origins of the two peak structure observed in the $UO_{2.2}$ IPS data is difficult due to the absence of theoretical calculations for $UO_{2.2}$. However, one tentative explanation for the two peak structure observed for $UO_{2.2}$ could be extrapolated from the interpretation of the UO_2 data. The small peak at 3.3 eV is almost

identical in position to the pre-peak in the UO_2 spectrum, and thus could be attributable to the $6d^1$ states. This would mean the main peak at 5.9 eV is from the $5f^3$ and $5f^2$ final states in the mixed valent oxide formed from U^{4+} and U^{5+}. The 0.9 eV increase in energy of the main peak from UO_2 to $UO_{2.2}$ is similar to the 0.8 eV increase observed in the XAS studies of these oxides [22]. In the previous study, this was attributed to the $3d$ to $5f$ (unoccupied) promotion confirming the peak at 5.9 eV originates from $5f$ final states.

With the origin of the IPS feature now ascribed it is of interest to discuss their influence on the shake up satellites in the uranium $4f$ XPS spectra. Baer and Schoenes attribute the shake up satellites for UO_2 in the uranium $4f$ spectrum, which occur at ~7 eV higher binding energy than the main $4f$ doublet, to the energy loss of the out going core photoelectron to promote a valance oxygen p electron to the unoccupied states. We apply this same argument to the unoccupied states of $UO_{2.2}$, which has a two peak structure separated by 2.6 eV (Fig. 3(b)). We would expect the XPS shake up satellites to consist of a two peak structure, with a separation of 2.6 eV. Furthermore, the oxygen p valance band starts at ~3 eV from the UPS data shown in Fig. 2(b). Therefore promotion to the unoccupied states will afford shake up peaks at ~6.3 and ~8.9 eV above the main core level peak. Indeed, this is what we observe (Fig. 1(b), *vide supra*).

Finally, we compare and contrast our experimental design to that of previous IPS and BIS apparatus used in the study of the light actinides. As mentioned previously, from the calculations of Yeh and Lindau we would expect our initial energy of 9.7 eV to focus predominantly on the uranium $6d$ electrons. The fact that we observe $5f$ unoccupied states with greater intensity than the $6d$ states is probably because they are so dominant in the light actinide metals and materials. From the 'universal curve' for the inelastic mean free path of electrons the depth penetration of the initial state energy used in this study is several monolayers less than that of the BIS study, and much greater than the previous IPS study [23]. The combined instrumental resolution of 1 eV is somewhat low, however, we are in the process of modifying our photon detector to the optimised design described by Schedin et al. which should afford a resolution <0.5 eV [9].

4. Conclusions

We have demonstrated our experimental apparatus, which has been designed to acquire IPS data from plutonium. Our initial study of UO_2 is almost identical to the previously reported BIS study, affording confidence in this technique when being applied to actinide materials. We have discussed the implication of the unoccupied states with respect to the shake up satellites in uranium $4f$ XPS. An IPS spectrum was acquired from a previously unstudied $UO_{2.2}$ surface, which afforded a two peak structure. This two peak structure has been tentatively assigned, with the feature occurring at ~3.3 eV ascribed to $6d$ states and the feature at 5.9 eV being ascribed to $5f$ states. Despite the low energy of the initial state used in our study, we have demonstrated that $5f$ final states can be detected with ease, and ascribe this to the dominance of the $5f$ empty states for the light actinide elements.

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