



An independent confirmation of the correlation of U4f primary peaks and satellite structures of U^{VI}, U^V and U^{IV} in mixed valence uranium oxides by two-dimensional correlation spectroscopy

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ABSTRACT

Two-dimensional (2D) correlation spectroscopy was used to resolve the positions and correlations among U4f primary peaks and satellite structures of U^{IV}, U^V and U^{VI} components on a dry mica surface. These different species resulted from the reduction of U^{VI}, initially sorbed/precipitated from solution, upon exposure to a high flux of monochromatic Al K α X-rays during X-ray photoelectron spectroscopy. Synchronous and asynchronous 2D maps of these results are consistent with previous assignments to U^{IV}, U^V and U^{VI} components of the solid. The synchronous spectra confirmed the negative correlation between U^{VI} and U^{IV} components and the asynchronous spectra confirmed the role of U^V as a reactive intermediate in the reduction reaction of U^{VI} to U^{IV}. Simulations of 2D correlation maps using synthetic spectra of the primary peaks showed that the presence of highly overlapped peaks centered within 2 eV of each other cannot be distinguished without the presence of additional cross-peaks. The maps have therefore confirmed the existence of three dominant oxidation states, and identified positions of U^{IV}, U^V and U^{VI} U4f primary peaks and satellite structures that are consistent with previous peak-fitting efforts. Satellite structures also showed out-of-phase correlations among the different oxidation states, further confirming their use as reliable indicators of oxidation state.

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1. Introduction

Numerous studies have focused on redox reactions of uranium compounds [1–17]. A subset of these efforts [9–17] has made use of X-ray photoelectron spectroscopy (XPS) to quantify systematic changes in the intensities of U^{IV}, U^V and U^{VI} components. For example, in a previous study by the present authors [16] a constant high flux of monochromatic Al K α X-rays was used to reduce uranyl sorbed on a mica substrate, to a mixture of U^{IV}–U^V–U^{VI} oxidation states (Fig. 1a). Peak-fitting the time-sequence spectra with U^{IV}, U^V and U^{VI} components (Table 1) derived from bulk standards yielded systematic trends in the concentrations of the three oxidation states as a function of beam time exposure (Fig. 1b). Not only were both primary peaks and satellite structures coherently modeled over a range of bonding environments but the latter were shown to be good diagnostic indicators of oxidation state. The data were also used in a kinetic model that provided evidence for two

distinct reduction pathways. The first consisted of a one electron transfer U^{VI} → U^V reaction producing a metastable pool of U^V which slowly converted to U^{IV} (Fig. 1b). The second reaction involved a different pool of U^V with negligible residence time and was therefore expressed as the two electron transfer U^{IV} → U^{IV} (Fig. 1b). We emphasize that these conclusions were derived from kinetic modeling of the component concentrations and that the peak-fitting itself did not provide any evidence for two distinct pools of U^V. In fact, a rank analysis of the spectroscopic data of Fig. 1 revealed only three distinct chemically-relevant eigenvectors associated with U^{IV}, U^V and U^{VI}.

Preliminary attempts (unpublished) were also made to extract spectral components from the spectra of Fig. 1 without any reference to standards. The kinetic model [16] of the data in Fig. 1b was used to extract pure component spectra using eigenvector rotation methods [18,19]. Although the resulting components were similar to the three oxidation state standards used in the curve fitting they recorded cross-contamination, indicating that the rotation of abstract eigenvectors to real chemical space was not sufficiently-well achieved with the model, nor with any other realistic variants. We ascribed this limitation to shortcomings arising from (1) covariance between components during portions of the reduction reaction and (2) potential variations in component

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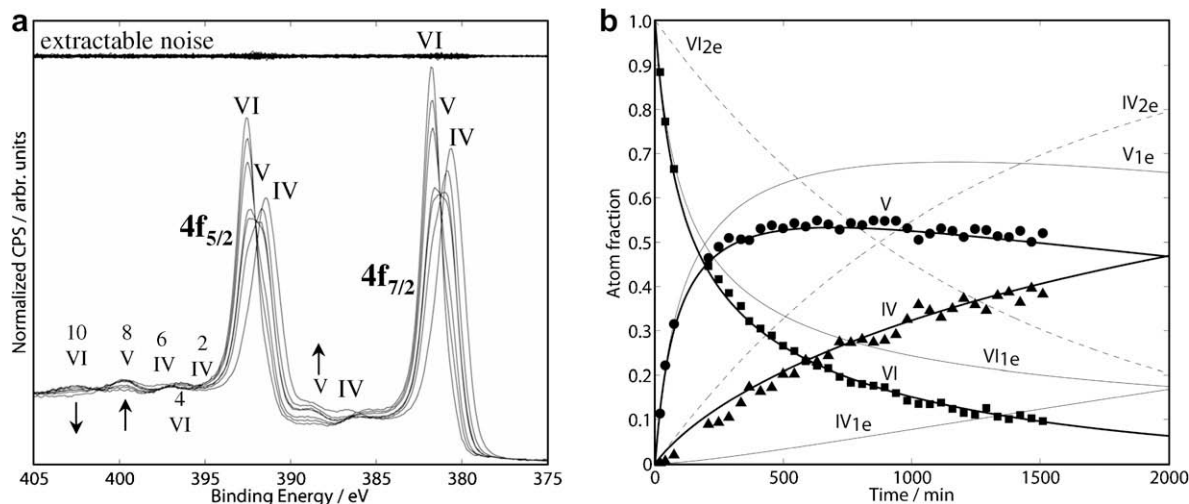


Fig. 1. (a) A selected subset of the 36 U4f XP spectra in Ilton et al. [16] showing X-ray induced reduction of sorbed/precipitated U^{VI} as a function X-ray beam exposure time. The positions of the various peaks elucidated by Ilton et al. [16] are marked by their corresponding oxidation states. These spectra were reconstructed from a SVD analysis of the raw spectra, removing up to 4% of the covariance originating from noise (shown on top portion of the figure). Arrows indicate increasing/decreasing intensity with exposure time. (b) Time-dependence of the total peak areas of the three uranium oxidation states from the constrained peak-fitting results [16]. The thick full lines show the overall kinetic model calibrated on these data. The thin dashed lines show the concentration-normalized fractional contributions of reduction pathways involving a rapid 2e process ($U^{VI} \rightarrow U^{IV}$) (labeled as '2e') and the thin full lines those involving a metastable pool of U^V ($U^{VI} \rightarrow U^V \rightarrow U^{IV}$) (labeled as '1e').

Table 1
Position of peaks (eV)

		$\Psi(v_1, v_2)_{max}^a$	Peak-Fitting ^b	Literature
4f_{7/2} primary				
U^{IV}		379.80–380.00	380.22–380.43	379.8 ^c , 379.9 ^d , 380.1 ^e , 380.0 ^f , 380.15 ^g , 379.9 ^h
U^V		380.80–380.94	380.77–380.98	380.4 ^c , 380.4 ^d
U^{VI}		381.78–381.91	381.67–381.93	381.0 ^c , 381.3 ^d
4f_{5/2} primary				
U^{IV}		390.58–390.75	391.04–391.25	390.9 ^c , 390.8 ^c , 390.8 ^f , 391.0 ^g
U^V		391.59–391.70	391.59–391.80	
U^{VI}		392.63–392.72	392.48–392.74	
4f_{7/2} satellite				
U^{VI}	(4)	384.9, 385.4	385.26–385.52	
U^{IV}	(6)	386.2	386.51–386.72	
		387.1		
U^V	(8)	388.8–388.9	388.91–389.38	
U^{VI}	(10)		n.a. ⁱ	
4f_{5/2} satellite				
U^{IV}	(2)	394.4–395.1	n.a. ^j	
U^{VI}	(4)	396.0–396.5	396.40–396.66	4.2 ^d , 4.0 ^e
U^{IV}	(6)	396.7	397.26–397.47	7.0 ^d , 397.6(6.7) ^e , 397.7 (6.8) ^e
U^V	(8)	399.6	399.71–399.92	8.5 ^d , 9.0 ^e
U^{VI}	(10)	402.8	402.26–402.52	10.0 ^d , 10.0 ^e

^a Asynchronous cross-peaks.

^b Peak-fitting from Ilton et al. [16] and calculated for this table as the average difference in binding energy to the average primary peak position. Those of the 4f_{5/2} primaries were obtained using spin-orbit splitting [16]. The values of the 4f_{7/2} satellite were obtained using the binding energy separation between the satellites and primary peaks of Ilton et al. [16].

^c Goldik et al. [15].

^d Santos et al. [14]. The satellite positions are relative to the U4f_{5/2} primary centered at an undisclosed position.

^e van den Berghe et al. [11].

^f Allen et al. [31] on a UO_{2.001} pellet.

^g Allen et al. [32] on monocrystalline UO₂.

^h Suresh Kumar et al. [33].

ⁱ This was modeled in [16] but lies under the U4f_{5/2} primary peaks.

^j Not modeled in Ilton et al. [16].

features, such as binding energy and spectral shape, as a function of changing bonding environment. Further attempts were also made with the multivariate curve resolution-alternating least square [20] method, which provides less stringent constraints on concentration profile, with, however, similar shortcomings.

Although careful peak-fitting using well characterized standards remains the most straight-forward approach to XPS curve resolution, the choice of peak parameters can often be subjective. Specifically, standards may not necessarily be fully appropriate for the bonding environment under investigation. Indeed, a non-con-

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