



Experiment title: Resonant inelastic x-ray scattering study of uranium compounds at M_{4,5} edges

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Report:

X-ray spectroscopy in the hard x-ray regime is a common technique for probing the electronic structure of actinide systems, since such experiments do not require the vacuum environment for the sample. X-ray absorption near edge spectroscopy (XANES) measurements performed at the L₃ edge of uranium (~17.166 keV) are the most commonly reported in the literature [1-3]. However, the large lifetime broadening at the 2*p* level (~7.4 eV for U) makes this method more valuable only at the extended X-ray absorption fine structure (EXAFS) region. This post-edge region in the spectra contains significant structural information on the coordination chemistry of actinides [4-6]. The shorter core hole lifetime broadening is achievable at the U M_{4,5} edge (3.5 – 3.7 keV) of XANES [2-3, 7]. Even the instrumental resolution is better at lower X-ray energies, which makes experiments at the M_{4,5} edge of actinides more attractive.

We performed XANES and resonant inelastic X-ray scattering (RIXS) measurements on two uranium systems with different oxidation states: uranium dioxide UO₂ with oxidation state of U⁴⁺ and torbernite mineral Cu(UO₂)₂(PO₄)₂*8H₂O with oxidation state of U⁶⁺. Spectra were recorded using X-ray emission spectrometer, based on a vertical Rowland circle geometry, exploiting the (8 8 0)

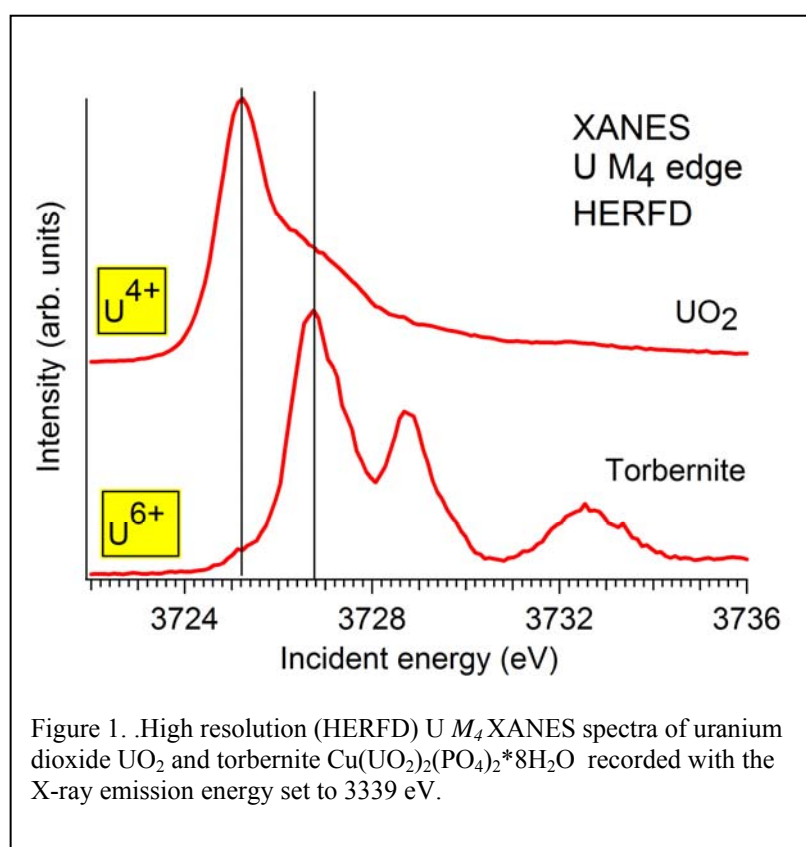


Figure 1. High resolution (HERFD) U M₄ XANES spectra of uranium dioxide UO₂ and torbernite Cu(UO₂)₂(PO₄)₂*8H₂O recorded with the X-ray emission energy set to 3339 eV.

reflection of four spherically bent 1m radius Si crystal analyzers for the core-to-core RIXS at the U M_4 edge experiment and the (10 10 0) reflection for the valence band RIXS measurements at the U M_5 edge. To reduce the flux losses at corresponding photon energies, the x-ray beam path in air was minimized and capton windows used in the x-ray emission spectrometer were replaced with polypropylene windows . A combined (monochromator and spectrometer) energy resolution of 0.8 eV was used as estimated from the FWHM of the elastic peak.

Figure 1 shows the high resolution fluorescence detected (HERFD) spectra of UO_2 and $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ across the U M_4 edge. The observed XANES transitions are due to the $3d \rightarrow 5f$ excitations. The energy position of the main line clearly indicates the oxidation state of uranium in the studied systems. Such a great sensitivity of the HERFD spectra can be taken advantage of in probing of species with varying oxidation states in more complex actinide systems.

Valence band RIXS results are displayed in Figure 2 as a 2D map where the vertical axis represents the energy of incident photons. The horizontal axis represents the energy transfer, i.e. the difference between the incident and emitted energies, labeled as final state energy in Figure 2. The elastic peak is set to 0 eV. The position of the elastic peak was established by comparative measurements of the elastic scattering from the Peek polymer. That allowed us to conclude that the observed structures within the 0-2 eV range in Figure 2 mostly arise from inelastic scattering. For the sake of an easy assignment of the scattering structures, the integrated intensity over the full 2D RIXS map is shown at the bottom of Figure 2.

The inelastic scattering structures follow the varying excitation energy and appear at constant energy transfer in the 0-2 eV region, at ~ 4.5 eV, 8.0 eV and 19.0 eV. The structures at 4.5 eV and 8.0 eV were already observed by Butorin and co-workers [8] and were assigned to the charge transfer excitations between U $5f - \text{O } 2p$ states. Later on, the same authors showed that spectral intensities of these charge transfer excitations are sensitive to the different scattering geometries [9]. The structure at ~ 19.0 eV corresponds to the U $6p_{3/2} - 3d_{5/2}$ transitions [8, 10].

The structures in the 0-2 eV range can be assigned to intra-atomic $f-f$ transitions within 5f shell. They can be

calculated within framework of the atomic multiplet theory for the U^{4+} ion. The behavior of these transition and changes in their spectral profile with varying energy of incident photons provide good fingerprints for the oxidation state of U in different systems. The existence of $f-f$ transitions in uranium systems were shown before by X-ray photoemission spectroscopy [11-12]. However, there are some advantages in utilizing the valence band RIXS at the $M_{4,5}$ edge, specifically for actinide compounds. Firstly, RIXS is a bulk-sensitive technique, which helps to avoid the confusion with additional states due to surface defects. Secondly, experiments at the $M_{4,5}$ edge do not require any high-vacuum environment as in the case of soft X-ray spectroscopy, and can be easily used for studies of in-situ reactions in actinide systems. Furthermore, RIXS experiments can be performed on very dilute systems, thus providing the opportunity to probe other actinides with higher radioactivity than uranium.

We believe that this kind of experiments can be performed for a variety of actinide materials and provide an access to important information for applied, environmental and fundamental science.

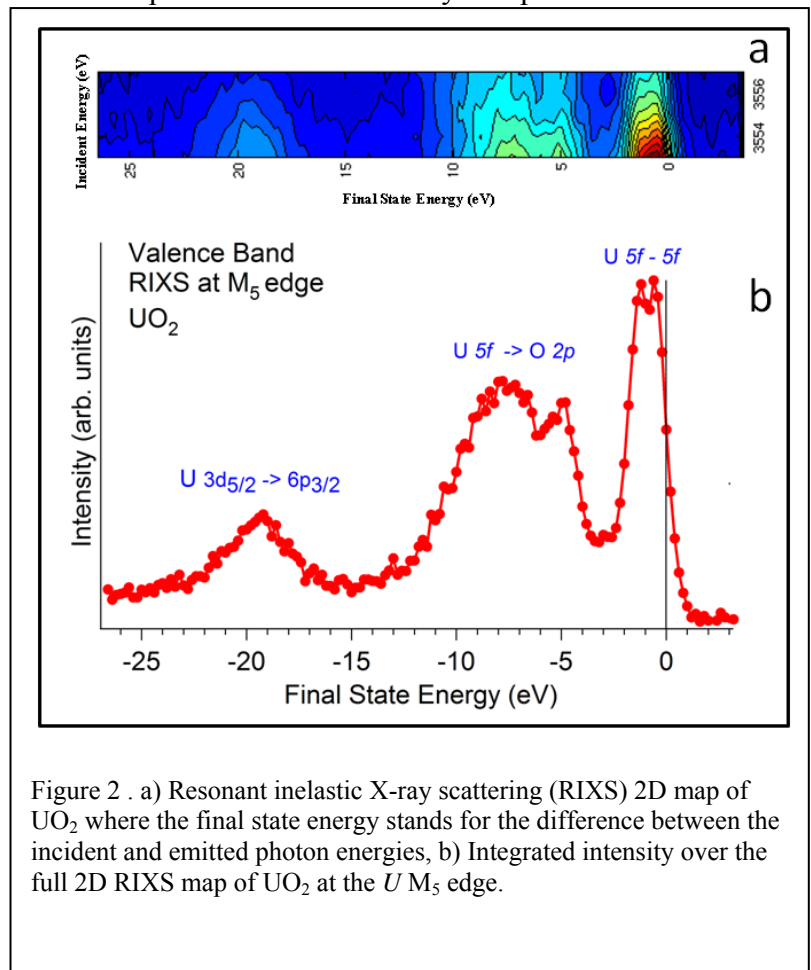


Figure 2 . a) Resonant inelastic X-ray scattering (RIXS) 2D map of UO_2 where the final state energy stands for the difference between the incident and emitted photon energies, b) Integrated intensity over the full 2D RIXS map of UO_2 at the $U M_5$ edge.

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