

Resonant inelastic X-ray scattering probe of inter- and intra-atomic interactions in uranium systems

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A central issue in the investigation of various properties of actinide systems is the nature of the $5f$ electrons in different systems. Many of the unusual properties found specifically in uranium (U) compounds are thought to be related to the delocalization of the partially filled U $5f$ electron states and their hybridization with the U $6d-7s$ states. However, due to the complexity of the physics involved, a complete understanding of the electronic structure of actinides has not yet been achieved.

An element-selective probe of the electronic structure is provided by inner-shell X-ray spectroscopy. Especially, hard X-ray spectroscopy is the ideal candidate for the actinide systems, since it does not require the high-vacuum environment around the sample. For the moment, the X-ray absorption near edge spectroscopy (XANES) at the L_3 edge of U (~ 17.166 keV) has been the most commonly reported. Nevertheless, the large lifetime broadening at the $2p$ level (~ 7.4 eV for U) renders the technique little sensitive to the electronic structure. Hämäläinen and co-workers [1-2] showed that the L_3 edge of lanthanides can be studied in considerably more details as compared to standard absorption spectroscopy by employing an X-ray emission spectrometer with an instrumental energy resolution similar to the core hole lifetime broadening.

We have studied the electronic structure of U systems in different oxidation states by means of resonant inelastic X-ray scattering (RIXS) via transitions between core levels and between core and valence levels at U L_3 edge. The pre-edge structure near the main L_3 edge is clearly resolved in U L_3 XANES spectra with a help of X-ray emission spectrometer. The general model for interpreting pre-edges of lanthanides is to consider them as quadrupole transitions into the empty f states. In order to analyze the possible existence of quadrupole transitions of U compounds we carried out FDMNES [3] calculations for the different U systems. Crystal field splitting of the U $6d$ states were observed in valence band RIXS spectra for UO_2 system and reproduced theoretically using LDA+ U [4] approximation.

On the other hand, the f shell can be directly probed via dipole transitions from $3d$ core levels (U $M_{4,5}$ absorption edge). RIXS spectroscopy has also been used to record changes of the oxidation state in the U systems, by directly observing $f-f$ interactions at U M_5 edge. The experimental results are supported by the atomic multiplet calculations[5]. The $f-f$ transitions uniquely identify the ground state configuration of the uranium ion and can therefore provide an indication of the valence state of U in different complex materials.

Reference:

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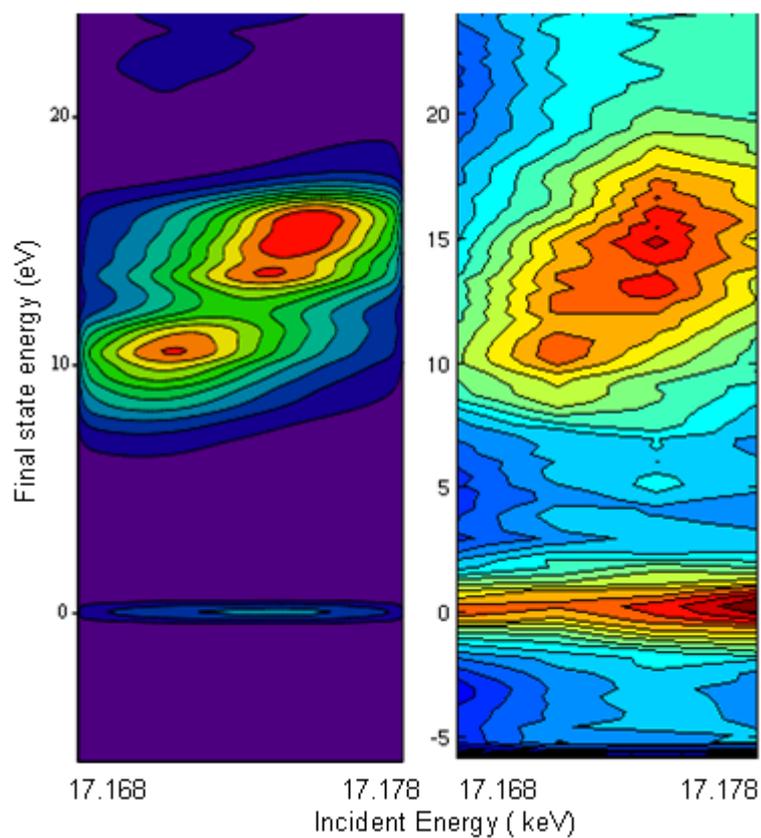


Fig.1. Theoretical (left) and experimental (right) valence band RIXS of UO_2 displayed as counter maps in two dimension planes versus incident and transferred energies over the $\text{U } L_3$ absorption edge

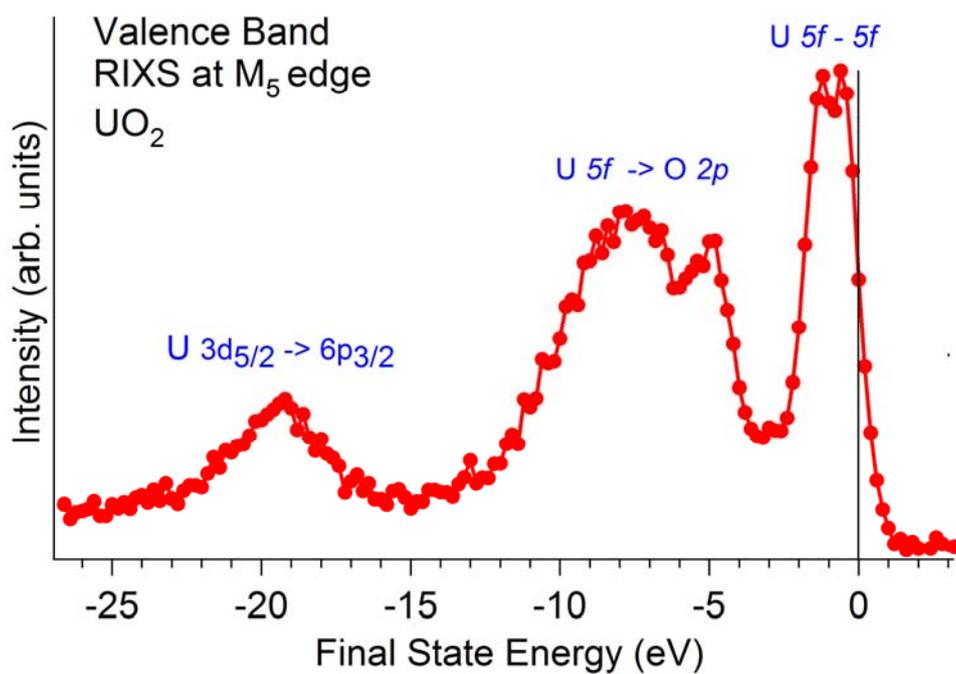


Fig. 2. Valence band RIXS spectra of UO_2 at $\text{U } M_5$ edge