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Report:

The experiment was designed to investigate the covalent bonding in the linear UO_2^{2+} ion, by measuring the polarised X-ray absorption and emission spectra at the Oxygen 1s edge. The absorption spectrum maps the Oxygen 2p contributions to the vacant valence orbitals, and the emission spectrum (if it takes place in the emission regime) maps the 2p population in the filled valence orbitals. Of particular interest is the role of the uranium 5f, 6p (pseudo-core) and 6d orbitals in the bonding.

A large single crystal (~15×6×3 mm) of $\text{Cs}_2\text{UO}_2\text{Cl}_4$ was mounted at the 70° intersection of the optical axes of the POLIFEMO monochromator preparing the incident beam and the AXES emission spectrograph on ID12B. Absorption was detected via the total fluorescence yield, using circularly polarised X-rays in the energy range 520-580 eV. The compound contains only one molecule per unit cell, and the O-U-O axis is readily located relative to the crystal habit. The crystal was mounted on a rotating holder, so that the same polished face was always exposed to the X-rays. In one orientation (labelled R) the O-U-O axis is directed almost parallel to the incident X-rays, and in the other (labelled S), almost perpendicular after a rotation of 180°. The AXES monochromator samples the emission nearly perpendicular to the O-U-O axis in the R configuration and nearly parallel to it in the S configuration. The R configuration therefore reveals absorption bands polarised perpendicular to the O-U-O axis but emission features polarised both parallel and perpendicular to it. In the S configuration the emission must be predominantly polarised perpendicular to O-U-O, while the absorption is a superposition of features polarised both parallel and perpendicular to the axis. Higher resolution absorption spectra were measured on a second crystal using the Dragon monochromator on ID-12B. Initially this was done with drain current detection, but no satisfactory polarisations

were found in the spectrum. The drain current detection is very surface sensitive, so it was inferred that the samples were susceptible to surface radiation damage. This was confirmed by slow changes in the spectrum with time during POLIFEMO absorption measurements, although no macroscopic chemical change could be seen under a microscope on the polished faces of the crystal. The damage was minimised by making small vertical (50 μm) translations of the sample every 15 minutes during the collection of emission data, during which time the changes in the absorption spectrum were negligible. Subsequent absorption measurements with the Dragon monochromator were made using linearly polarised X-rays and fluorescence detection, on a crystal oriented to permit measurements either perpendicular or parallel to O-U-O.

Figure 1 shows the polarised POLIFEMO absorption spectrum for both the R and S configurations. We show both spectra since they were measured in the configuration used for the emission spectra, i.e. circularly polarised x-rays and incidence either parallel or perpendicular to the O-U-O bond axis. The linear dichroism in absorption is shown in the polarised Dragon spectra in Figure 2, measured with linearly polarised radiation having E vector parallel or perpendicular to the O-U-O bond. The feature labelled C is clearly polarised parallel to the O-U-O axis, whereas those labelled B and D are perpendicularly polarised. The main perpendicularly-polarised bands are found at 531.8 and 536.3 eV, while the strong parallel-polarised feature is at 534.6 eV. Figure 3 shows that the emission spectra are, for the most part, quite insensitive to the excitation energies (see Figure 2 for the location of these). The emission is not therefore a resonant Raman process, but rather fluorescence. The only difference in the emission spectrum is a small (0.5 eV) shift in emission energy with excitation E. At this energy the core electrons have sufficient energy to be directly ionised, whereas the lower energy excitations create an electron in a bound orbital. The shift to higher emission energy on ionisation is consistent with reduced screening of the core hole. Moreover there is no appreciable difference between R and S emission spectra (apart from the detail discussed below). For this reason Figure 3 shows only R spectra.

Empty antibonding molecular orbitals with significant oxygen $2p$ contributions are expected to have predominantly $5f_{\sigma}$, $5f_{\pi}$, $6d_{\sigma}$ and $6d_{\pi}$ character. Transitions to the s -orbitals must be polarised parallel to O-U-O, and transitions to the p -orbitals perpendicular to it. We therefore assign band B to the transition to f_{π} , band C to the transition to f_{σ} , and D to the transition to d_{π} . The location of the d_{σ} component is not obvious, but preliminary theoretical calculations suggest that it may be close to degenerate with f_{σ} . The almost equal intensities of these features show clearly that the $6d$ and $5f$ orbitals make almost equal contributions to the covalent bonding interactions.

There should be four oxygen- $2p$ based filled valence orbitals responsible for emission near 525.5 eV. The separate transitions are apparently unresolved in an envelope with a width of ~ 3 eV. There is no appreciable linear dichroism in the emission, so the s and p -symmetry orbitals must be nearly degenerate. This near degeneracy indicates a strong similarity between the magnitude of the s and p bonding interactions, and also between the $5f$ and $6d$ bonding interactions. Finally, we observe a weak emission feature at 516.0 eV (see inset in Fig. 3), that only

appears in the R configuration, and which we therefore interpret as a parallel polarised transition, and must therefore involve an orbital of *s*-symmetry. According to theoretical calculations, and photoelectron spectroscopy data, this is at the energy expected for the $6p_{1/2}$ (*s*) component of the uranium pseudo core orbital. Calculation also shows that the overlap of this orbital with the oxygen-2*p* is not negligible, and the emission spectrum clearly confirms this.

FIGURES

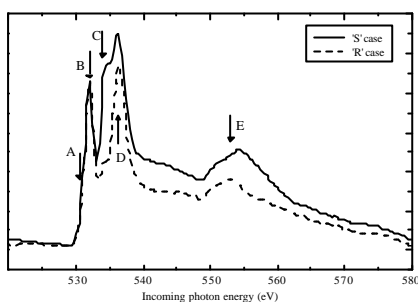


Figure 1. Oxygen X-Ray absorption spectra measured in Total Fluorescence Yield with circularly polarized radiation. In the 'R' case the incident beam is nearly parallel to the O-U-O bond, in the 'S' case nearly perpendicular. The arrows point to the excitation energies used for emission spectra.

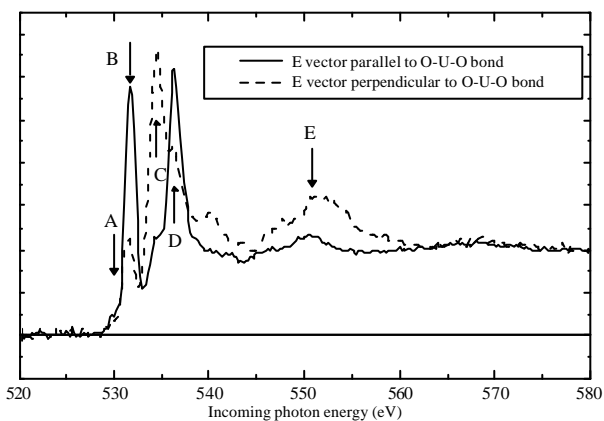


Figure 2. Oxygen X-Ray absorption spectra measured in Total Fluorescence Yield using linearly polarized radiation with E vector parallel and perpendicular to O-U-O bond. The arrows point to the excitation energies used for emission spectra.

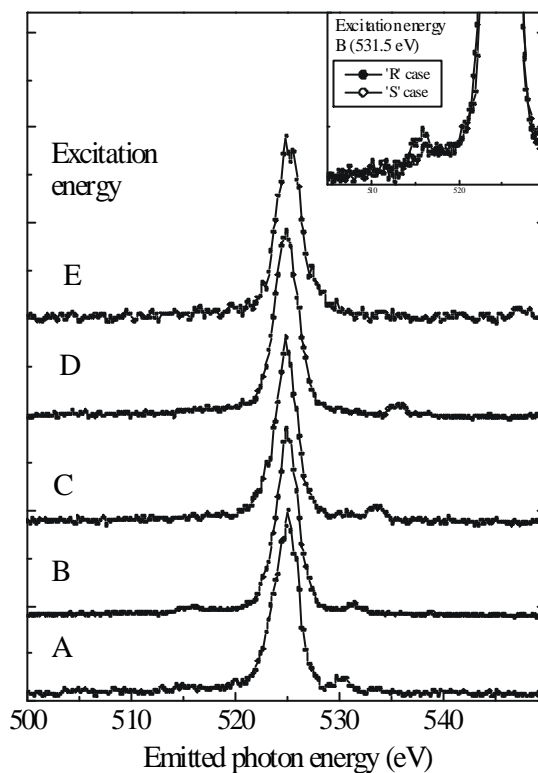


Figure 3. Emission spectra of Oxygen measured in 'R' geometry (incident beam parallel to O-U-O bond, outgoing beam perpendicular to O-U-O bond). The excitation energies are as shown on the absorption spectra. The inset shows the linear dichroism on the feature emitted at 516 eV when the excitation energy is set to 531.5 eV.