Invisible structures in the X-ray absorption spectra of actinides

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ABSTRACT

The X-ray absorption spectra of actinides are discussed with an emphasis on the fundamental effects that influence their spectral shape, including atomic multiplet theory, charge transfer theory and crystal field theory. Many actinide spectra consist of a single peak and it is shown that the use of resonant inelastic X-ray emission spectra (RIXS) has the potential to reveal many new features in the X-ray absorption spectra of actinides. The new range of RIXS beamlines will allow the determination of new structures in the X-ray absorption spectra that have been hitherto invisible. This has the potential to become an important tool in the determination of the electronic structure of actinides.

1. Introduction

This paper discusses some fundamental aspects of the X-ray absorption spectra (XAS) of actinides. The focus is on the general aspects that influence the spectral shape. Details on specific actinide systems, for example the heavy fermion systems, are not included. A detailed review of the spectroscopy of the 5f states in actinides has been recently published by Moore and van der Laan [1].

The central aspect of the electronic structure of an actinide is the partly filled 5f band. The 5f electrons are more delocalized than the rare earth 4f electrons, but less delocalized as the d-electrons of the 3d, 4d and 5d transition metal systems. Because of the relatively strong localization of the 5f electrons, the atomic interactions are important if one excited a core electron. As an indicator for the atomicity of an orbital we use the cubic crystal field strength (10Dq) as a measure. The crystal field strength is a measure of the splitting of 4f, 5f and 3d states due to the inhomogeneity of the surroundings, for example an octahedral symmetry. Typical crystal field strengths for oxides are 0.03 eV for 4f systems, 0.25 eV for 5f systems and 1.5 eV for 3d systems. In other words a 4f state is approximately 5 times more localized than a 5f electron and a 3d electron is ~5 times less localized. As such one would expect the general behavior of 5f electrons to be intermediate between 4f and 3d systems.

2. Atomic aspects in 5d XAS spectra

The 5d XAS spectra of uranium and other actinides are dominated by many peaks and structures related to multiplet effects. In contrast, all other XAS spectra (4d, 3d, 2p) do show only a single peak that does not seem to contain fine structure. We explain the atomic features of the actinides by its 5d XAS spectrum, which has the strongest coupling between the core state and the 5f states. The main features of the 5d XAS spectra of actinide systems can described with an isolated atom or ion. This allows us to explain some of the fundamental issues concerning 5d5f ($O_{4,5}$) edges, in particular the importance of 5f5f intra-atomic interactions and the 5f spin-orbit coupling.

X-ray absorption spectra of free atoms can be described with atomic multiplet theory. The atomic Hamiltonian is usually divided into large energy terms consisting of the kinetic energy, the nuclear energy and the spherical averaged electron–electron interaction. Together these three interactions determine the energy of a certain configuration. The remaining two smaller energy effects, i.e. the non-spherical electron–electron interaction and the spin–orbit coupling determine the splitting of the states (indicated with term symbols) within a certain electron configuration. This splitting of a certain $5f^n$ configuration is indicated as multiplet splitting. The ground state is given by the Hunds rules, i.e. (1) maximum S, (2) maximum L and (3) maximum J, if the shell is more than half-full. An isolated U^{4+} ion has an electronic configuration $5f^2$. The ground state configuration of the two 5f electrons is given by the Hunds rule, which yields a ground state with L = 5 and S = 1, represented by a ^3H term symbol. The ^3H state is split into three substates by the 5f spin-orbit coupling and the ground state has $^3H_4$ symmetry. The 5f spin-orbit coupling is 0.26 eV, too large to be affected

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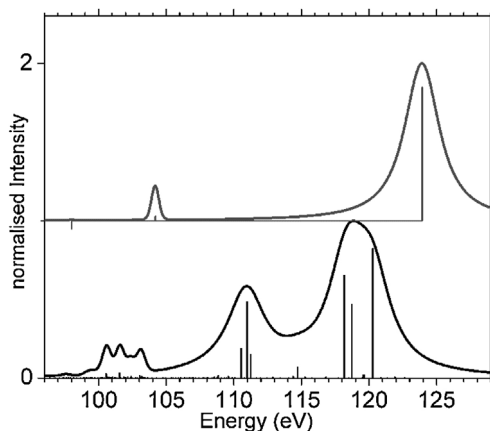 E-mail address: f.m.f.degroot@uu.nl (F.M.F. de Groot).

Fig. 1. Atomic multiplet calculations for the 5d5f transition of $5f^2$ U^{4+} (bottom) and $5f^0$ U^{6+} (top). The $O_{4,5}$ edge is spread over 20 eV due to large 5d5f and 5f5f multiplet effects. The broadened spectra use a broadening that cannot be achieved with normal 5d XAS experiments to highlight the potentially observable spectral features.

by temperature effects. Fig. 1 shows the 5d X-ray absorption spectrum that can be calculated by performing an atomic multiplet calculation of the final state in which a 5d electron has been excited to a 5f state, which corresponds to a $5d^9 5f^3$ configuration. The 5d spin-orbit coupling is relatively small (3.2 eV) and the O_4 and O_5 edges overlap in energy. The 5d5f multiplet interaction, in other words the higher order interaction of the electron–electron repulsion term coupling the 5d and 5f electronic states is large (F^2 = 10.6 eV), resulting in a combined $O_{4,5}$ multiplet spectrum that spreads over 20 eV. For more details regarding the use of atomic multiplet theory in X-ray absorption spectroscopy, we refer to *The Theory of Atomic Structure and Spectra* [2], the *Hitchhiker's guide to multiplet calculations* [3] and *Core Level Spectroscopy of Solids* [4].

3. Other X-ray absorption spectra of uranium

UO_2 and UF_4 have a $5f^2$ ground state. Fig. 2 shows its L_3 edge ($2p_{3/2}\rightarrow$6d) at ~17,180 eV, M_3 edge ($3p_{3/2}\rightarrow$6d) at ~4310 eV, M_5 edge ($3d_{5/2}\rightarrow$5f) at ~3550 eV and N_5 edge ($4d_{5/2}\rightarrow$5f) at ~730 eV show essentially a single peak at the edge, followed by additional structure at higher energy. These X-ray absorption spectra taken over a larger energy range should correspond closely to single particle calculations. The resolution of the spectra does not allow any detailed multiplet analysis of the edge structure. As discussed above, only the $O_{4,5}$ spectrum (5d→5f) at ~100 eV shows significant fine structure, related to the $5d^9 5f^3$ final state multiplet. The $5d^9 5f^n$ multiplet spectrum is similar to the $4d^9 4f^n$ multiplet for the rare earths, with a series of small pre-edge peaks followed by a large absorption peak [5]. In contrast the 4d XAS spectrum ($N_{4,5}$ edges) seem to show only a single Lorentzian peak. The reason that only a single peak is visible is the large lifetime broadening of approximately 6 eV [6].

Fig. 3 shows the atomic multiplet calculation of the 4d XAS spectrum, where only the $4d_{5/2}$ (N_4) edge is shown. If one could lower the lifetime broadening to 0.5 eV, one would observe clear fine structure due to atomic multiplet effects. The $4d_{7/2}$ (N_5) edge has less fine structure than the N_4 edge and is not shown. It will be shown below how such fine structure could be made visible.

4. The screening of the core hole: charge transfer effects

The theory of X-ray spectroscopy of open shell systems is based on the charge transfer model, as introduced by Kotani and Toyozawa [7]. The charge transfer method is based on the Anderson
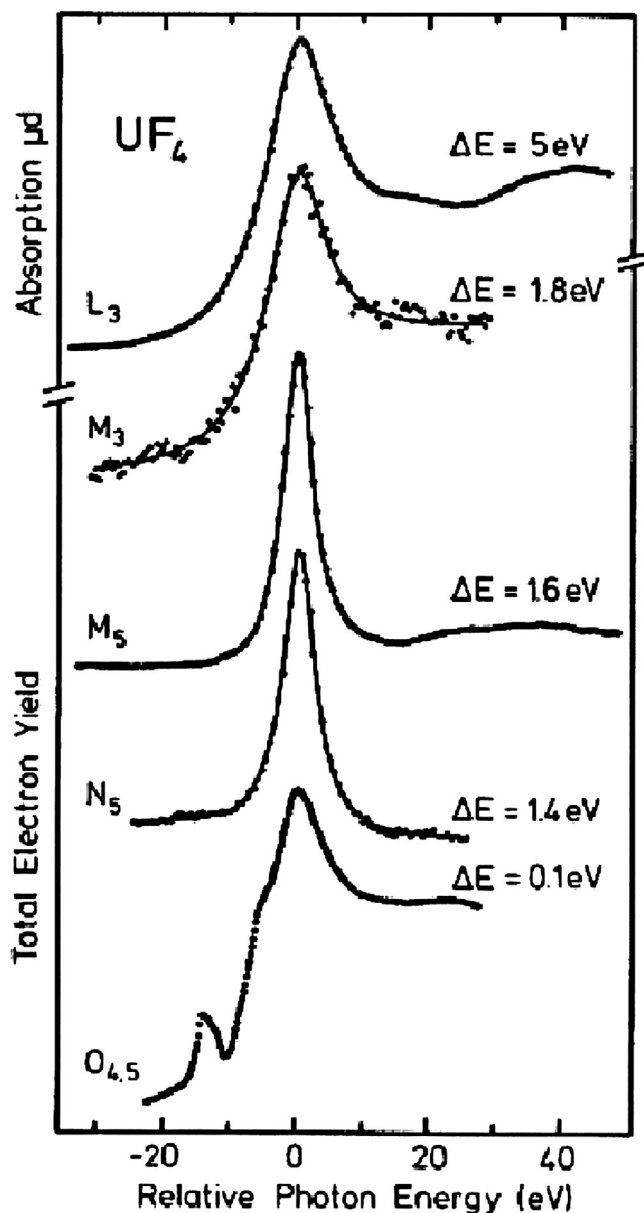

Fig. 2. The L_3, M_3, M_5, N_5 and $O_{4,5}$ edges of UF_4. Reprinted from [4].

impurity model and describes a localized state, the $5f^n$ state, which interacts with delocalized electrons in bands. One can combine this configuration with other low-lying configurations similar to the way configuration-interaction works. The charge-transfer model adds a configuration $5f^{n+1}\underline{L}$ to the $5f^n$ ground state. In the case of a actinide oxide, in a $5f^{n+1}\underline{L}$ configuration an electron has been moved from the oxygen 2p valence band to the actinide 5f band and the $\underline{L}$ represents a ligand hole. The energy difference between the $5f^n$ and $5f^{n+1}\underline{L}$ configurations is defined as the charge-transfer energy.

The effects of charge transfer are particularly apparent in the 4f XPS spectra of actinides [8]. In case of 4f XPS the ground state of U^{4+} can be described $5f^2 + 5f^3\underline{L}$ and the final state as $4f^{13} 5f^2 \varepsilon + 4f^{13} 5f^3 \underline{L} \varepsilon$. In the XPS final state, the 4f core hole modifies the ordering of the 5f configurations and the final state with the lowest energy will change from $5f^2$ to $5f^3$. Charge transfer multiplet calculations can take care of these effects in detail as explained by Kotani and Ogasawara [8]. It is important to note the large difference between XPS and XAS in this respect. XPS of open shell systems is often
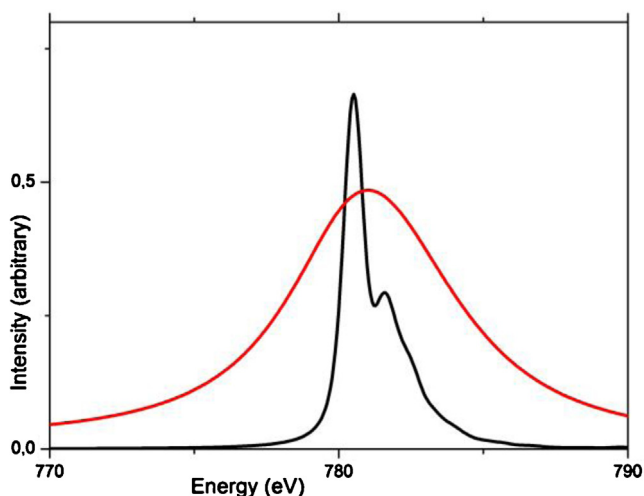
Fig. 3. Atomic multiplet calculations for the 4d5f transition of $5f^2$ U^{4+}. The N_4 edge is visible as a single Lorentzian with 6 eV lifetime broadening (red). With 0.5 eV lifetime broadening fine structure is visible (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 5. Experimental 3d5f RIXS data of UO_2 at different excitation energies close to the U $3d_{5/2}$ (M_5) edge compared with results of atomic multiplet calculations for the free U^{4+}, U^{5+} and U^{6+} ions. Red and green curves show RIXS data of UO_2 recorded at two different excitation energies. Enhanced inelastic part below 0 eV represents the ff transitions in RIXS spectra.

dominated by charge transfer because the core hole rearranges the ordering of the $5f^n$ configurations. In contrast XAS is a self-screened process as the core electron will be excited to the 5f shell and this process will screen the core hole effectively. One could state that the surroundings hardly notice that something has happened when a 4d electron has moved to a 5f state, as the local charge is maintained. In fact this explains the success of atomic multiplet theory to explain the XAS spectra of 4f and 5f systems [9,10]. Fig. 4 indicates the energy levels of $5f^2$ and $5f^3\underline{L}$ in respectively XPS and XAS. In XAS the final state charge transfer value is given as $\Delta + U - Q$ and because the core hole potential (Q) is essentially equal to the Hubbard U, this final state charge transfer value is equal to the initial state charge transfer value.

The ground state is often dominated by one 5f configuration, which implies that it is still possible to describe most aspects of the XPS spectral shapes without the inclusion of charge transfer effects. Such approach has been used to explain the 4f XPS spectra of UO_2 [11] and also to explain the 3d XPS in Gd systems [12].

5. Detecting crystal field effects

Crystal field effects in actinides are usually below 0.5 eV, which makes it difficult to detect them in XAS and XPS experiments due to the intrinsic broadening effects. Ilton and Bagus included crystal field effects to explain the 4f XPS spectra of UO_2 [11] and the effects are potentially detectable, but the situation is not very clear. At least not as clear as for the 3d transition metals where crystal field theory is used to explain their XAS spectra [13,14].

The starting point of crystal field multiplet theory is the approximation that the transition metal is an isolated ion with its electronic
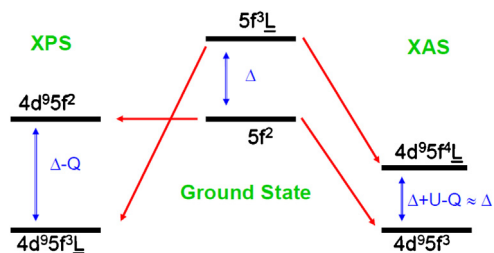

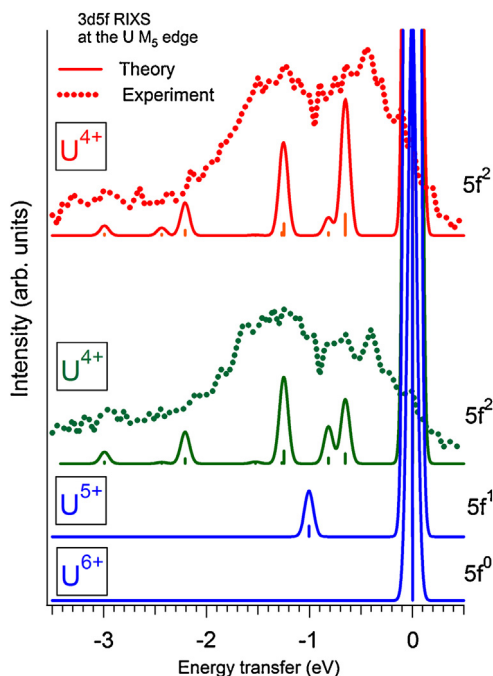**Fig. 4.** Configurations in 4d XPS and 4d XAS of a $5f^2$ U^{4+} system.

structure surrounded by a distribution of structure-less point charge sources, which mimic the symmetry around the central ion. Excellent textbooks on crystal field theory include *Spectroscopy of Transition-Group Complexes* [15] and *Ligand Field Theory and the Properties of Transition Metal Complexes* [16]. The effect of the cubic crystal field is that the seven 4f orbitals will lose their degeneracy and become split in energy into three distinct representations, respectively with T_1, T_2 and A_2 symmetry. The $^3H_4$ ground state of UO_2 will split into four sub-states and if the crystal field is of similar magnitude as the 5f spin–orbit coupling it also can mix the $^3H_4$, $^3H_5$ and $^3H_6$ characters into a new ground state. The actual nature of the ground state is difficult to determine from XAS or XPS spectra due to their natural broadening.

6. Resonant Inelastic X-ray Scattering as a tool to make invisible peaks visible

Resonant Inelastic X-ray Scattering (RIXS) is able to make invisible structures visible by effectively removing the lifetime broadening. Hamalainen et al. used the example of the 2p XAS spectrum of a rare earth spectrum to reveal the quadrupole 2p4f pre-edge peaks before the main 2p5d peak due to the dipole transitions [17]. Such experiments are known as high energy resolution fluorescence detection (HERFD).

We first discuss the use of RIXS to reveal ff transitions, which gives the option to detect the crystal field splitting of actinides. It has been shown in case of rare earths that 4d4f RIXS is able to determine the effects of the crystal field [18]. Because the crystal field effect is larger for actinides one would expect that 4d5f RIXS or 5d5f RIXS would be able to study these crystal field effects in great detail. Such experiments have been performed for uranium [19,20], neptunium [20] and curium [21], though that study focused on the valence determination making use of atomic multiplet calculations. In recent years the overall resolution of RIXS experiments have been improved to below 100 meV and 4d5f RIXS or 5d5f RIXS
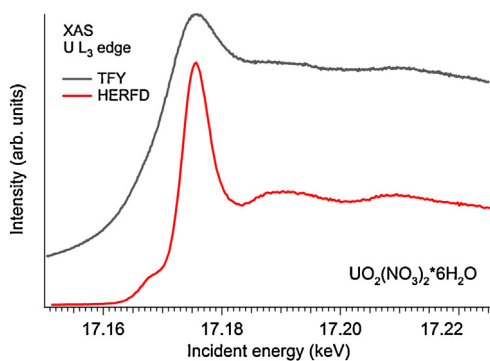
Fig. 6. U 2p (L$_3$) XAS of UO$_2$(NO$_3$)$_2$·6H$_2$O recorded with the X-ray emission spectrometer set to Lα$_1$ emission line (~13.616 eV) and compared to total fluorescence yield (TFY) curve recorded using a photodiode.

Fig. 7. Schematic diagram of XAS and RIXS processes at the U L$_3$ edge.

experiments on actinides with such resolution can be expected to provide detailed information on the ground state symmetry, including its crystal field effects. For more details regarding the use of atomic multiplet theory in soft X-ray spectroscopy, we refer to *Resonant Inelastic Soft X-Ray Scattering Spectroscopy of Light-Actinide Materials* [22].

We show below similar experiments performed in the intermediate x-ray energy range (~3550 eV). Fig. 5 illustrates 3d5f RIXS experiment of UO$_2$ compared with the theoretical calculations using the atomic multiplet theory for the free U^{4+}, U^{5+} and U^{6+} ions. Red and a green curves show RIXS data of UO$_2$ recorded at two different excitation energies near the maximum of the U 3d$_{5/2}$ XAS (U M$_5$ absorption cross section). There are two types of features observed in both spectra – elastic (at 0 eV in energy transfer scale) and inelastic scattering (few eV below the elastic scattering). The inelastic scattering process of U^{4+} has been described by transitions from the ground state 5f^2 to the intermediate states
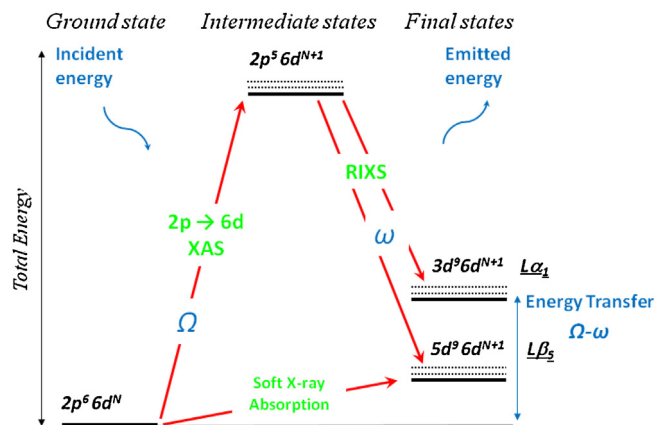
of the 3d^{9}5f^3 configuration and then to the final states of the 5f^2 configuration. The 3d5f RIXS spectra have been calculated from the Kramers–Heisenberg formula using the same scaling for the Slater integrals as in Ref. [21]. The ground state of U^{5+} and U^{6+} ions is described by 5f^1 and 5f^0 configurations respectively. The energy separation between elastic and inelastic excitations is very different for U^{4+} and U^{5+} ions. In a similar way to 4d5f or 5d5f RIXS, the inelastic scattering features are assigned to 5f-5f intra-atomic transitions. The shape of those transitions strongly depends of the number of 5f electrons available in the systems. These structures are absent in the U^{6+} spectra due to the formal 5f^0 configuration of the U^{6+} ion. Such RIXS experiments have their present resolution defined by the response function from the instrumentation. The spectra in Fig. 5 were collected by the X-ray emission spectrometer [23]. The paths of the incident and emitted X-rays through air were minimized in order to avoid losses in intensity due the
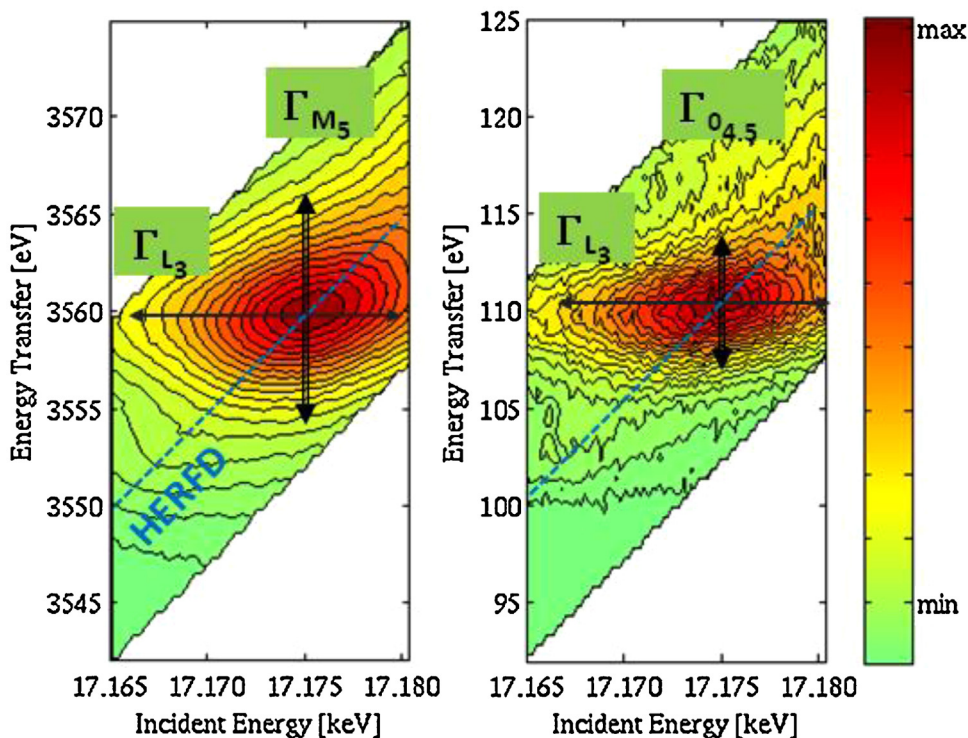

Fig. 8. Experimental RIXS maps displayed as contour maps with axes corresponding to incident and transferred energies over the U L$_3$ absorption edges near the Lα$_1$ (left panel) and Lβ$_5$ (right panel) emission lines for UO$_2$(NO$_3$)$_2$·6H$_2$O. A HERFD spectrum corresponds to diagonal cut (dashed line) through the RIXS planes at the maximum of the emission line. The energy transfer axis relates to the excitation energy in M$_5$ and O$_{4,5}$ edge XAS.

air absorption. Obviously development of X-ray spectrometers adjustable for intermediate X-ray energies will improve quality of collected data and help to resolve the fine structure due to atomic multiplet effects. Kavcic et al. recently reviewed the development of X-ray spectrometers in intermediate X-ray energy range [24].

RIXS can also be used to effectively sharpen the XAS spectra by detecting HERFD spectra [23,25]. Vitova et al. [26] measured the 2p3d RIXS of some uranium compounds. They clearly show the pre-edge structure related to the 2p5f transitions at 17,170 eV before the 2p6d edge at 17,175 eV (Fig. 6). In that experiment the X-ray emission spectrometer was tuned to the maximum of $L\alpha_1$ ($3d_{5/2} - 2p_{3/2}$) transitions and the 2p XAS was recorded by monitoring the $L\alpha_1$ intensity as a function of the incident energy. Schematic diagram of 2p3d RIXS and 2p XAS processes is illustrated in Fig. 7. The intermediate states of RIXS (or final states of XAS) exhibit a core-hole making the techniques element selective. RIXS final states contain a core-hole depending on the energy transfer (or the emission line) that is chosen for the experiment. Thus the spectral sharpening or the observation of new features in HERFD spectra will strongly depend of the lifetime broadening of the chosen final states.

Fig. 8 shows RIXS data at the uranium L_3 edge of UO_2 recorded at emission lines $L\alpha_1$ ($3d_{5/2} - 2p_{3/2}$) and $L\beta_5$ ($5d_{3/2,5/2} - 2p_{3/2}$). Incident energies in both RIXS maps are identical (the intermediate states are similar) but the final states (energy transfer scale) are different. The energy transfer in RIXS near the $L\alpha_1$ emission line is large (~3550 eV) while it is smaller near the $L\beta_5$ emission line (~105 eV). Spectral features in the horizontal direction are broadened by the core-hole life time broadening (Γ_{L3}) of the uranium 2p level. Final states broadening ($\Gamma_{O4,5}$) of X-ray emission line $L\beta_5$ is shorter (~1 eV) for compare to Γ_{M5} broadening of $L\alpha_1$ line (~4.2 eV). Intensity distribution in vertical direction through the RIXS maps clearly demonstrates this effect. Consequently the diagonal scan (dash line in Fig. 8 marked as HERFD) at the maximum of the $L\beta_5$ emission line will have better resolution and reveal more features in HERFD spectrum. Interestingly to notice that energy transfer axis relates to the excitation energies in 3d (M_5) XAS (left panel Fig. 8) and 5d ($O_{4,5}$) XAS (right panel Fig. 8) and illustrated schematically in Fig. 7. For more information we refer to Ref. [23,27] were the crystal field splitting of the uranium 6d states in UO_2 was resolved. More details about RIXS experiments at the uranium L_3 edge can be found in Ref. [28,29].

Butorin et al. [30] measured the 3d5f RIXS spectra of UO_3. Using the 3d5f X-ray emission channel, the 3d XAS spectrum could in principle be measured with very good resolution. Fig. 9 shows an example of the U $3d_{3/2}$ (M_4) XAS measured at the maximum of U $M\beta$ emission line ($4f_{5/2} - 3d_{3/2}$ transitions). Total fluorescence yield spectra (recorded using a photodiode) show only a single peak profile while HERFD spectra reveal a variety of absorption features that reveal much greater details [31]. Atomic multiplet calculations of those spectra are reported in Ref. [31]. The 3d5f RIXS experiments can be performed on dilute systems that give the opportunity to probe other actinides with higher radioactivity than uranium. Similarly the 4d5f X-ray emission channel would allow the measurement of the 4d XAS spectrum with a resolution as indicated in Fig. 3. Such high-energy-resolution XAS spectra would be useful to determine the effects of the crystal field and charge transfer on the atomic transitions. For more information about possible RIXS experiments at intermediate and hard X-ray energies we refer to Ref. [27].

7. Future developments

For future developments the use of RIXS experiments seems crucial. There are three factors that can be considered:
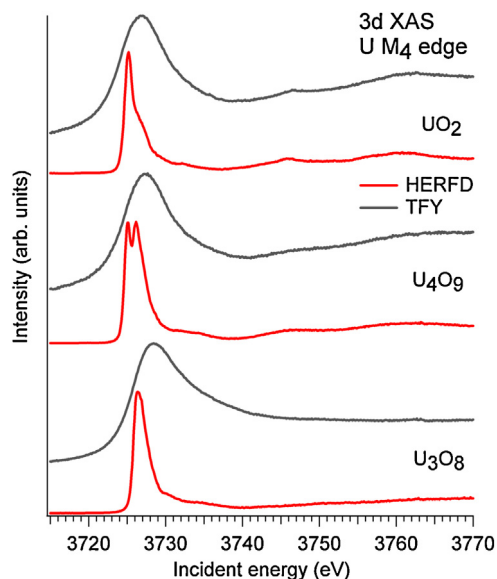

Fig. 9. The U $3d_{3/2}$ (M_4 edge) XAS of UO_2, U_3O_8, U_4O_9 recorded with the X-ray emission spectrometer set to $M\beta$ emission line (~3336 eV) and compared with TFY curves recorded using a photodiode.

1. The resolution of soft X-ray RIXS will go down to below 100 meV and of hard X-ray RIXS beamlines to 0.3 eV.
2. There will be a number of new beamlines available that will have this kind of resolution. In a few years beamlines should exist at SLS, ESRF, ALS, SSRL, Diamond, Soleil, Spring8, NSRRC, APS and NSLS.
3. The gap between soft X-ray RIXS (below 1 keV) and hard X-ray RIXS (above 3 keV) will be closed in the next years with detectors that allow the intermediate X-ray energy range to be detected.

The larger availability of RIXS beamlines will allow future experiments on actinides, in particular:

(a) HERFD experiments at the 2p edge to reveal the quadrupole 2p5f peak and fine structure.
(b) HERFD experiments at the 3d and 4d edges to reveal the fine structure in the $M_{4,5}$ and $N_{4,5}$ edges, allowing the potential determination of crystal field and charge transfer effects and as such of the electronic structure of actinides.
(c) The measurement of ff transitions in actinide systems, using the 3d, 4d or 5d core levels.

This will yield a wealth of new information on uranium systems and on other actinides.

8. Concluding remarks

In this paper we have discussed some fundamental aspects of the X-ray spectra of actinides. We have seen that the XAS spectra of actinides are dominated by atomic multiplet effects. The effects due to charge transfer and crystal field effects are present, but their influence on the spectral shape is much more difficult to determine from experimental spectra, partly due to intrinsic broadening effects. A great promise for future studies of the electronic structure of actinides are the RIXS experiments that promise the possibility to determine the electronic structure of actinides with great detail.

Acknowledgement

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