

Chemical shift of U L₃ edges in different uranium compounds obtained by X-ray absorption spectroscopy with synchrotron radiation

D JOSEPH[†], C NAYAK^{††}, P VENU BABU[#], S N JHA[†] and D BHATTACHARYYA^{††,*}

[†]Nuclear Physics Division, ^{††}Applied Spectroscopy Division, [#]Nuclear Agriculture and Biotechnology Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

MS received 28 February 2013; revised 7 June 2013

Abstract. Uranium L₃ X-ray absorption edge was measured in various compounds containing uranium in U⁴⁺, U⁵⁺ and U⁶⁺ oxidation states. The measurements have been carried out at the Energy Dispersive EXAFS beamline (BL-08) at INDUS-2 synchrotron radiation source at RRCAT, Indore. Energy shifts of ~2–3 eV were observed for U L₃ edge in the U-compounds compared to their value in elemental U. The different chemical shifts observed for the compounds having the same oxidation state of the cation but different anions or ligands show the effect of different chemical environments surrounding the cations in determining their X-ray absorption edges in the above compounds. The above chemical effect has been quantitatively described by determining the effective charges on U cation in the above compounds.

Keywords. U L₃ edge; EXAFS; synchrotron radiation; energy shift; oxidation state; effective charge.

1. Introduction

It is well known that the X-ray absorption edge of a metal ion present in a compound shifts to higher energy due to increase in the binding energy of its core level electrons, if the oxidation state of the ion increases in the compound. Moreover, the X-ray absorption process involves two orbitals, one core and the other the lowest empty energy level, the core level being affected by the oxidation state and crystal field effects, while the empty level is affected by direct bonding effects. Therefore, even for the same oxidation state of the metal ion, its X-ray absorption edge may appear at different energies in different materials, depending on the nature of ligands attached to the metal ion, coordination number, covalent character of the bond, electronegativity of the anion or in other words the chemical environment of the metal ion. The change in absorption edge which could be attributed to different chemical environment of a metal ion inside a compound is generally known as the chemical shift.

In the present study, the effect of chemical environment on shifting of L₃ X-ray absorption edge of uranium ion has been investigated by X-ray absorption spectroscopy (XAS) measurements with synchrotron radiation on few uranium compounds, viz. UF₄, U₃O₈, ammonium diuranate and uranyl nitrate hexahydrate. A relationship between the energy shift and effective charges on U atom in the compounds has been found out.

2. Experimental

The X-ray absorption spectroscopy (XAS) measurements on the uranium compounds were carried out at the dispersive EXAFS beamline (BL-8) in transmission mode at the INDUS-2 synchrotron source (Basu *et al* 2012, 2013; Neetika *et al* 2012). The beamline uses a 460-mm long Si (111) crystal having $2d$ value equal to 6.2709 Å mounted on an elliptical bender, which can bend the crystal to take the shape of an ellipse (Bhattacharyya *et al* 2009). The crystal is first set in such a fashion that the central portion makes the proper Bragg angle (θ_0) w.r.t. the incident beam and it selects the energy (E_0) corresponding to the absorption edge of interest. Due to the divergent nature of the synchrotron beam, the angle of incidence varies from ($\theta_0 - \Delta\theta$) at one end of the crystal to ($\theta_0 + \Delta\theta$) the other end and hence, a band energy of $E_0 + \Delta E$ is selected by the crystal, which then falls on the sample due to the elliptical bending of the crystal. The elliptical optics offer minimum aberration. The radiation transmitted through the sample is detected by a position-sensitive CCD detector having 2048 × 2048 pixels. The plot of absorption vs photon energy is obtained by recording the intensities I_0 and I_T , as the CCD outputs, without and with the sample, respectively, and the absorption coefficient, μ is obtained using the relation

$$I_T = I_0 e^{-\mu x}, \quad (1)$$

where x is the thickness of the absorber. Thus, using the above beamline, the full EXAFS spectrum of the sample at any specified absorption edge can be obtained as a single shot within a time frame of 300 ms.

*Author for correspondence (dibyendu@barc.gov.in)

For the present measurement on uranium samples, the Si (111) crystal has been set at a proper Bragg angle to obtain a band of energy around 17,166 eV for XAS measurement at U L₃ edge. Samples of appropriate weight of UF₄, U₃O₈, ammonium diuranate ((NH₄)₂U₂O₇) and uranyl nitrate hexahydrate ((UO₂)₂(NO₃)₂·6H₂O), estimated to obtain reasonable edge jumps, were taken in powder form and mixed thoroughly with cellulose powder to obtain the total weight of about 100 mg and homogenous pellets of 15 mm diameter were prepared using an electrically operated hydraulic press.

It should be noted here that the present measurements have been carried out with synchrotron radiation as a source, unlike most of the other results reported in the reference list where much weaker laboratory sources have been used. For each sample at least 200 spectra were recorded and average was taken to have a better accuracy in the data. This has been possible due to the high flux of synchrotron radiation and very fast read out time of the CCD (300 ms) detector used in the present measurement. It should also be mentioned here that generally in the normal operation of the beamline, an energy resolution of ~1 eV at 9 keV ($E/\delta E \sim 10^4$) is achieved, when a spatially dispersed band of 1 keV falls on 2000 pixels of the CCD detector. However, in case of the present measurements, since we are only concerned with the XANES part (X-ray near edge absorption spectra or regions of absorption spectra near the absorption edge), the goniometer is positioned in such a way that a smaller band of 150 eV falls on the CCD spreading over its 2000 pixels and hence, a much better energy resolution is obtained in this case (~0.1 eV).

3. Results and discussion

Normalized X-ray absorption spectra ($\mu(E)$ vs E) for U L₃ edge are shown in figure 1 for all the uranium samples. The white line observed for UF₄ sample is more intense and narrower than the other samples. This is due to the less occupancy of 6*d* levels in the UF₄ sample as has been observed by Kalkowski *et al* (1987) also. However, contrary to the report by the above authors, we have not observed any double-peak or shoulder-like hump in the white line region in any of the samples which is generally believed to be caused by the presence of considerable amount of covalent 5*f* character in hexavalent uranium compounds (Sampathkumaran *et al* 1985). The XANES data show considerable shifts in U L₃ absorption edge from sample to sample. The actual edge position of the samples have been obtained from the zero crossing of the second derivative of their respective $\mu(E)$ vs E spectrum and the edge shift (ΔE) value, i.e. the difference in their edge energy w.r.t. the edge energy of U metal which is 17,166 eV (X-ray data booklet 2009), have been tabulated in table 1. The edge shifts (ΔE) in UF₄, U₃O₈ and

uranyl nitrate hexahydrate (UO₂(NO₃)₂·6H₂O) compounds which are in the range of 2–3 eV agree well with the values reported by Kalkowski *et al* (1987) by synchrotron radiation based NEXAS measurements.

As has been discussed in the ‘Introduction’ section, the above edge shift (ΔE) values depend on the chemical environment of the absorbing species in the compound. It has also been shown by various authors (Nigam and Gupta 1974; Kondawar and Mande 1976; Ballal and Mande 1977; Apte and Mande 1981; Chetal *et al* 1988; Pandey *et al* 1990; Hinge *et al* 2011; Joseph *et al* 2012, 2013) that the effect of chemical environment can quantitatively be presented by ‘effective charge’ (q). Formation of chemical bond in a compound involves redistribution of valence electrons of the constituent atoms and effective charge is a hypothetical parameter which gives a measure of the charge residing over the cation, when it forms a bond with a ligand. Apart from the valency, it takes care of the electronegativity of the pair of atoms forming the bond, covalent nature of the bond, coordination number, etc. and thus, quantitatively takes care of the chemical environment around the absorbing metal ions.

Several empirical relations have been proposed in the literature (Mande and Apte 1981; Chetal *et al* 1988), to estimate the effective charge on a metal cation in a compound. According to Suchet’s (1965) method, the

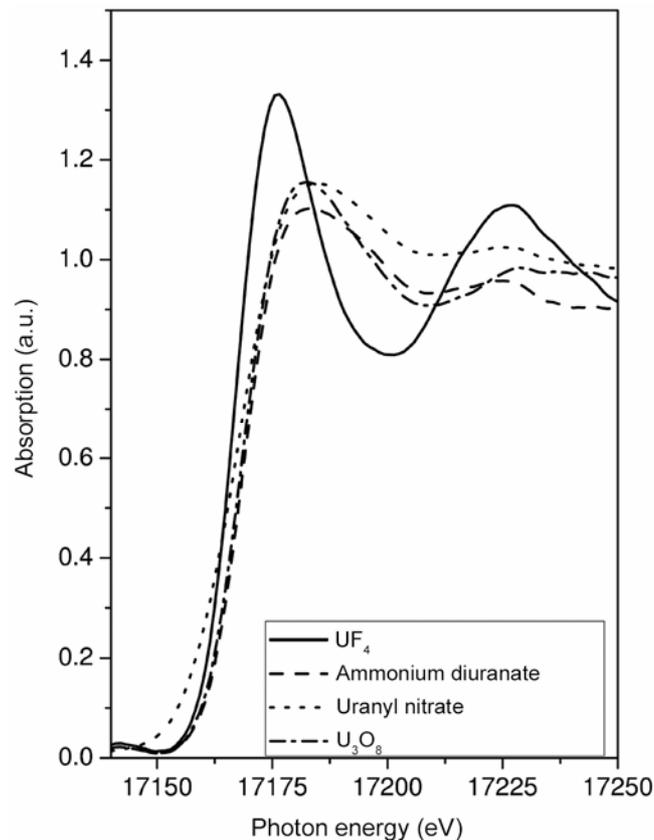


Figure 1. XANES spectra of different uranium compounds around U L₃ edge.

Table 1. Chemical shift of uranium L₃ edge and estimated effective charge on uranium ion in compounds.

Compounds	Oxidation state			
	Suchet	Pauling	Effective charge	Energy shift (eV)
UF ₄	+4	0.18	3.63	1.3
U ₃ O ₈	5, +6	0.46	3.927	2.7
Ammonium diuranate ((NH ₄) ₂ U ₂ O ₇)	+6	0.55	3.923	2.75
Uranyl nitrate hexahydrate ((UO) ₂ (NO ₃) ₂ ·6H ₂ O)	+6	0.67	4.44	2.61

effective charge on a cationic species involved in formation of a chemical bond is given by:

$$q = n \left[1 - 0.01185 \left(\frac{Z}{r'} + \frac{Z'}{r} \right) \right], \quad (2)$$

where Z , r and n are respectively, the total number of electrons, the ionic radius and the oxidation number of the cation and the primed symbols refer to the anion in the compounds. For complex samples, viz. ammonium diuranate and uranyl nitrate hexahydrate, the effective charges have been calculated approximately by considering the first coordination shell around the absorbing atom. Using the above formula, the effective charge on U in the uranium samples have been estimated and given in table 1.

Another formula to estimate the effective charge was suggested by Pauling (1960). By Pauling's method, the effective charge is given by:

$$q = nI, \quad (3)$$

where n is the valence of the absorbing ion and I the ionicity of the metal–ligand bond given as below:

$$I = 1 - \frac{n}{c} \exp \left[-\frac{(X_1 - X_a)^2}{4} \right], \quad (4)$$

where X_1 and X_a are the electronegativities of the ligand and the absorbing atom, respectively, and c the coordination number of the absorbing atom. The effective charge on U in the uranium samples has also been calculated using this formula and tabulated in table 1. It can be seen that there is difference between the effective charge values obtained by the two methods for all the samples.

This difference mainly arises due to the different ways in which 'ionicity' is defined in solids. The Pauling's method is based on purely ionic concept, where the number of bonding electrons possessed by the cations are equal to the number of the electrons transferred to the anion (Catlow and Stoneham 1983). However, the Suchet's (1965) method is based on the 'iono-covalent' concept of bonds in a real crystal, where it is assumed that valence electrons are not fully transferred to the anion and hence the ionicity and effective charge is reduced accordingly.

The Suchet's method seems more appropriate for the present system of molecular solids in which the ionic models like the Pauling's method do not hold good. As suggested by Suchet (1965), in compounds involving high Z elements like in U, the increase in atomic weight results in mutual polarization of the electron clouds whose interpenetration results in return of covalent characteristics resulting in lower values of effective charge as obtained here by Suchet's method. Hence the effective charge values estimated by Suchet's method have been considered for further analysis.

It has been suggested by Sarode *et al* (1978) that the energy shift is related to the effective charge by the relation:

$$\Delta E = aq + bq^2,$$

where a and b are constants. This relation has also been justified on theoretical grounds using the proportionality between the energy of the core levels E_i and $(Z - Z_i)^2$ where Z is the atomic number of the absorbing atom and Z_i is the screening of the i th core electron. However, later studies by Mande and Apte (1981) have showed deviations from the above result. Also, these studies were mainly based on transition metal compounds. In order to investigate the variation of the energy shift with effective charge for compounds having rare earth metal, we have tried to fit the data for the present uranium compounds with the different polynomial equations (Pandey *et al* 1990):

$$\Delta E = Aq \text{ (linear)}, \quad (5)$$

$$\Delta E = Aq + Bq^2 \text{ (quadratic)}, \quad (6)$$

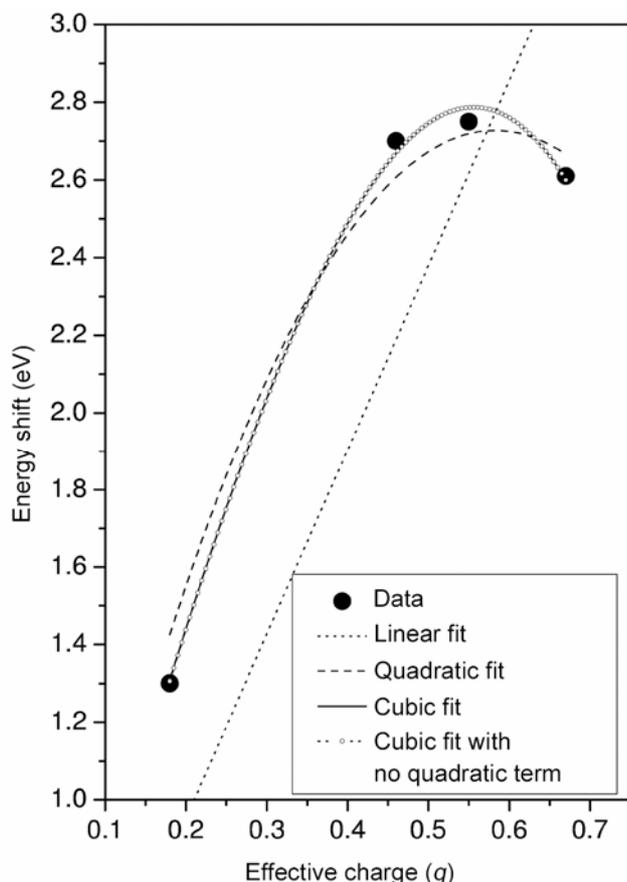
$$\Delta E = Aq + Bq^2 + Cq^3 \text{ (cubic)}, \quad (7)$$

$$\Delta E = Aq + Cq^3 \text{ (cubic with no quadratic term)}, \quad (8)$$

where A , B , C are constants which are obtained by fitting the experimental data. Figure 2 shows fitting of the ΔE vs q data to the above polynomial relations and the values of the fitting parameters A , B , C and the correlation coefficient have been tabulated in table 2. It should be noted that in the above exercise, the effective charge values obtained from Suchet's formula have been considered. It can be seen from table 2 that in this case, the maximum

Table 2. Fitting parameters of ΔE vs q curve with different polynomials.

Fitting	A	B	C	R^2 correlation coefficient
Linear	4.76	–	–	0.954
Quadratic	9.37	–8.04	–	0.971
Cubic	7.56	–0.16	–7.9	0.995
Cubic with no quadratic term	7.52	0	–8.1	0.998

**Figure 2.** ΔE vs q for U compounds with polynomial fit, where effective charges have been calculated using Suchet's formula.

value of correlation coefficient have been obtained for fitting with the polynomial given by (8). This suggests that the cubic polynomial with no quadratic term is the most suitable to describe the relation between energy shift and effective charge for our samples. The linear term corresponds to the hole-site effect and the cubic term is due to the Watson Bennet Davenport type energy term corresponding to overlap and hybridization effects and the valence d orbital effect (Pandey *et al* 1990). From table 2, it can be inferred that for the present set of samples, the parameter A which corresponds to the hole-site effect enhance the energy shift, while the parameter C corresponding to the overlap and hybridization effects and the valence d orbital effects lowering in the shift.

4. Conclusions

X-ray absorption spectroscopy measurements have been carried out at U L_3 edge around 17,166 eV in various compounds containing uranium in U^{4+} , U^{5+} and U^{6+} oxidation states. The measurements have been carried out at the energy dispersive EXAFS beamline at INDUS-2 synchrotron radiation source at RRCAT, Indore. It has been observed that the U L_3 edges in the compounds are shifted by 2–3 eV compared to its value for elemental U. The U L_3 edge energy is found to be shifted by different amounts in different compounds due to the different chemical environment around the U cation. The above chemical effect has been quantitatively described by determining the effective charges on U cation in the above compounds. It has been observed that a cubic relationship with no quadratic term, exists between the edge energy shifts and the effective charges on the cation.

Acknowledgements

The authors wish to acknowledge Dr N K Sahoo, Head, Applied Spectroscopy Division and Dr V M Datar, Head, Nuclear Physics Division, Bhabha Atomic Research Centre, Mumbai, for their keen interest during this work.

References

- Apte M Y and Mande C 1981 *J. Phys. Chem. Sol.* **42** 605
- Ballal M M and Mande C 1977 *J. Phys. Chem. Sol.* **38** 1383
- Basu S, Varma Salil, Shirsat A N, Wani B N, Bharadwaj S R, Chakrabarti A, Jha S N and Bhattacharyya D 2012 *J. Appl. Phys.* **111** 053532
- Basu S, Varma Salil, Shirsat A N, Wani B N, Bharadwaj S R, Chakrabarti Aparna, Jha S N and Bhattacharyya D 2013 *J. Appl. Phys.* **113** 043508
- Bhattacharyya D, Poswal A K, Jha S N, Sangeeta and Sabharwal S C 2009 *Nucl. Instrum. Meth. Phys. Res.* **A609** 286
- Catlow C R A and Stoneham A M 1983 *J. Phys. C: Sol. St. Phys.* **16** 4321
- Chetal A R, Mahto P and Sarode P R 1988 *J. Phys. Chem. Sol.* **49** 279
- Hinge H K, Joshi S K, Shrivastava B D, Prasad J and Srivastava K 2011 *Ind. J. Pure & Appl. Phys.* **49** 168
- Joseph D, Basu S, Jha S N and Bhattacharyya D 2012 *Nucl. Inst. Meth. Phys. Res.* **B274** 126
- Joseph D, Yadav A K, Jha S N and Bhattacharyya D 2013 *Bull. Mater. Sci.* (in press)

- Kalkowski G, Kaindl G, Brewer W D and Krone W 1987 *Phys. Rev.* **B35** 2667
- Kondawar V K and Mande C 1976 *J. Phys. C: Sol. St. Phys.* **9** 1351
- Mande C and Apte M Y 1981 *Bull. Mater. Sci.* **3** 193
- Neetika, Das A, Dhiman I, Nigam A K, Yadav A K, Bhat-tacharyya D and Meena S S 2012 *J. Appl. Phys.* **112** 123913
- Nigam A K and Gupta M K 1974 *J. Phys. F: Metal Phys.* **4** 1084
- Pauling L 1960 *The nature of chemical bond* (NY: Cornell Univ. Press)
- Pandey S K, Chetal A R and Sarode P R 1990 *J. Phys. Soc. Japan* **59** 1848
- Sampathkumaran E V, Kaindl G, Krone W, Perscheid B and Vijayraghavan R 1985 *Phys. Rev. Lett.* **54** 1067
- Sarode P R, Ramasesha S, Madhusudan W H and Rao C N R 1979 *J. Phys. C: Sol. St. Phys.* **12** 2439
- Suchet J P 1965 *Chem. Phys. Semiconductors* (London: Van Nostrand)
- X-ray Data Booklet 2009 Centre for X-ray Optics and Advanced Light Source (www.xdb.lbl.gov)