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XAS study of actinide and lanthanide solvent extraction compounds—I. $UO_2(NO_3)_2(TIBP)_2$ and $UO_2(NO_3)_2(TBP)_2$ (with TIBP = tri-isobutylphosphate and TBP = tributylphosphate)

C. Den Auwer,[a]* C. Lecouteux,[a] M. C. Charbonnel,[a] C. Madic[a] and R. Guillaumont[b]

[a] CEA, DCC/DRDD, Service d'études et de modélisation des procédés, ValRho, BP 171,
3027 Bagnols-sur-Cèze, France

[b] Institut de Physique Nucléaire d'Orsay, BP 6, 91406 Orsay, Cedex, France

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Abstract—For the design of new liquid–liquid extracting agents, which may or may not coordinate with elements to be separated, knowledge of the coordination polyhedra of the metal ions is important. In this paper, this information was obtained for the solvate $[UO_2(NO_3)_2(TBP)_2]$ (with TBP = tributylphosphate) using X-ray absorption spectroscopy. It includes the analysis and *ab initio* calculation of the EXAFS and XANES spectra corresponding to the model compound $[UO_2(NO_3)_2(TIBP)_2]$ (with TIBP = tri-isobutylphosphate) for which the crystal structure is known. The EXAFS results show little differences between the coordination polyhedra of the uranium ions engaged in both compounds, at low (77 K) or room (295 K) temperatures. The uranium eight-coordination polyhedron is composed of two uranyl oxygens located at 1.76 Å, four nitrate (bidentate) oxygens located at 2.51 Å and two phosphate oxygens located at 2.42 Å. Finally, investigation of the XANES spectra fully confirmed these results. © 1997 Elsevier Science Ltd

Keywords: Uranyl nitrate; extraction; nuclear fuel cycle; EXAFS; XANES; phosphate.

Reprocessing of the nuclear irradiated or used fuels permits the recycling of valuable fissile materials, i.e. uranium and plutonium, and to separate fission and activation products, as well as minor actinides (neptunium, americium and curium) which can be vitrified to give nuclear glass blocks. These waste packages would be buried in a deep-site geological repository. To achieve this goal, the liquid–liquid solvent extraction method is used world-wide in the so-called PUREX process [1]. In this process, uranium and plutonium are extracted from the aqueous nitric acid nuclear fuels solution with an organic phase which contains tri-n-butylphosphate extracting agent (TBP), diluted into an aliphatic solvent. The extracted solvates are $[UO_2(NO_3)_2(TBP)_2]$ and $[Pu(NO_3)_4(TBP)_2]$.

It was recently considered that the long-term hazards associated with a deep site nuclear repository could be minimized if the long-lived radionuclides, mostly the minor actinides, and some fission products, would not be present in these wastes. To achieve such a goal, separation and transmutation methods of these radionuclides must be intensively investigated. This is the aim of the OMEGA and SPIN programmes launched respectively in 1989 in Japan [2] and in 1991 in France at the CEA [3] (in the frame of the law voted by the French parliament on 30 December 1991).

Consequently, new actinide separation methods must be proposed and new liquid–liquid solvent extraction processes must be conceived using new extractants giving less secondary wastes than the PUREX one. Of course, in such a research it is of prime importance to have a good knowledge of the coordination polyhedron of the metal ions to be

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* Author to whom correspondence should be addressed. Permanent address: Université Paris-Sud, LURE, bat 209 D, 91405 Orsay Cedex, France.

extracted. This is required for molecular modelling, which was selected as one of the tools to help in the molecular design [4,5]. It also contributes to the understanding of the species reactivity, *via* a better insight in the coordination patterns.

The first step of our research in this field is the determination of the coordination sphere of the uranium ion in the $[UO_2(NO_3)_2(TBP)_2]$ solvate. X-ray absorption spectroscopy (EXAFS and XANES) and IR spectroscopy were selected as tools to probe the uranium local order. The choice of X-ray absorption spectroscopy was mainly motivated in this work by the possibility to obtain bond structure information from liquid phase samples.

The use of EXAFS spectroscopy requires reliable phase and amplitude parameters. Experimental phases and amplitudes have to be excluded here because of overlapping Fourier transformed features (contributions from different neighbour types are not deconvoluted). Therefore, *ab initio* calculated phases and amplitudes (using FEFF6 code [6]) are particularly attractive. The validity of these calculated phases and amplitudes was first tested on the model compound $[UO_2(NO_3)_2(TIBP)_2]$ (with TIBP = tri-i-butylphosphate) of known structure at 77 K [7], as fully described in the experimental section. To evaluate the effect of the temperature on the bond length, we also recorded the spectrum of $[UO_2(NO_3)_2(TIBP)_2]$ at the same temperature as for $[UO_2(NO_3)_2(TBP)_2]$ in solution, i.e. 295 K. It must be noted that EXAFS spectroscopy was demonstrated to be very fruitful in a recent published study related to uranyl carbonate complexes in aqueous solution [8].

EXPERIMENTAL

Synthesis

$UO_2(NO_3)_2(TIBP)_2$ was synthesized from 10.14 g of $UO_2(NO_3)\cdot 6H_2O$ and 10 cm^3 of tri-isobutyl phosphate (TIBP, stoichiometric ratio TIBP/U^{VI} = 2). The mixture was stirred at 46°C and the water formed was removed. Then, the yellow paste was dried *in vacuo*, leading to the formation of a yellow powder. IR spectra [1 mg in 80 mg of KBr pellet; cm^{-1}: 2963 (str, br), 2874 (str, br), 2552 (m), 2298 (s), 1832 (s), 1776 (s), 1729 (s), 1622 (s, br), 1533 (m, br), 1472 (m), 1385 (str), 1269 (m, br) 1172 (m), 1031 (str, br), 938 (m), 882 (m, br), 747 (m), 597 (m), 543 (m. br)] exhibit the well-known stretching frequency for the uranyl group at 938 cm^{-1}. The bands between 2500 and 1700 cm^{-1} are combination bands which are often observed with nitrate compounds [9].

$UO_2(NO_3)_2(TBP)_2$ solvate was prepared in an excess of tri-n-butylphosphate (TBP) by dissolving 10.32 g of $UO_2(NO_3)\cdot 6H_2O$ in pure TBP. Uranium(VI) concentration was 142 g dm^{-3}. IR spectra of the liquid phase [on a ZnSe horizontal Attenuated Transmitted Reflectance crystal; cm^{-1}: 2962 (str, br), 2878 (str, br), 1522 (str), 1474 (m), 1382 (w), 1278 (m), 1182 (m), 998–1030 (str, br), 937 (m), 811 (m), 747 (m)] are similar to the IR spectrum of $UO_2(NO_3)_2(TIBP)_2$.

EXAFS and XANES

EXAFS and XANES measurements were carried out at LURE at the DCI high energy ring on the EXAFS IV experimental hutch [10]. Transmission detection mode was used with two ionization chambers filled with argon. Spectra were taken at the uranium L$_{III}$ edge (17,166 eV) using a double crystal Si 311 monochromator.

Samples were weighed in order to obtain an absorption jump of 1 after the edge. Solid state samples (71 mg mm^2) were diluted in cellulose to obtain solid pellets placed in a sample holder. Low temperature measurements were carried out using a liquid nitrogen cryostat. Liquid samples were measured in an *in house* [11] liquid cell (path length = 3 mm) at room temperature.

Data treatment was carried out using *in house* codes [12]. Electronic parameters used to fit the spectra of the unknown compounds (electron mean free path Γ, ionization energy threshold ΔE_0) were extracted from the adjustment (using Round Midnight [12] fitting procedure) of the experimental spectrum of model compound [solid-state $UO_2(NO_3)_2(TIBP)_2$ at 77 K] of known structure (space group $P\bar{1}$) [7]: 2 O (from UO_2) at 1.76 Å; 2 O (from TIBP) at 2.37 Å and 4 O (from NO_3) at 2.51 Å. Phases and amplitudes were extracted from *ab initio* calculations of the EXAFS spectrum of solid-state $UO_2(NO_3)_2(TIBP)_2$ at 77 K using FEFF6 code [6]. Adjustment of the experimental model compound spectrum was carried out in two steps: (i) filtering and fit of the Fourier transformed EXAFS spectrum between 0.7 and 1.7 Å corresponding to the contribution of the oxygen atoms of the UO_2 group; (ii) filtering and fit of the Fourier transformed EXAFS spectrum between 0.7 and 2.4 Å corresponding to the contributions of the oxygen atoms from UO_2, TIBP and NO_3 groups. All the parameters determined in (i) for the UO_2 layer were transferred and kept constant in this three-layer adjustment. Treatments of the experimental spectra of the unknown products [i.e. solid-state $UO_2(NO_3)_2(TIBP)_2$ at room temperature and liquid $UO_2(NO_3)_2(TBP)_2$ in TBP solution at room temperature] were carried out in the same way.

RESULTS AND DISCUSSION

Comparison in Fig. 1 of the Fourier transformed EXAFS spectra of solid-state $[UO_2(NO_3)_2(TIBP)_2]$ at 77 K, solid-state $[UO_2(NO_3)_2(TIBP)_2]$ at 295 K and $[UO_2(NO_3)_2(TBP)_2]$ in solution in TBP at 295 K shows no major differences up to 2.5 Å. We conclude that the first coordination of uranium in these three

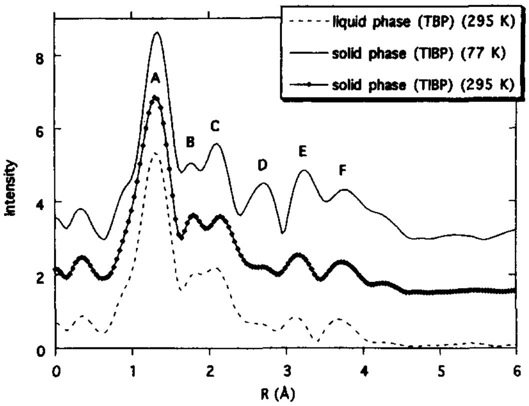

Fig. 1. Comparison between the moduli of the Fourier transformed EXAFS spectra of solid state $[(UO_2)(NO_3)_2(TIBP)_2]$ at 77 K, solid-state $[(UO_2)(NO_3)_2(TBP)_2]$ at 295 K and $[(UO_2)(NO_3)_2(TBP)_2]$ in solution in TBP at 295 K (distances are not phase-shift corrected).

samples are comparable. Quantitative analysis was undertaken with our fitting code, Round Midnight. It is based on the single scattering approximation of the data treatment. Thus, only the part of the experimental spectra where multiple scattering is negligible can be adjusted. *Ab initio* calculations of the EXAFS spectrum of solid-state $[UO_2(NO_3)_2(TIBP)_2]$ at 77 K using FEFF6 code allowed both assignment and determination of the scattering multiplicity of each contribution of the Fourier transformed EXAFS spectrum. The six major peaks of the Fourier transformed spectrum (Fig. 2) were assigned to: (i) single scattering of oxygen atoms of the uranyl group for peak A, (ii) single scattering of the closest oxygen atoms of the phosphate and nitrate groups for peaks B and C, (iii) single scattering involving the nitrogen atoms of the nitrate groups as well as multiple scattering of the oxygen atoms of the uranyl group for peak D, (iv) single and multiple scattering involving the phosphate atoms of the phosphate groups for peak E and (v) multiple and single scattering involving mainly the further oxygen atoms of the phosphate groups for peak F. Figure 2 shows the contribution of multiple scattering from the third and fourth orders. This calculation shows that multiple scattering is negligible between 0.7 and 2.4 Å. This is the region I where no major differences can be seen between Fourier transformed spectra of $[UO_2(NO_3)_2(TIBP)_2]$ at 77 and 295 K, and $[UO_2(NO_3)_2(TBP)_2]$ in TBP solution. On the other hand, the region between 2.4 and 5 Å (region II, much more complex to analyse because of the preponderant weight of multiple scattering) exhibits slight intensity differences between the spectra of the three samples.

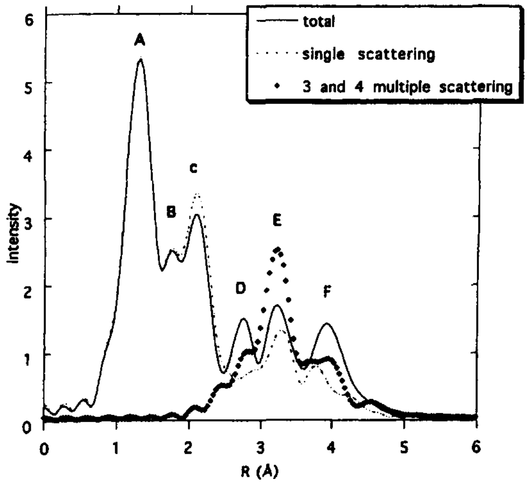

Fig. 2. FEFF6 simulation of the Fourier transformed EXAFS spectrum of $[(UO_2)(NO_3)_2(TIBP)_2]$ solid at 77 K. The total spectrum is shown, including single, double, triple and quadruple multiple scattering processes. Multiple scattering (triple and quadruple) as well as single scattering contributions to the total spectrum are also shown. (Distances are not phase-shift corrected).

Region I analysis

Quantitative determination of structural parameters R (distances) and N (number of neighbours) is highly correlated to the phases and amplitudes used. In previous studies related to uranium(VI) compounds and solutions, distances and number of neighbours have been shown to depend on the choice of the experimental phases and amplitudes [13,14].

In our case of interest, dispersion of the U—O distances associated with the non-deconvulated peaks A, B and C, precludes the use of experimental phases and amplitudes [15]. This is the reason why *ab initio* calculated (FEFF6) phases and amplitudes have been used in this work. Adjustments with Round Midnight of the contributions of the three spectra between 0.7 and 2.4 Å confirm the structural similarities of the three samples. Best-fit parameters are presented in Table 1. Figure 3 shows the adjustment of the spectrum of $[UO_2(NO_3)_2(TBP)_2]$ in TBP solution at 295 K. Figure 4 shows the extracted EXAFS oscillations of this compound as well as the influence of the different U—O layers on the fit results of the filtered oscillations. There are no differences between the U—O distances in solid-state $[UO_2(NO_3)_2(TIBP)_2$ at 295 K and in $[UO_2(NO_3)_2(TBP)_2]$ in TBP solution at 295 K. However, the results show a lengthening of the U—O (phosphate groups) bonds in solid-state $[UO_2(NO_3)_2(TIBP)_2]$ from 2.37 Å at 77 K to 2.42 Å at 295 K and 2.42 Å for $[UO_2(NO_3)_2(TBP)_2]$ in TBP solution at 295 K. In the fitting procedure, the number of neighbours of uranium in $[UO_2(NO_3)_2(TBP)_2]$ in TBP solution was fixed. This is because the Debye–Waller factors extracted from $[UO_2(NO_3)_2(TIBP)_2]$ at 295 K in the solid state are not transferable to the liquid phase case. Reasonable assumption for the coordination sphere of U in $UO_2(NO_3)_2(TBP)_2$ is: (i) 2 O for the uranyl group (the oxidation state of *U* stays constant upon

Table 1. Best-fit parameters of the EXAFS spectra of solid $[(UO_2)(NO_3)_2(TIBP)_2]$ and $[(UO_2)(NO_3)_2(TBP)_2]$ solvate in TBP

	N (U—O)	σ (Å)	R (Å)	O type
$[(UO_2)(NO_3)_2(TIBP)_2]$	2.0[a]	0.067	1.76[a]	From UO_2 group
at 77 K.	2.0[a]	0.160	2.37[a]	From 2 TIBP groups
$\rho = 3.0\%$	4.0[a]	0.094	2.51[a]	From 2 NO_3 groups
$[(UO_2)(NO_3)_2(TIBP)_2]$	2.0[a]	0.069	1.76	From UO_2 group
at 295 K	2.0[a]	0.190	2.43	From 2 TIBP groups
$\rho = 0.9\%$	4.0[a]	0.093	2.51	From 2 NO_3 groups
$[(UO_2)(NO_3)_2(TBP)_2]$	2.0[a]	0.064	1.76	From UO_2 group
in solution at 295 K	2.0[a]	0.280	2.41	From 2 TIBP groups
$\rho = 1.5\%$	4.0[a]	0.104	2.51	From 2 NO_3 groups

[a] Indicates fixed parameters equal to the crystallographic parameters of $[(UO_2)(NO_3)_2(TIBP)_2]$ found in the literature [7]. N is the number of O neighbours, σ is the Debye–Waller factor and R is the U—O distance. For all layers $\Gamma = 0.58$ Å^{-2} and $\Delta E_0 = -1.0$ eV; 10.7 eV and 6.4 eV for the first, second and third layers respectively.

ρ is the figure-of-merit of the fit: $\rho = \dfrac{\sum_k [\chi_{exp}(k) - \chi_{fit}(k, P_i)]^2}{\sum_k [\chi_{exp}(k)]^2}$, where χ is the EXAFS signal and P_i the number of fitted parameters.

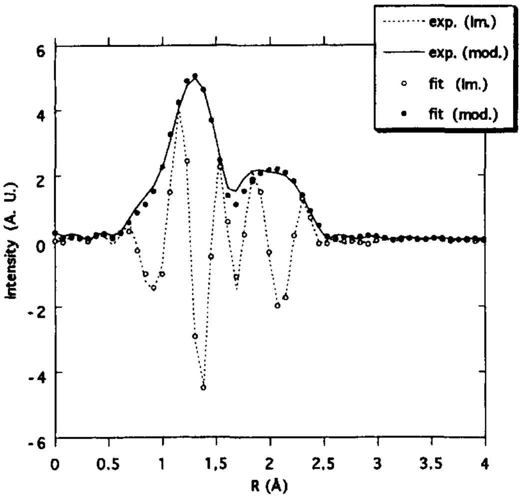

Fig. 3. Fit of the modulus (mod.) and the imaginary part (Im.) of the Fourier transform of the EXAFS spectrum of $[(UO_2)(NO_3)_2(TBP)_2]$ in solution at 295 K (distances are not phase-shift corrected).

solvatation and going from TIBP to TBP), (ii) 2 O for the phosphate groups, and (iii) 4 O corresponding to 2 bidentate NO_3^- groups, as in the solid state. The choice of monodentate NO_3^- was precluded because of the presence of the two characteristic [8,16] stretching frequencies of bidentate NO_3^- ligand in the liquid phase sample that also appear in the solid state $[UO_2(NO_3)_2(TIBP)_2]$ (1522 and 1278 cm^{-1} for the liquid; 1533 and 1269 cm^{-1} for the solid).

The large Debye–Waller factor adjusted for the U—O(PO_3R_3) bond in $[UO_2(NO_3)_2(TBP)_2]$ (0.28 Å with regards to 0.19 Å in the solid state at the same

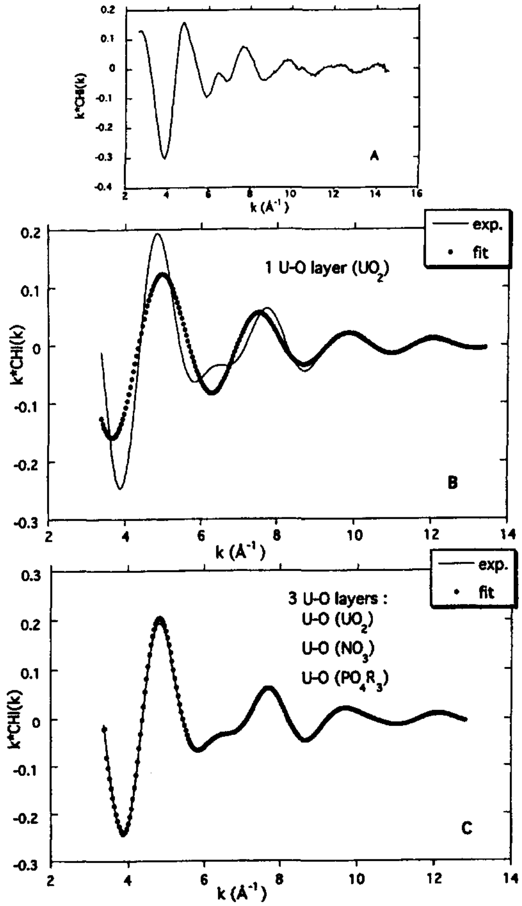

Fig. 4. Extracted EXAFS spectrum of $[(UO_2)(NO_3)_2(TBP)_2]$ in solution at 295 K and fit of the filtered EXAFS oscillation: (a) experimental EXAFS spectrum; (b) contribution of the two uranyl oxygen atoms; (c) contribution of all the oxygen atoms.

temperature) reflects the additional disorder upon solvatation.

Region II analysis

In order to extract additional structural information about the coordination sphere of $[UO_2(NO_3)_2(TBP)_2]$ in solution we next investigated the multiple scattering contributions to the absorption spectrum. It is well known that bond angles close to 180° favour enhanced multiple scattering contributions [17,18]. To illustrate this in our compounds, Table 2 gives the scattering relative intensities of some remarkable scattering paths, as calculated by FEFF6. Paths 5 and 6, involving linear arrangement of the scattering atoms, contribute to the spectrum to almost the same extent as paths 2 and 3, which involve single scattering contributions. Path number 4 is a good example of the falling intensity of multiple scattering when the atoms involved are not aligned anymore.

As mentioned above, region II includes predominant multiple scattering contributions. It should therefore be sensitive to any structural changes [especially involving bond angle changes in the UO_2 and $O(PO_3R_3)$ groups, as we have seen the importance of multiple scattering in these groups because of bond angles close to 180°] going from $[UO_2(NO_3)_2(TIBP)_2]$ to $[UO_2(NO_3)_2(TBP)_2]$. Since the XANES part of the absorption spectrum predominantly includes multiple scattering contributions, we expect to extract from its study further information on bond angle modifications that may occur going from TIBP ligand in the solid state to TBP in the liquid phase. The XANES spectra (U L_{III} edge) of both $[UO_2(NO_3)_2(TIBP)_2]$ and $[UO_2(NO_3)_2(TBP)_2]$ were recorded and further simulated by FEFF6 [19]. Simulation of $[UO_2(NO_3)_2(TIBP)_2]$ at 77 K in the multiple scattering approach reproduces the two shoulders B and C exhibited by the experimental spectrum, as shown in Fig. 5. However, the very weak shoulder A is not clearly reproduced by the calculated spectrum. Further investigation of the calculated spectrum shows that shoulder B is due to multiple scattering paths of the UO_2 group (paths of type 5 in Table 2). Shoulder C is mainly due to single scattering contributions as shown by the calculation carried out in the single scattering approximation. Its shift towards higher energy and its intensity decrease in the experimental spectrum are due to additional destructive multiple scattering contributions of the oxygen atoms of both uranyl and phosphate groups. The XANES spectrum of $[UO_2(NO_3)_2(TBP)_2]$ (Fig. 5) exhibits the same features as the one of solid-state $[UO_2(NO_3)_2(TIBP)_2]$ at 77 K. However, because of increased Debye–Waller factors

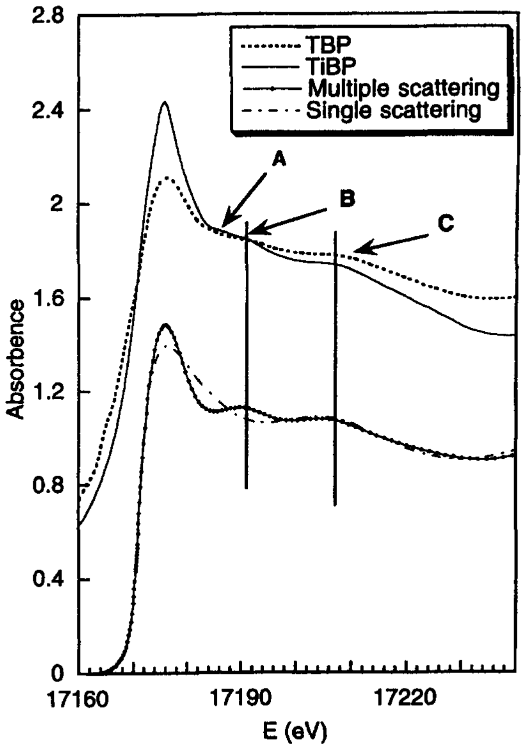

Fig. 5. Experimental XANES spectra of $[(UO_2)(NO_3)_2(TIBP)_2]$ at 77 K (TIBP) and $[(UO_2)(NO_3)_2(TBP)_2]$ in TBP solution at 295 K (TBP). Theoretical spectra (FEFF6) were calculated in both single scattering approximation and multiple scattering approach. A cluster of 8 Å was used for the potential calculation and up to 6 scattering multiplicity were taken into account. The two calculated spectra were shifted towards higher energies of 21 eV. This is a reasonable value for such calculations [19].

Table 2. Some calculated (FEFF6) multiple scattering paths of $[(UO_2)(NO_3)_2(TIBP)_2]$ at 77 K

Path index	Scattering multiplicity	Relative amplitude[a]	Atoms involved and paths half length (Å)
1	Single	100	U—O(UO_2)—U, 1.76
2	Single	45	U—O(PO_3R_3)—U, 2.37
3	Single	38	U—O(NO_3)—U, 2.51
4	Triple	7	U—N—O(NO_3)—U, 3.37
5	Quadruple	22	U—O—U—O—U, 3.51 all O from (UO_2)
6	Triple	33	U—O(PO_3R_3)—P—U, 3.83

[a] All path amplitudes are calculated with respect to the highest one, set to 100%.

in the liquid phase at 295 K compared with $[UO_2(NO_3)_2(TIBP)_2]$ at 77 K (as observed in the EXAFS treatment), the white line intensity as well as shoulders A, B and C are weaker [20]. In particular, shoulder A is not visible. The similarity of their two spectra (position of B and C shoulders) shows that no dramatic structural changes occur, going from the TIBP ligand in the solid state to the TBP ligand in the liquid phase. We confirm here the results obtained by the EXAFS analysis.

CONCLUSIONS

The main result of this study is that solid-state $[UO_2(NO_3)_2(TIBP)_2]$ and liquid $[UO_2(NO_3)_2(TBP)_2]$ in TBP solution, at 295 K, have the same structure. To our belief, both solvation effects (going from solid state to liquid phase in TBP) and steric effects of the alkyl part of the two phosphate groups (going from TIBP to TBP) could have slightly modified the first coordination sphere in $[UO_2(NO_3)_2(TBP)_2]$, compared with $[UO_2(NO_3)_2(TIBP)_2]$. This was not observed in this work. Further studies involving EXAFS measurements on $[UO_2(NO_3)_2(OPO_3R_3)_2]$ (where R is an alkyl group) in solution should determine the influence of the steric effect of the alkyl group on the U—O bond lengths.

The use of *ab initio* calculations was proved to be particularly useful for the attribution of the scattering contributions to the total absorption spectrum. We think that, although quite limited, the results presented in this study demonstrate the value of X-ray absorption spectroscopy in solvent extraction of actinide compounds, in order to extract structural information (such as bond distances) on the coordination sphere of the central atom.

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