Structure of the Aqua Ions and Fluoride Complexes of Uranium(IV) and Thorium(IV) in Aqueous Solution an EXAFS Study

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The structures of aqueous M^{4+}(aq) and MF^{3+}(aq), where M is uranium(IV) or thorium(IV), have been determined by L_{III} edge EXAFS using data from solutions of 1.5 M $HClO_4$ in which the M(IV) concentrations ranged from 0.03 to 0.3 M. A least-squares refinement of the data for the aqua ions indicated 10.8 ± 0.5 water molecules in the first hydration sphere of both ions and M−O bond distances for U(IV) and Th(IV) of 2.42 ± 0.01 and 2.45 ± 0.01 Å, respectively. By considering both previous structure information and the EXAFS data, we selected $N = 10 \pm 1$ as the most likely coordination number of both M(IV) aqua ions. EXAFS measurements from acidic aqueous uranium(IV) and thorium(IV) solutions containing fluoride show that large changes in the first coordination sphere occur. The experimental data indicates an asymmetrical distribution of the distances, probably as a result of differing M−F and M−O bond lengths. These can be described by a model that contains two different bond distances, one M−F distance at 2.10 Å and one M−O distance at 2.45 Å for U(IV); for Th(IV), the corresponding distances are 2.14 and 2.48 Å. The total coordination number in this model is unchanged from the aqua ions, i.e., 10 ± 1.

Introduction

Extended X-ray absorption fine structure (EXAFS) spectroscopy is a standard technique, providing information of coordination numbers and distances of a chosen atom to its nearest neighbors.[1] The application of synchrotron-based X-ray absorption spectroscopy (XAS) in actinide research is becoming more and more important.[2]

As part of our ongoing studies of the water exchange on actinide ions,[3] we determined the bond distance and number of coordinated water molecules in the first hydration sphere of Th(IV) and U(IV) in acidic solutions from their L_{III} edge EXAFS spectra. The coordination of Th(IV) and U(IV) in aqueous solutions containing perchlorate, chloride, and nitrate has previously been studied by large angle X-ray scattering (LAXS).[4−6] This technique, however, requires higher M^{4+} concentrations than does EXAFS investigations. The number of coordinated water molecules in the first hydration sphere of U(IV) was determined from LAXS results to be 8.2 ± 0.4, with

an average bond distance of 2.44_1 Å;[4,5] for thorium,[5,6] 8.0 ± 0.5 water molecules at 2.48_5 Å were reported. Evidence that the number of coordinated water for these tetravalent actinides is larger than eight is available from different sources: from the metal-water bond distances in M(IV) compared to M(III) ions with the same ionic radius, vide infra p 000, and from a previous EXAFS study for Np^{4+} by Allen et al. This study indicates that 9 to 11 water molecules are bonded at a distance of 2.40 Å.[7]

We have observed changes in the rate of water substitution between M^{4+}(aq) and MF^{3+}(aq) ions (M = U, Th) as studied by ^{17}O NMR relaxation.[3] To deduce the mechanisms for these reactions, in particular if they have associative or dissociative activation, it is necessary to have information on their coordination numbers. To achieve this, it is important that EXAFS measurements be made in the same concentration range as the kinetic measurements. LAXS measurements were performed at such high concentrations that both the activity and the concentration of water in the test solution differed greatly from those in more dilute systems used in the kinetic study. Therefore, the U and Th L_{III} edge EXAFS measurements were made using approximately 0.05 M M^{4+} in 1.5 M $HClO_4$ and F^- concentrations ranging from 0.05 to 0.09 M.

Different metal ion concentrations were investigated to determine if the measured EXAFS oscillations exhibit any concentration dependence. The structural parameters were obtained using different data evaluation procedures and then compared to those observed in LAXS experiments. To evaluate which structural model agreed best with the experimental data, we compared results to structure data from the aqua species of Er^{3+}, which has the same ionic radius as U^{4+}. We also studied

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Table 1. Summary of Sample Composition, Sample Cell Path Length, and Calculated and Measured Absorption Edge Jumps

sample	$[M^{4+}]$ and $[F^-]^a$	speciation	path (mm)	edge jump expected	edge jump measured
A	U^{4+}, 0.3	82% U^{4+} 18% UOH^{3+}	3	1.13	1.4
B	U^{4+}, 0.2		5	1.31	1.5
C	U^{4+}, 0.2		3	0.79	1.0
D	U^{4+}, 0.055		13	0.97	1.0
E	U^{4+}, 0.05		13	0.85	1.0
F	Th^{4+}, 0.03	100% Th^{4+}	13	0.60	0.4
G	Th^{4+}, 0.05		13	1.01	1.0
H	U^{4+}, 0.055 + F^-, 0.055	88% UF^{3+} 12% U^{4+}	13	0.97	1.0
I	U^{4+}, 0.055 + F^-, 0.09	63% UF_2^{2+} 37% UF^{3+}	13	0.97	1.0
J	Th^{4+}, 0.05 + F^-, 0.05	80% ThF^{3+} 10% ThF_2^{2+} 10% Th^{4+}	13	1.01	0.9

^{a} Expressed as molar concentrations; medium was 1.5 M $HClO_4$.

the changes in the first coordination sphere of Th^{4+} and U^{4+} caused by the formation of fluoride complexes.

Experimental Section

Sample Preparation. The U^{4+} and Th^{4+} perchlorate stock solutions were prepared as described earlier.[8,9] The U^{4+} stock solution was prepared from acidified $UO_2(ClO_4)_2$ solution by electrolysis, using a two-compartment cell with separated mercury cathode and platinum anode, at a potential of 4 V. The solution was stored under argon. Samples were prepared from appropriate aliquots of the stock solutions in 1.5 M $HClO_4$. Solutions containing fluoride concentrations from 0.05 to 0.09 M were made from NaF (Merck). The sample information is summarized in Table 1. The hydrated U^{4+} and Th^{4+} ions are the major species in all solutions without fluoride (samples A–G). UF^{3+} and ThF^{3+} were the dominant species in solutions H–J, whereas sample I contained a mixture of UF_2^{2+} and UF^{3+}. The speciation calculations were made using known equilibrium constants and the program SOLGASWATER.[10] The sample cell path length of the aqua ion solutions was varied between 3 and 13 mm (Table 1) to obtain edge jumps of 1.3 or less, so that amplitude distortions from thickness effects[11] could be avoided. Three different solid test substances were measured. Crystalline $UO_2(s)$ used was supplied by ASEA ATOM, ThO_2 was prepared as described in ref 9, and $Ba_2U(C_2O_4)_4 \cdot 8H_2O$ was prepared and characterized as described in ref 12. The solid samples were prepared by mixing approximately 25 mg of MO_2 or 100 mg of $Ba_2U(C_2O_4)_4 \cdot 8H_2O$ with polyethylene and were pressed as 13 mm diameter pellets. These amounts were selected to obtain an edge jump of ~1.0 across the Th and U L_{III} absorption edges.

EXAFS Measurements. The EXAFS spectra were collected in transmission mode at room temperature at SSRL, Stanford, and HASYLAB, Hamburg. The measurements at SSRL were performed on wiggler beamline 4-1 using a Si(220) double-crystal monochromator. Spectra measured at HASYLAB were recorded at the beamline A1 using a Si(311) and a Si(220) double-crystal monochromator. The incident beam flux in all cases was reduced to ~50% of its maximum. Three EXAFS scans were collected from each sample and then averaged. For energy calibration of the sample spectra, the spectrum from a yttrium foil was recorded simultaneously. The ionization energy

of the U L_{III} and the Th L_{III} electron, E_0, was arbitrarily defined as 17 166 and 16 300 eV, respectively.

EXAFS Data Analysis. The data were treated using the WinXAS software.[13] The EXAFS oscillations were isolated using standard procedures for preedge subtraction, data normalization, and spline removal.[1] The spline parameters used were $k_w = 3$, points = 8, and k-region ranging from 0.4 to 13 Å^{-1}. Theoretical backscattering phase and amplitude functions, $\delta(k)$ and $F(k)$, used in data analysis were calculated for the test compounds, ThO_2,[14] UO_2,[15] and $UF_4 \cdot 2.5H_2O$[16] using the FEFF7[17] program. Samples with eight-coordination (UO_2 and ThO_2) and nine-coordination ($Ba_2U(C_2O_4)_4 \cdot 8H_2O$) were used as structural models when interpreting the data from the M(IV) solutions. First-shell EXAFS data, Fourier-filtered between 1.5 and 2.5 Å (not phase-shifted), were used for fits to the EXAFS equation to determine structure parameters. The amplitude reduction factor, S_0^2, was held constant at 1.0 in all the fits. ΔE_0 values were set at 4 eV for the M^{4+}-(aq) samples (A–G) and at 5 eV for the MF^{3+} solution samples (H–J).

The theoretical U–O and Th–O phase and amplitude functions calculated with FEFF7 were tested by fitting Fourier-filtered first-shell EXAFS results of MO_2 and $Ba_2U(C_2O_4)_4 \cdot 8H_2O$. The MO_2 results showed an average coordination number and bond distance of 6.9 ± 1 and 2.34 Å for uranium(IV) and 7.6 ± 0.8 and 2.41 Å for thorium-(IV). These values for coordination numbers are within 13.7% and 5% and the bond distances are within 0.03 and 0.01 Å of those reported for X-ray diffraction (XRD) results on UO_2 and ThO_2, respectively.[14,15] For $Ba_2U(C_2O_4)_4 \cdot 8H_2O$, we found 9.0 ± 0.7 oxygen atoms at 2.38 Å, which compares well with values from XRD of a coordination number of 9 and an average U–O bond length of 2.407 Å.[12]

It is not possible to distinguish between O and F backscatterers using EXAFS. If the difference between the M–O and M–F bond distance in the MF^{3+} solution species is sufficiently large, however, they can be differentiated indirectly. Therefore, we tested different models, one assuming one Gaussian M–(O, F) pair distribution (model A), the second taking into account the asymmetry in the M–(O, F) pair distribution that different M–O and M–F distances would induce (model B), and the third using separate M–F and M–O distances (model C). Least-squares refinements using model C yielded coordination numbers of the M–F distance of 1.0 ± 0.25. The coordination numbers obtained for fluoride in samples H and J are in good agreement with the speciation calculations shown in Table 1. The value determined for sample I deviates much more from the theoretical value 1.63. This is not due to deficiencies in the equilibrium model but rather reflects the difficulty in determining precise coordination numbers from EXAFS data. The residual value, Res, was used to compare the goodness of fit for each of the models. However, Res is the difference between the theoretical EXAFS function and experiment and does not depend on the experimental error.

Results and Discussion

A preliminary account of this study has been presented as a poster.[18] In this communication, we have made more extensive modeling of the experimental data and their effects on the M–O distance, coordination number, standard deviations, and the asymmetry of the M–O distance distribution.

The isolated EXAFS oscillations and the corresponding Fourier transforms for samples A–G are shown in Figure 1.

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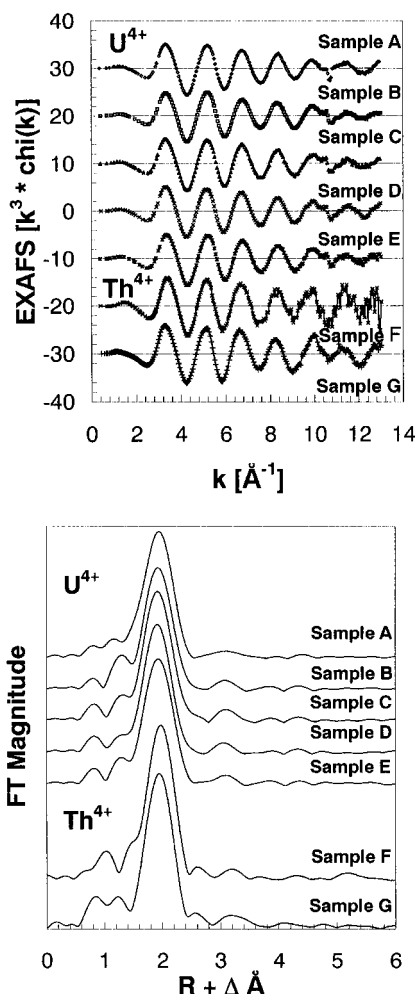
Figure 1. Raw U and Th L_{III} edge k^3-weighted EXAFS data for samples A−G and corresponding Fourier transforms (transformation in the k-range shown in Table 2, using a Bessel window).

The FTs are not corrected for the EXAFS phase shift, so peaks appear at shorter distances ($R + \Delta$) than the true near-neighbor distances (R). The FT peaks below 1.5 Å (without phase shift) are artifacts of the spline removal and are not associated with any coordination distance. The EXAFS oscillations of all samples are dominated by the M−O interaction in the first hydration sphere. The EXAFS amplitudes in Figure 1 are nearly the same for all the acid U^{4+} solutions and Th^{4+} samples and are independent of the concentration, indicating a similar coordination number in all of these samples.

The EXAFS oscillations of samples F and G containing Th^{4+} at 0.03 and 0.05 M, respectively, have a slightly shorter period length than that for samples A−E. This is a result of a longer Th−O bond distance. The bond lengths and coordination numbers obtained from fits to Fourier-filtered first-shell data are summarized in Table 2. Fits to the raw data of all samples (not shown) yielded similar bond length and coordination numbers. The coordination numbers obtained were similar for all M^{4+} aqua samples, 10.8 ± 0.5. The bond length difference between U−O ($R = 2.42 \pm 0.01$ Å) and Th−O ($R = 2.45 \pm 0.01$ Å) in the aqua ion is about 0.03 Å, close to the difference of the effective ionic radii of U^{4+} and Th^{4+}, 0.04 Å.[19] This also suggests that the coordination number is the same in both systems (see Table 2). If the number of coordinating water molecules was different, the change in their M−O bond distance

Table 2. Fit Parameters to U and Th L_{III} Edge Fourier-Filtered (1.5−2.5 Å, without Phase Shift) EXAFS Data for Samples A−F and The Fourier Transform k-Ranges Used; ΔE_0 Set at 4.0 eV

sample	FT range ($Å^{-1}$)	scattering path	N	σ^2 ($Å^2$)	R (Å)	Res
A	2.82−12.66	U−O	10.5 ± 0.9	0.0084	2.41_7	9.2
B	2.85−12.55		10.1 ± 0.9	0.0087	2.41_2	11.1
C	2.84−12.67		11.0 ± 1.0	0.0089	2.41_6	14.7
D	2.83−12.55		10.8 ± 1.0	0.0089	2.42_3	19.2
E	2.86−12.47		10.7 ± 1.0	0.0088	2.41_0	10.2
F	2.92−11.85	Th−O	11.0 ± 0.9	0.0067	2.43_7	10.2
G	2.86−12.50		11.2 ± 0.9	0.0071	2.44_8	19.8
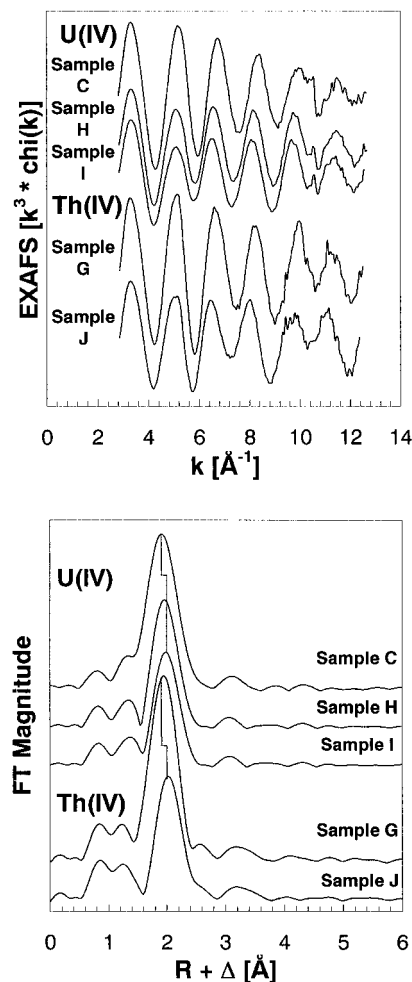
Figure 2. Raw U and Th L_{III} edge EXAFS data and corresponding FTs for samples H−J in comparison to the data measured for the aqua ions (samples C and G).

would differ from that between their ionic radii. The EXAFS analysis gave a slightly shorter U−O bond distance, 2.42 Å, and a larger coordination number, 10.8 ± 0.5, than LAXS results.[4,5] The EXAFS measurements indicated a Th−O distance of 2.45 Å and a coordination number of 10.8 ± 0.5, which is larger than that estimated by Johansson et al.[5,6]

Additional information on the coordination number of the M(IV) aqua ions may be obtained by comparing structure data from Er^{3+} with that from U^{4+}. These cations have nearly the same ionic radii; the difference is less than 0.01 Å.[19] The coordination number of trivalent lanthanides has been discussed for nearly fifty years, but both kinetic evidence[20] and diffraction

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Table 3. Fit Parameters to U and Th L_{III} Edge Fourier-Filtered (1.5−2.5 Å, without Phase Shift) EXAFS Data; ΔE_0 Set at 5.0 eV[a]

sample	fit model	FT range (Å⁻¹)	scattering path	N	σ^2 (Å²)	σ' (Å³)	R (Å)	Res
H	A		U−O	7.2 ± 0.6	0.0067		2.45$_8$	28.0
	B	2.85−12.73		6.9 ± 0.5	0.0054	0.000 87	2.49$_5$	11.1
	C		U−F	0.9 ± 0.2	0.0034		2.09	10.3
			U−O	8.7 ± 0.6	0.0089		2.45	
I	A		U−O	5.6 ± 0.5	0.0055		2.47$_0$	30.8
	B	2.85−12.56		5.4 ± 0.5	0.0041	0.000 88	2.51$_2$	16.0
	C		U−F	1.1 ± 0.2	0.0023		2.11	11.0
			U−O	8.2 ± 0.6	0.0091		2.46	
J	A		Th−O	8.0 ± 0.9	0.0076		2.49$_8$	22.2
	B	2.86−12.40		7.6 ± 0.8	0.0065	0.000 57	2.52$_1$	17.6
	C		Th−F	1.0 ± 0.3	0.0043		2.14	11.8
			Th−O	10.0 ± 0.9	0.0097		2.48	

[a] For samples H−J, different fitting methods were tested: A, fit to the EXAFS equation assuming a symmetrical (Gaussian) pair distribution; B, fit results taking the asymmetry of the pair distribution into account; and C, fit results using two different distances, one M−F(O) and a M−O.

data from solution[21] indicate that Er^{3+}(aq) is eight-coordinated, with an average bond distance of 2.36$_0$ Å. If U^{4+}(aq) also is eight-coordinate, one would expect a similar or slightly shorter bond distance for these electrostatically dominated metal−oxygen interactions. The experimentally determined U^{4+}−water distance, 2.42 Å, is significantly longer, which can only be explained by a coordination number larger than eight. For comparison, the average Er−H_2O bond distance in the solid-state structure of $[Er(H_2O)_9](C_2H_5SO_4)_3$, in which erbium is nine-coordinated, is 2.42 Å.[22]

The amplitude of the EXAFS oscillations of a coordination shell in general increases with increasing number of equidistant near-neighbor atoms, vide infra p 000, around the absorbing atom. Fourier-filtered first-shell EXAFS oscillations for U^{4+} in sample A, UO_2, and $Ba_2U(C_2O_4)_4\cdot8H_2O$ are compared in Figure S1 in the Supporting Information. Both UO_2, where U(IV) is eight-coordinate, and $Ba_2U(C_2O_4)_4\cdot8H_2O$, where U(IV) is nine-coordinate, exhibit amplitudes smaller than the U^{4+} aqua species. The larger amplitude indicates a coordination number which is higher than eight or nine in U^{4+}(aq). Furthermore, an average bond distance of 2.38 Å in the first coordination sphere of the nine-coordinated U(IV) in $Ba_2U(C_2O_4)_4\cdot8H_2O$ was measured, which supports a coordination of 10 in U^{4+}(aq). By considering both the available structure information and the EXAFS results, we selected $N = 10 \pm 1$ as the most likely coordination number of both M(IV) aqua ions.

Figure 2 compares isolated EXAFS oscillations and the corresponding Fourier transforms from U^{4+} and Th^{4+} in acidic solution (samples C and G) with those of the fluoride-containing samples (samples H−J). The difference between the two sets of spectra is pronounced; both a shortening of the period length of the EXAFS oscillations and a decrease in their amplitude is observed in the fluoride samples. This is also evident in the FTs, where the peak maxima of samples H−J are shifted to longer bond distances and the area under these peaks has decreased. Fits to the Fourier-filtered data (model A, Table 3) yielded longer bond distances in the first coordination sphere and a lower coordination number in the fluoride-containing samples compared to the aqua ions. However, the goodness of the fit results for the MF^{3+} samples, as judged by the relatively large Res values (Table 3), was clearly less satisfactory than the fits to the M^{4+}(aq) spectra. The largest difference between experimental and theoretical EXAFS oscillations was detected at higher k-values, where a phase shift between the measured

Fourier-filtered data and the calculated EXAFS was observed. This can result from an asymmetrical distribution of the M−(O,F) distances in the first coordination shell. There is also evidence for an asymmetric M−O distance distribution (Figure S2) in the M^{4+}(aq) samples. However, the apparent mean M−O distance increases only by 0.01−0.02 Å, which is close to the experimental error. Therefore, the results presented for the M^{4+}-(aq) species are based on the fits using a Gaussian pair distribution.

The EXAFS Debye−Waller factor, σ^2, takes the fluctuation in interatomic distances between the absorbing and backscattering atoms into consideration. It includes a dynamic term due to the thermal motion of the atoms and a static term due to structural disorder, which is essentially temperature independent. It does not account for large local disorder ($\sigma^2 > 0.01$ Å²), however. Therefore, we included the next higher moment of the absorber−backscatter distribution in the analysis to account for pair distribution asymmetry. This was done using the method of cumulant expansion,[23] including the third cumulant or σ', in the XAS formula in the WinXAS program:[13]

$$\chi(k) = \sum \frac{N_j \cdot S_0^2(k) \cdot F_j(k)}{k R_j^2} \cdot \exp(-2k^2\sigma_j^2) \cdot \exp\left(\frac{-2R_j}{\lambda}\right) \cdot$$

$$\sin\left[2kR_j + \delta_j(k) - \frac{4}{3}\sigma_j' k^3\right]$$

λ is the mean free path of the photoelectron, N is the coordination number, and R is the bond distance for atoms in coordination shell j.

The quality of the fits including σ' improved significantly (40−80% decrease in Res). Figure 3 depicts the experimental Fourier-filtered EXAFS function for sample H and the best theoretical fit obtained with and without σ' (models A and B). The high k phase shift between the experimental and theoretical EXAFS for the fits assuming a symmetrical distribution disappears when an asymmetrical distribution is accounted for. The coordination number obtained from these fits, however, remained less than that found for the corresponding aqua ions. This is because the third cumulant only affects the phase of the EXAFS oscillations. The next higher or fourth cumulant affects the oscillation amplitude and, hence, the coordination number.

Instead of including this fourth cumulant into the data analysis, we chose to analyze the data with a structural model using different M−F and M−O distances, model C. Differences in M−F and M−O bond distances can produce the unsym-

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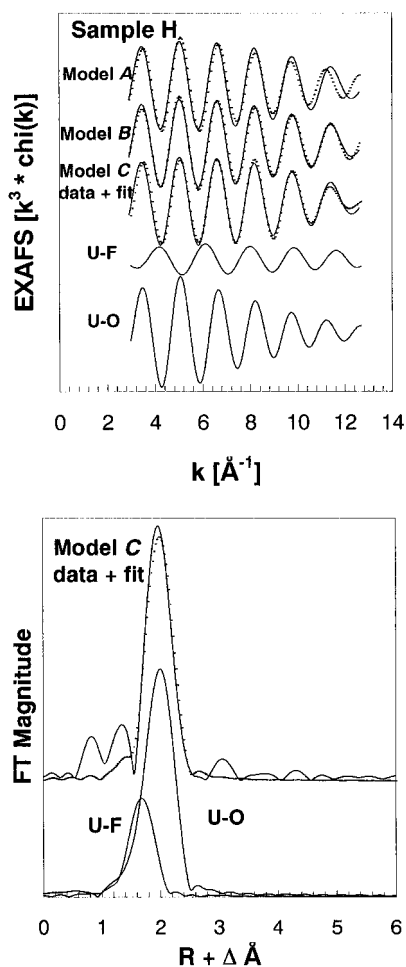
Figure 3. Experimental EXAFS oscillations for sample H (continuous line) and the best theoretical fits (squared): A, fit to the EXAFS equation assuming a symmetrical (Gaussian) pair distribution; B, fit results taking the asymmetry of the pair distribution into account; and C, fit results using two different distances, one M−F(O) and a M−O, including curve-fit deconvolution in *k*-space and *R*-space.

metrical distribution observed for the fluoride samples. Fits to the data using this model yielded average M−(O, F) coordination numbers similar to those obtained in the M^{4+} aqua species. For uranium(IV), one fluoride at 2.10 Å and 8.4 ± 0.6 water molecules at 2.46 Å were observed, and for thorium(IV), one fluoride at 2.14 Å and 10.0 ± 0.9 water molecules at 2.48 Å.

The relative magnitude and position of the fluoride and oxygen contributions to the fit of the spectrum of sample H are compared in Figure 3. The smaller EXAFS amplitude measured is explained using model C by an interference of the EXAFS oscillation of a backscatterer with a short distance with the M−O interaction at a somewhat longer distance, as shown in Figure 3. It is not due to an actual decrease in coordination number, as was obtained in models A and B. We prefer model C, because similar short M−F distances, 2.10−2.20 Å, are reported for several U(IV) solid-state structures, e.g., TlUF$_5$[24] or Rb$_2$UF$_6$.[25]

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It is also unlikely that a lower coordination number would correspond to an increase in the mean M−(O, F) distance. By combining EXAFS data with other structure information, it is in this case possible to select a proper model, which is not possible by using EXAFS data alone.

Conclusion

The results presented in this paper suggest that the number of bonded water molecules in the first hydration sphere of Th^{4+} and U^{4+} is larger than eight, in contrast to previous reports.[4−6] The EXAFS results are compatible with coordination numbers in the range 9−11 because of the uncertainty in the S_0^2 value. Comparisons of bond distances and coordination numbers between U^{4+} and Er^{3+}, which have the same ionic radii, indicate that nine- or ten-coordination is most likely for the M^{4+}(aq) ions. Comparison of EXAFS amplitudes for U(IV) compounds having eight- and nine-coordination with that of the U^{4+} aqua species and available structure information indicate that 10 water molecules are bonded to U^{4+} and Th^{4+}. The M−O bond distances for U^{4+} and Th^{4+} are 2.42 ± 0.01 and 2.45 ± 0.01 Å, respectively. Our experimental results are consistent with structural parameters for Np^{4+}(aq) of $N = 9-11$ and $R = 2.40$ Å.[7]

A significant change in the coordination sphere is observed when the complexes MF^{3+}(aq) and presumably MF_2^{2+}(aq) are formed. With one model, the coordination number decreases to 7 ± 1 and the mean M−(O, F) distance increases to 2.46 and 2.49 Å for uranium(IV) and thorium(IV), respectively. Better agreement between theoretical and experimental data, however, was obtained using a model having two different bond distances in the coordination sphere, one M−F distance at 2.10 Å and one M−O distance at 2.45 Å for U(IV); for Th(IV), the corresponding distances are 2.14 and 2.48 Å. In this case, the same coordination numbers as were obtained for the M(IV) aqua species, 9−11, were obtained. As indicated above, we prefer the latter model. To support this result, we have started quantum chemical calculations to obtain optimized geometries and energies of different structure models, which then may substantiate the interpretation of the EXAFS experimental findings.

Supporting Information Available: Comparison of the Fourier-filtered first-shell EXAFS data for U^{4+} (sample A), UO_2, and $Ba_2U(C_2O_4)_4$·$8H_2O$, and the best theoretical fits (S1); experimental EXAFS oscillations for sample D and G and the best theoretical fits, (*A*), fit to the EXAFS equation assuming a symmetrical (Gaussian) pair distribution, and (*B*), fit results taking the asymmetry of the pair distribution into account (S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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