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Experimental Coordination Environment of Uranyl(VI) in Aqueous Solution

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The coordination environment of a molecular UO_2^{2+} ion in aqueous solution is determined with X-ray scattering and interpreted taking into account the electron redistribution around the uranyl ion. The data indicate that uranyl coordinated to five water molecules is the dominating species, although a small percentage of the uranyl ions are coordinated to four waters. We argue that our result, taken together with calculated relative stabilities of 4- and 5-coordinated UO_2^{2+}, are consistent with a dynamic equilibrium that favors five coordinating H_2O. The data further indicate that electron transfer from the uranium(VI) to the uranyl-oxygen is incomplete and that the effective charge of the uranium is less than indicated by its formal valence. In addition, a partial electron transfer from the hydrating waters to the uranium takes place, further lowering the effective charge of the uranium atom. The results described herein are in agreement with recent density functional calculations for an actinyl−water cluster embedded in a dielectric continuum.

Introduction

In this paper we present information obtained by X-ray scattering on the coordination environment of a molecular ion dissolved in water, specifically of the uranyl(VI) UO_2^{2+} ion. The linear dioxo-U(VI) ion has received considerable interest due to its importance for the environmental chemistry of radioactive elements, its complex electronic behavior, and its role as a benchmark system for higher actinides. As a result, a number of theoretical calculations on the uranyl and higher actinyl ions have appeared within the last four years,[1−9] all highlighting the importance of charge transfer in this system. Theoretical studies of these systems are complicated by the large number of electrons in U ($Z = 92$) and the large nuclear charge, which introduces relativistic effects. In contrast, the large number of electrons makes it an excellent candidate for study with high-energy ($E > 60$ keV) X-rays, as the scattering signal is large.

X-ray scattering data are used herein to probe the coordination environment of a uranyl ion in aqueous solution. X-ray scattering studies of uranium and actinide solutions have been rare,[10−17] and direct structural information on these systems has been mainly obtained by extended X-ray absorption fine structure (EXAFS) measurements.[18−26] Uranyl salts of strong acids hydrolyze in aqueous solution with resultant pH values near 2.[27−30] The choice of the counterion is crucial, since UO_2^{2+} is known to form relatively strong complexes with several counterions. It is accepted, however, that the perchlorate ClO_4^- ion is noncoordinating.[31] At higher pH values, UO_2^{2+} ions do form various oligomeric species,[32] but this study is restricted to acidic solutions, the solution as it forms on dissolution of the salt. Thus, the species we are investigating is the “isolated” uranyl ion, that is, UO_2^{2+} surrounded in its first coordination sphere by only water molecules.

Square-planar and hexagonal-planar coordination was once thought to be the dominant coordination of the UO_2^{2+} ion in the crystal, but Evans[33] made the case for planar-pentagonal coordination being equally as prevalent as four- and six-coordination. Since then, the number of crystal structures with five-coordinated uranyl has outnumbered those in which four- and six-coordination are found. Of particular note to the work presented here, five-coordination is also found in crystalline $UO_2(ClO_4)_2 \cdot 7H_2O$.[34] In the solid state, the coordination environment is necessarily static, but there are documented cases in which different coordination environments coexist in the same crystal.[35] Although 5-fold coordination has been found by the majority of the experimental studies[26] in solution, recent EXAFS[31] and NMR[36] studies of perchlorate solutions do report coordination numbers systematically below five.

X-ray scattering experiments are sensitive to the electron density distribution, and therefore the determination of atomic coordination numbers is correlated to some extent with the attribution of electrons to specific atoms. Since core electrons can be attributed with high confidence, this is generally a small effect, and the simplest approximation, the independent atom approximation, is by far the most commonly used in the interpretation of liquid scattering experiments. Discussion of electron densities in crystalline samples is not uncommon,[37,38] however, and a few studies have appeared recently aimed at accounting for the electron density modifications induced by chemical bonding in liquids.[39−42] We will discuss the implications on the derived coordination numbers in limiting cases of the charge redistribution between the uranium and its surrounding oxygen and hydrogen atoms.

Experimental Section

Uranyl solutions have been prepared by dissolution of $UO_3 \cdot 0.8H_2O$ in dilute perchloric acid. The powder-diffraction pattern of the $UO_3 \cdot 0.8H_2O$ was in agreement with literature.[43] In a separate experiment, the concentration of UO_2^{2+} of a solution of the $UO_3 \cdot 0.8H_2O$ in dilute sulfuric acid was determined by titration with a standardized NaOH solution (Aldrich) as described in the literature.[44] The composition of the solutions was determined directly from the mass of $UO_3 \cdot 0.8H_2O$, perchloric acid, and water added and measured with a precision better than 1%. The composition of the individual solutions is given in Table 1. The average UO_2^{2+} concentration of the three $UO_2(ClO_4)_2$ solutions is 0.500(5) mol kg^{-1} water or 111 water molecules per UO_2^{2+} ion. The $LiClO_4$ samples, which were used for data reduction procedures, were prepared either by dissolution of the salt or by neutralization. Several independently

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TABLE 1: Composition of the Individual Solutions Used in the Experiments (in mol %)[a]

	UO_2^{2+}/mol %	Li^+/mol %	ClO_4^-/mol %	H_2O/mol %
$UO_2(ClO_4)_2$ [1]	0.858		1.74	97.4
$UO_2(ClO_4)_2$ [2]	0.882		1.78	97.3
$UO_2(ClO_4)_2$ [3]	0.892		1.76	97.4
$LiClO_4$ [1]		1.81	1.71	96.5
$LiClO_4$ [2]		1.82	1.82	96.4

[a] The fraction of the three components UO_2^{2+} or Li^+, ClO_4^-, and H_2O are given as percentage of molecules of a given type relative to the total number of molecules, counting UO_2^{2+} or Li^+, ClO_4^-, and H_2O as single particles.

prepared UO_2^{2+} and Li^+ solutions, three UO_2^{2+} and two Li^+ solutions were prepared, sealed, and measured.

The samples were sealed in thin-walled, 3.0 mm diameter quartz capillaries for the X-ray scattering measurements. The capillaries were mounted within two superimposed containers of increasing diameter with Kapton windows, thus triple-encapsulating the radioactive sample. The data were collected in two different data acquisition periods at the high-energy scattering beam-line 11-ID-C[45] of the BESSRC−collaborative access team at the Advanced Photon Source. To minimize absorption, the energy for the scattering experiment was set to 115.1 keV, which is just below the K-absorption edge of uranium. Under these conditions the measured attenuation of the beam transmitted through a 3 mm sample of 0.5 M UO_2^{2+} solution is 8%, in agreement with the attenuation calculated from tabulated absorption cross sections. Data were collected covering the momentum transfer range $Q = 4\pi/\lambda \sin \theta$ from 0.3 to 35 $Å^{-1}$, corrected for detector dead-time, background (empty container), polarization and tangential detector movement, normalized to a cross section per formula unit and extrapolated to $Q = 0$ using standard procedures.[46]

The raw data from the $UO_2(ClO_4)_2$ solutions are shown in Figure 1a. Despite the need to triple-encapsulate the sample and the presence of air scattering, the signal-to-background ratio is about 10 at higher Q values. The proximity of the direct and scattered beams at $Q < 0.45$ Å vitiates a reliable background subtraction for this region; therefore, the first five points have been excluded from further analysis. The derived structure functions (defined below) are shown in Figure 1b. For the difference-structure function, this curve represents the average of the three independent measurements.

Calculation of Coordination Numbers from X-ray Scattering Data. The intensity of X-rays scattered from a liquid is proportional to the differential cross section ($d\sigma/d\Omega$) of the sample. For a noncrystalline system, the differential cross section, including Compton scattering, can be written[47] as a sum of a distinct- and a self-term, the latter of which does not depend on the interatomic structure:

$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\frac{d\sigma}{d\Omega}\right)_{\text{distinct}} + \left(\frac{d\sigma}{d\Omega}\right)_{\text{self}}$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{distinct}} = \sigma_{\text{Th}}(Q)\sum_{j,i} f_i(Q) f_j(Q)\gamma_i\gamma_j \int 4\pi\rho r^2[g_{ij}(r) - 1] j_0(Qr)\, dQ$$
$$= \sigma_{\text{Th}}(Q)\sum_{j,i} f_i(Q) f_j(Q)\gamma_i\gamma_j[s_{ij}(Q) - 1]$$

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{self}} = \sigma_{\text{Th}}(Q)\sum_i \gamma_i f_i^2 + \sigma_{\text{KN}}(Q)\sum_i \gamma_i C_i(Q) \qquad (1)$$

The $\sigma_{\text{Th}}(Q)$and the $\sigma_{\text{KN}}(Q)$ are the Thompson and the Klein-Nishina cross-sections which depend on the polarization of the X-rays; the $f_i(Q)$ and $C_i(Q)$ are the atomic form-factors and Compton intensities. The $g_{ij}(r)$ are the partial pair distribution functions between two atomic species and contain the information on the interatomic structure of the sample; the $s_{ij}(Q)$ are the partial structure factors. The γ_i are the concentration of species i and are conveniently taken such that $\sum_i \gamma_i = 1$ and $j_0(x) = \sin(x)/x$ is the zeroth-order Bessel function. The self-scattering dominates liquid scattering at high momentum transfers and can be used for absolute normalization, that is, for determining the proportionality between the measured intensity and the differential cross section.

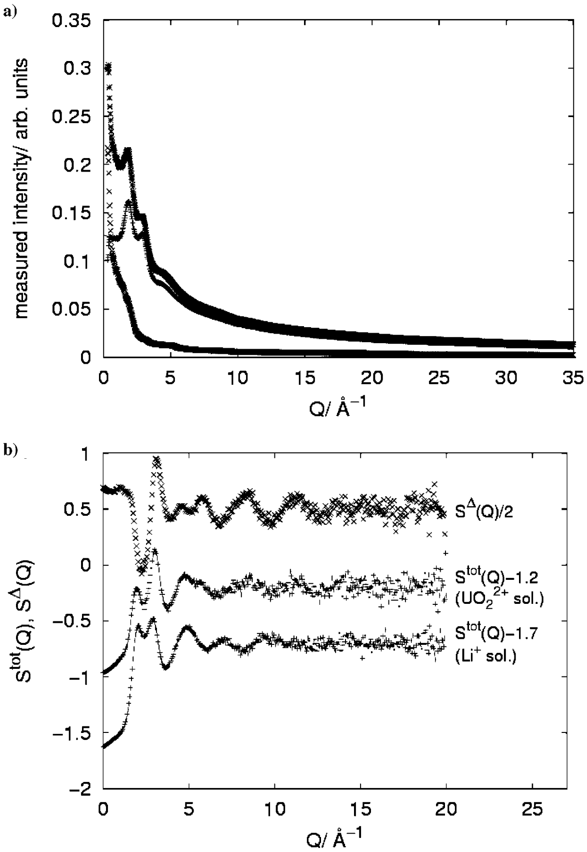

Figure 1. (a) Experimental scattering intensities from the $UO_2(ClO_4)_2$ solution. From top to bottom: Sample + background intensity, background-corrected intensity, and background intensity. At $Q < 0.45$ $Å^{-1}$, a reliable background subtraction is not possible and consequently the data are extrapolated. (b) The structure factors $S(Q)$ for the $LiClO_4$ and the $UO_2(ClO_4)_2$ solution and the difference function $S^{\Delta}(Q)$. The structure functions are scaled and shifted as indicated in the plot. The momentum-transfer range $Q > 20$ $Å^{-1}$ has been used for normalization only.

It is apparent from eq 1 that the correlations between all atoms contribute to the scattering intensity. We are interested in the local environment of the U-atom. A weighted difference between the differential cross section of $UO_2(ClO_4)_2$ and a $LiClO_4$ solution:

$$\Delta\left(\frac{d\sigma}{d\Omega}\right) = (\gamma_{H_2O}^{Li^+})^2\left(\frac{d\sigma}{d\Omega}\right)_{UO_2ClO_4} - (\gamma_{H_2O}^{UO_2^{2+}})^2\left(\frac{d\sigma}{d\Omega}\right)_{LiClO_4} \qquad (2)$$

eliminates to a first approximation the correlations between H_2O itself, H_2O and ClO_4^-, and ClO_4^- itself. Here $\gamma_{H_2O}^{Y}$ is the concentration of water in the solution containing the Y ion. The factor γ^2 reflects the fact that the total number of particles in the $UO_2(ClO_4)_2$ and $LiClO_4$ solutions is slightly different.

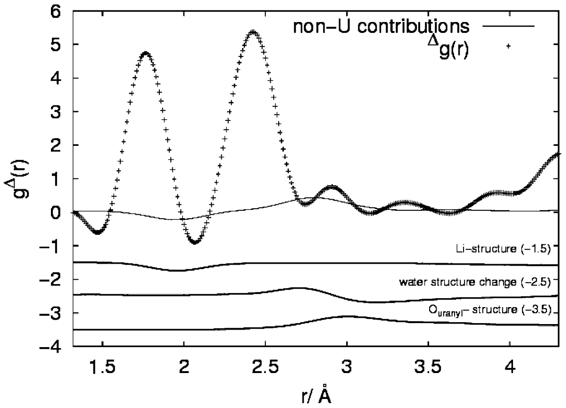

Figure 2. The difference pair distribution function $g^\Delta(r)$ obtained by FT of the structure factor $S^\Delta(Q)$. The three non-uranium contributions to $g^\Delta(r)$ corresponding to the three trailing terms in eq 4 are shown. These curves are shifted as indicated in the figure. The total non-uranium contributions to $g^\Delta(r)$ are shown with a thin line.

With the definition of a structure function $S^\Delta(Q)$ corresponding to the differential cross section:

$$S^\Delta(Q) - 1 = \frac{\Delta\left(\frac{d\sigma}{d\Omega}\right)_{\text{distinct}}}{\sigma_{\text{Th}} N^\Delta(Q)} \tag{3}$$

—$N^\Delta(Q)$ is a factor to normalize the sum of the weighting factors: $\sum w_{ij}(Q) = 1$ of the partial structure factors—$S^\Delta = \sum w_{ij} s_{ij}$ can be written as a sum of four groups of partial structure factors:

$$S^\Delta N^\Delta = \sum_i w_{\text{U},i} s_{\text{U},i}^{\text{UO}_2^{2+}} - \sum_i w_{\text{Li},i} s_{\text{Li},i}^{\text{Li}^+} + \sum_{i,j \neq \text{U,Li,O}_\text{U}} w_{ij}(s_{ij}^{\text{UO}_2^{2+}} - s_{ij}^{\text{Li}^+}) + \sum_i w_{\text{O}_\text{U},i} s_{\text{O}_\text{U},i}^{\text{UO}_2^{2+}} \tag{4}$$

the (composite) uranium structure factor $S_{\text{UX}} = \sum_i w_{\text{U},i} s_{\text{U},i}^{\text{UO}_2^{2+}}$, the lithium structure factor, the structure changes induced by the presence of either UO_2^{2+}or Li^+ on the structure functions not involved in the exchange, especially those structural changes induced in the water structure,[48] and the uranyl-oxygen structure factor. The contribution of the non-U partial structure factors, the last three terms in eq 4, is small, and we believe their contribution can be reasonably estimated from extrinsic information. Their contribution to the pair distribution function $g^\Delta(r)$ obtained from a molecular dynamics simulation of $LiClO_4$ and $UO_2(ClO_4)_2$ is shown in Figure 2, the pair distribution function given by the Fourier-Bessel transform of $S^\Delta - 1$. All three non-U components together do not exceed 8% of the peak height of g^Δ. The experiment reported here is, hence, not an isomorphic g^Δ substitution experiment in the sense the term has been used by Skipper et al.[49] In fact such an experiment would not be possible, as the dioxo-ion chemistry of the actinides does not have a correspondence in lighter-element chemistry.

The coordination number $N_{j(i)}$ of particles type j around a particle type i can be obtained by integration of the partial pair distribution function.[50] For a composite pair distribution function like g_{UX} the weight $w_{ij}(0)$ of the s_{ij} in S_{UX} has to be taken into account in the calculation of the coordination number. Whereas the shape of $w_{ij}(Q)$ influences the detailed shape of a peak in g_{UX}, the integral over that peak only depends on the value $w_{ij}(0)$, hence the use of $w_{ij}(0)$ in the following equation (compare Appendix):

$$N_{j(i)}(r_u) = \frac{N^\Delta(0)}{2\gamma_i\gamma_i f_i^*(0)\, f_j^*(0)} \int_0^{r_u} 4\pi\rho_j r^2 g_{\text{UX}}(r)\, \mathrm{d}r \tag{5}$$

with $\rho_j = \gamma_i\rho$, and the factor 2 is valid for $i \neq j$. In this equation, $N^\Delta(0)$ needs to be calculated in a manner consistent with eq 4; the atomic form-factors $f(Q)$, however, have been replaced by the form-factors $f^*(Q)$ of the actual, charged atoms present in the sample. For uranium, as an example, $f_\text{U}^*(0)$ could vary between 86 for U^{6+} and 92 for neutral uranium, since the value of the form factor at $Q = 0$ is identical to the number of electrons Z^* associated with that atom:

$$f_i^*(0) = Z_i^* \tag{6}$$

Thus, to accurately determine the atomic coordination number, the charge of the atoms must be known. Alternatively, if the atomic coordination number is known, the charge state of the atoms can be deduced, while only an electronic coordination number can be calculated if the atomic coordination number is unknown.

If we calculate instead of the atomic coordination integral in eq 5 an electronic coordination integral:

$$N'_{\text{el}}(r_u) = \frac{N^\Delta(0)}{2\gamma_i} \int_0^{r_u} 4\pi\rho r^2 g_{\text{UX}}(r)\, \mathrm{d}r = f_i^*(0)\, f_j^*(0)\, N_{j(i)} \tag{7}$$

we obtain the product of the number of electrons on atom i and j multiplied with the atomic coordination number. This electronic coordination number is independent of the attribution of electrons to specific atoms. Since the relative change of electron density in uranium is small, compared to the change in the oxygen and hydrogen surrounding it, it is convenient to calculate:

$$N_{\text{el}}(r_u) = \frac{N'_{\text{el}}}{f_\text{U}(0)} = \frac{f_\text{U}^*(0)}{f_\text{U}(0)} f_j^*(0)\, N_{j(U)} \approx Z_j^* N_{j(\text{U})} \tag{8}$$

$N_{\text{el}}(r_u)$ is thus approximately the number of electrons of the ligand atoms within $r = [0, r_\text{u}]$ from the uranium atom projected onto the nuclear positions.

Results and Discussion

The experimental difference pair distribution function g^Δ and the derived uranium pair distribution function g_{UX} are shown in Figure 3a and 4a. The position of the peak maxima originating from the uranyl U=O double bonds and the water molecules coordinated to UO_2^{2+} are at 1.766(1) and 2.420(1) Å. There is an additional broad peak centered at $r = 4.46$ Å (off the figure), that is attributed to the second water coordination shell[15] and, potentially, to solvent-separated UO_2^{2+} ClO_4^- pairs. It is noted that the uranyl peak position (1.766 Å) is slightly larger than 1.761 Å, the average value of 76 crystal structures containing uranyl with water coordination[3] and within the range of distances obtained by EXAFS spectroscopy from solutions (1.75−1.78 Å, 1.765 on average[26]). The value obtained earlier by an X-ray scattering measurement in solution, 1.702 Å,[15] is significantly shorter than any of these distances. The peak position for the UO_2^{2+} water-oxygen peak (2.420 Å) is likewise in good agreement with other experimental results. The distances determined with EXAFS spectroscopy vary in the range 2.40−2.46 Å,[26] with an average of 2.43 Å, and the value found by

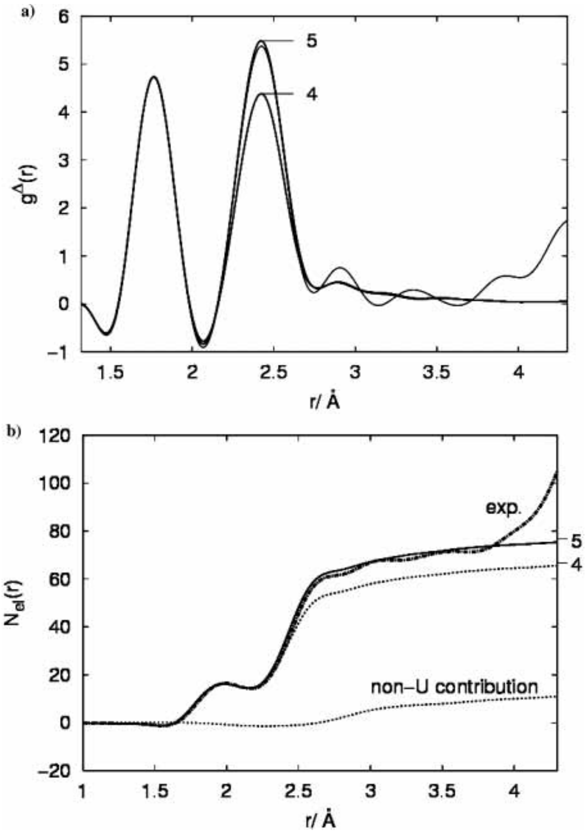

Figure 3. The difference pair distribution function $g^{\Delta}(r)$ (a) and integrated electron numbers $N_{\mathrm{el}}(r)$ (b) for the UO_2^{2+} in perchlorate solution compared to the theoretical functions for uranyl coordinated to four and five water molecules. The theoretical curves corresponding to the four- and five-coordinated cluster[1] are annotated with the corresponding number, the unmarked solid line is the experimental result.

the earlier scattering experiment,[15] 2.421(5) Å, agrees well within the error. The values reported here are the peak positions, hence should be interpreted as the most likely bond distance. They do not take into account any anharmonicity corrections and do not reflect a possible deviation of the average bond distance from the most likely bond distance.

The two peaks at 1.766 and 2.420 Å give rise to two steps in the electron integral as shown in Figures 3b and 4b. The peak at 1.77 Å—this peak belongs to the uranium- uranyl-oxygen correlation and uranium's atomic coordination number with uranyl-oxygen is unambiguously two—is found to give an average value of the N_{el} integral in the interval [2.0 Å $< r <$ 2.15 Å] of 16.4(8) (Figure 4c). This error estimate is the deviation of the maximum and minimum value from the average. (See the Appendix for the discussion of this uncertainty estimate.) The experimental value for this integral is close to the value of 16, expected in the independent, neutral-atom approximation, and significantly below 20, expected if each of the uranyl oxygens acquires two electrons from uranium. The integral value found corresponds to the transfer of considerably less than one electron per oxygen. Apart from the results of quantum mechanical calculations discussed later, there are independent indications that a complete electron transfer of two electrons to the uranyl-oxygen does not occur. Guilbaud et al.[51] optimized a potential of charged Lennard-Jones particles for use in molecular dynamics simulation to agree with relative solvation enthalpies and found the best agreement for charges of +2.5 for the U and −0.25 for each of the uranyl oxygens. Denning et al.[9] interpreted their X-ray absorption and photoemission data on crystalline $Cs_2UO_2Cl_4$ with models that exhibit a charge of −0.5 at each oxygen.

The N_{el} integral of the uranium−water peak at 2.42 Å is 46.1(7) (Figure 4d). This value represents the average taken in the interval [3.5 Å $< r <$ 3.7 Å] and thus includes the contribution from the water-hydrogen electrons. That is considerably less than the value of 50 electrons one would expect from simple arguments, if five water molecules coordinate uranyl and there is no charge transfer from water to uranium.

In contrast to the case of the uranyl-oxygens, the atomic coordination number for the solvation water molecules is not known a priori. As detailed in the Introduction, planar-pentagonal coordination is the dominant coordination in the solid state and is also found in crystalline $UO_2(ClO_4)_2{\cdot}7H_2O$.[34] However, recent EXAFS[31] and NMR[36] studies of perchlorate solutions do report coordination numbers systematically below five. The value of the electron integral can be interpreted either as an electron transfer from the water molecules to the uranyl or as an average atomic coordination number below five. The quantum mechanical calculations[1−9] cited in the Introduction do predict a back-transfer of electron density from the water ligands to the uranium atom in the order of 0.3 electrons. This effect reduces the integral value to be expected for the five-coordinated complex to 48.5, still above the experimentally determined value. It is difficult to argue that each water molecule can transfer almost a full electron to the uranium. An alternate interpretation, that the average atomic coordination number of UO_2^{2+} is below five in perchlorate solution, is more consistent with our results.

The above arguments are approximate as expressed by eq 8 and by the limitation explained in the Appendix; however, they do not require any assumptions about thermal vibration parameters or about the orientation of the hydrating water molecules relative to uranyl. We use two uranyl−water clusters, with four and five water ligands, whose electronic structures have been previously discussed[1] as a starting point for further discussion, and we compare in Figures 3 and 4 the experimental result with the pair distribution functions, $g^{\Delta}(r)$ and $g_{\mathrm{UX}}(r)$, and the electron integrals, $N_{\mathrm{el}}(r)$, of these clusters. We first note that the integral N_{el} of the clusters follow the experiment very closely in the region between the peaks. We can therefore fix the charge on the uranyl-oxygen at the value of −0.25 obtained in the density functional calculation.[1] The charges on the water-hydrogen and -oxygen atoms are more problematic as they are correlated to the ratio of the five-/four-coordinated species. If we fix the water charges to the values obtained by the quantum mechanical calculations, we can fit the ratio between five- and four-coordinated uranyl ions and obtain a ratio of 88:12. We can also determine the two limiting values for the five/four ratio assuming no electron back-transfer (i.e., the charge of the coordinating water molecules is zero) or complete electron back-transfer (i.e., the charge of the uranyl ion is zero and the positive charge is completely assumed by the coordinating water molecules). In these cases, the best fit is reached for 79% and 94% five-coordinated complex, respectively. Thus, even for the rather extreme assumption of a complete electron back-transfer, the integral of the peak at 2.42 Å is lower than required for ideal 5-fold coordination. Turning the focus back to the first peak, we compare the values of the local maxima and minima of the integral in the region between the peaks in $g(r)$. For the 88:12 mixture of clusters we find 17.03 at the maximum and 15.62 at the minimum, which is 16.33 on average. The amplitude of the oscillation found experimentally is larger with 17.21 at the maximum and 15.58 at the minimum, but the average of

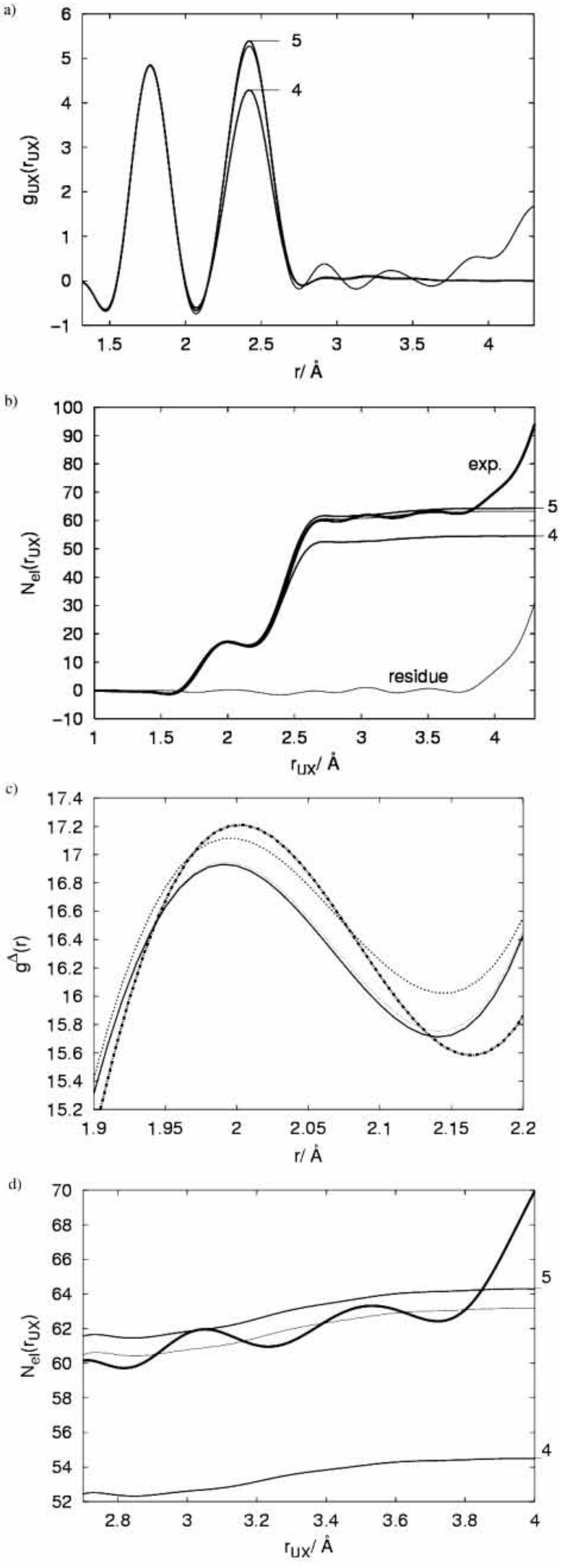

Figure 4. The uranium pair distribution function $g_{UX}(r)$ after correction for the non-uranium contributions (a) and integrated electron numbers $N_{el}(r)$ (b) for the UO_2^{2+} in perchlorate solution compared to the theoretical functions for uranyl coordinated to four and five water molecules. The result of a fit of the ratio of five- and four-coordinated uranyl as well as the residue of that fit are also shown as thin lines. Close-ups showing $N_{el}(r)$ in the regions [1.9 Å < r < 2.2 Å] and [2.7 Å < r < 4 Å] are shown in (c) and (d).

16.39 is in remarkable agreement, justifying the choice of a uranyl-oxygen charge of −0.25.

A mixed coordination of uranyl with water implies that the energies of the five- and the four-coordinated species are comparable in the aqueous solution under investigation. Calculations[1] indicate that significant changes in the relative energies of the four-, five-, and six-coordinated complexes occur if the environment is altered from an isolated cluster in the gas phase to a cluster embedded in a dielectric continuum, mimicking the influence of water molecules surrounding the uranyl-water cluster. Under these conditions the stability of the four-coordinated cluster is increased. This statement is supported by the calculations of Farkas et al.[3] The atomic coordination number therefore is expected to be sensitive to the environment of the uranyl−water cluster. Four- and five-coordination are both realized in the solid state depending on the environment, even within the same crystal, as outlined in the Introduction. We argue that our result, taken together with calculated relative stabilities of 4- and 5-coordinated UO_2^{2+}, are consistent with a dynamic equilibrium that favors the five-coordinated state. Temperature-dependent measurements could address this hypothesis, and indeed high-temperature EXAFS measurements on $UO_2(NO_3)_2$ solutions[52] indicate the breakdown of five-coordination at 478 K. It should be finally noted that a more complex mixture of 5-4-, and 6-fold coordination with the same average coordination number cannot be ruled out from our results. However the relative stability of the 6-fold coordination has been found the lowest in the density functional calculation.[1] In the crystal, 6-fold coordination is found mainly with bidentate ligands. Both facts argue against the presence of 6-fold coordinated uranyl in perchlorate solution.

Conclusion

In this paper we demonstrate that liquid X-ray scattering experiments with high-energy X-rays can give a detailed picture of the coordination environment of UO_2^{2+} in perchlorate solution. The integral of the first peak in g^{Δ} and g_{UX} originating from the uranyl-oxygens is consistent with the charges assigned to the uranyl-oxygen in previously published calculations. The electron density found on the equatorial water molecules is best interpreted in terms of a dynamic equilibrium of four and five coordinating waters. The exact value of the ratio of five- to four-coordination depends on the assumed electron back-transfer from ligand water to the uranyl ion. Assuming the electron back-transfer from the density functional calculations, a mixture of four- to five-coordinated uranyl ions containing 12% of four-coordinated uranyl fits the data best. Under the extreme assumptions of no or of complete electron back-transfer, this value varies from 21 to 6%.

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Appendix: Error Estimation

Calculation of the influence of statistical errors within the data on the derived pair distribution function and the coordination integrals is straightforward and implies only calculation of error propagation in a sum.[46] The experimental g_{UX}, depicted in Figure 4a, shows small oscillations (with maxima, e.g., at 2.8, 3.3, and 3.8 Å). Such oscillations are often interpreted as the truncation effect that results from a limited available Q space for the Fourier transform. The theoretical g_{UX}, for the water cluster, which has been obtained via a Fourier transform over

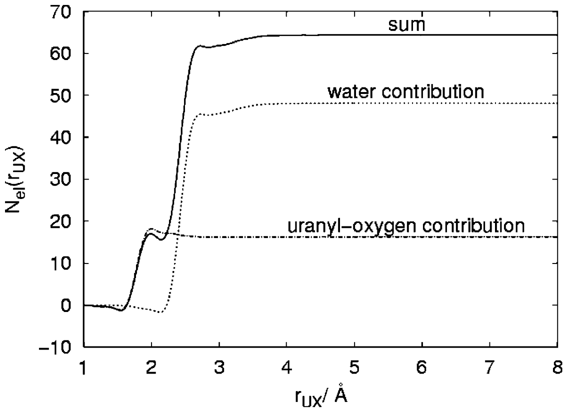

Figure 5. Individual contributions of the uranyl-oxygen and the water shell to the integral $N_{el}(r)$ for the five-coordinated model.

the same Q-range, shows these oscillations to a much lesser extent, indicating that the truncation effect is not the only and not the dominating reason for these oscillations. Instead, it is the limited, but still high, statistical accuracy of the data that is responsible for these oscillations. Due to the random nature, these oscillations have both a positive and a negative contribution to the coordination integrals and its influence is, hence, smaller there.

More difficult is the evaluation of systematic errors. In liquid scattering experiments at X-ray energies given by the typical X-ray tubes 8−22 keV, errors associated with absorption, fluorescence, and multiple scattering corrections dominate. These errors almost vanish at high energies.[53] The measured intensity has to be normalized to the self-scattering to obtain a differential cross section in absolute units. The self-scattering is calculated from form-factors and the Compton scattering amplitudes calculated within the independent atom approximation[54] from atomic electron densities. It has been pointed out that deviations from the independent atom approximation are not expected to affect the normalization since the form factors are dominated by core electron contributions at high Q. The form-factor of hydrogen, whose relative magnitude varies the most as a function of its charge, does not affect the normalization as it is entirely due to valence-electron density and therefore confined to the low-Q region. The limit of Compton scattering amplitudes at high Q converges to the total number of electrons and is also left unchanged upon charge redistribution. However, two other factors limit the accuracy with which normalization can be done. The atomic electron distributions—the input to form-factor calculations—do have a limited accuracy, and published values of the atomic form-factor vary by 6.5% at $Q = 35$ Å^{-1} for uranium.[54,55] It is noted that this uncertainty is introduced by the uncertainty in the core electron distribution and therefore manifests itself at high Q. That makes it relevant for the normalization and introduces an uncertainty of about 2%. The other source of error is the anomalous (resonant) contributions to the form-factor. This contribution can be safely neglected at the high energies for all elements present in the sample except uranium. According to Chantler's tabulation,[56] the resonance contribution to the uranium form-factor at the energy of the experiment is −3.6 electron units. However, this calculation assumes a sharp U−K edge and is therefore considered as an upper limit for the anomalous contribution. In principle, choosing an energy farther away from the absorption edge can largely eliminate this effect. Thus, the resonant contribution to the uranium scattering also introduces an error in the order of 2% to the normalization constant.

The integral of eq 5 and eq 7 of one individual shell of coordinating atoms is only reached asymptotically as demonstrated in Figure 5. Here, the contributions of the peaks are integrated individually for the five-coordinated model. The oscillation between the peaks can be seen to result in a sum of a positive deviation from the asymptotic value of the integral of the uranyl-oxygen peak and a negative deviation of the integral of the hydration-water peak. Since this oscillation occurs for the model distribution, it cannot be the result of statistical errors but is rather the effect of the convolution with a Q-dependent weighting-factor. This is important and means that estimating the error on the uranyl-oxygen charge by the amplitude of this oscillation is an overestimation. However, this behavior limits the accuracy of the model-free interpretation of the integral followed in the first part of the discussion as that requires the approximate compensation of the positive and negative deviations from the asymptotic value of both peaks.

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