

# A theoretical study of uranyl solvation: Explicit modelling of the second hydration sphere by quantum mechanical methods

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## Abstract

The inclusion of an explicit second sphere in the hydration of the uranyl ion is investigated by DFT. We study model complexes that contain two water molecules in the second sphere hydrogen-bonded to each water molecule in the first. Compared with single-sphere models, significant changes are observed for the uranium–water first-sphere distance, the uranium–“yl” oxygen distance and the uranyl stretching vibrational frequencies. For each of these observables, agreement with experiment is improved with our new model. Charge transfer to uranyl is substantially enhanced when the second hydration sphere is present. Effects of third and subsequent hydration spheres appear to be small, but the influence of water molecules linked to the apical oxygens by a hydrogen-bonding network is probably not negligible. Models based on a polarizable continuum are less satisfactory, particularly for the vibrational frequencies. The uranyl stretching frequencies are highly correlated with charge transfer from water molecules to the “yl” oxygen atoms and with the uranyl bond length.

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## 1. Introduction

Quantum mechanical (QM) calculations have been applied to various aspects of the chemistry of the uranyl ion ( $\text{UO}_2^{2+}$ ): topics such as the structure [1], the vibrational frequencies [1], complexation with various neutral or charged ligands [2], ligand exchange [3], reduction potentials [1] and solvation [4] have all been studied, with generally pleasing success. However, the treatment of solvation still requires development, because it is one of the dominating terms for most of those topics and the results obtained to date are not completely satisfactory in a quantitative sense. The main problem to be treated is not the high atomic number of uranium, but the nature of solvation itself: the large number of water molecules required, the

unknown structure of the aquo-complexes, and the multiplicity of co-existing structures due to thermal agitation. A completely satisfactory treatment of solvation in aqueous media will of course require dynamics to be taken into account, but we are not there yet; we limit ourselves in the present work to a static description, since even that is a substantial challenge.

The influence of the solvent can be represented in various ways. In continuum models (CM), the solvent is described as a homogeneous medium [5,6]. These models account for long-range interactions, but cannot fully describe any “chemical” interactions with the solute, since a proper model will necessarily be explicit, implying a QM treatment. With appropriate corrections, these models can, however, include dispersion and repulsion phenomena between the solute and the solvent. They are most suitable when no covalent bonds are involved. CM do not allow for any charge transfer between the medium and the solute [7],

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though this can be important for a solvent that includes hydrogen bonds and for a highly charged solute such as the uranyl ion. However, the addition of a continuum around a uranyl ion solvated by a first shell of water molecules that are treated by QM methods does induce some charge transfer, through polarization of the continuum. The solvation of the uranyl ion using CM approaches has been studied in [8,9] with the COSMO formalism, and in [10] with the IEFPCM. The results obtained for the U=O bond length show that a treatment using only the CM approach is unsatisfactory. Significant improvement is obtained if the first hydration shell is treated explicitly by QM methods, and a relatively small change is obtained if the (ion + first hydration shell) is solvated by a CM.

It is also possible to treat solvation by molecular mechanics (MM). In approaches based on this philosophy, the solute is described explicitly by QM methods, but the solvent molecules are treated by empirical parameters. One advantage of this approach is that it is possible to include a very large number of solvent molecules in the chemical system, but the data needed for extraction of the parameters are rarely available. It is possible to combine QM and MM approaches, as for example in [4].

It is not currently easy to use a completely QM approach for a full treatment of solvation, since the electrostatic interactions between a highly charged ion such as uranyl and a polar solvent such as water extend over a very long range, meaning that a very large number of water molecules need to be described. A model potential developed for the treatment of uranyl–water systems shows that interactions involving water molecules in the third solvation “shell” are still of the order of 25 kJ/mol, i.e., larger than those between adjacent water molecules in the bulk [11]. There have been a few studies adopting explicit QM descriptions of solvation. In [12], Hartree–Fock calculations were reported of  $[\text{UO}_2(\text{H}_2\text{O})_n]^{2+}$ , with  $n = 5$  and 6. Partial geometry optimization was undertaken and the effects of the addition of a second sphere on electronic populations were explored. The geometry of some uranyl nitrate hydrate complexes was studied in [13] with DFT methods, where it was shown that addition of a partial second sphere gave results in much better agreement with the structure found in the solid state.

A recent publication uses CPMD to study the coordination of uranyl in water [14]. The use of both quantum mechanics and molecular dynamics should result in a very realistic calculation, although the high computational cost reduces the number of solvent molecules that can be treated. Static methods, such as those we use in the present paper, allow a step-by-step analysis (1 hydration sphere, 2 hydration spheres, apical links). For this reason, we believe that static and dynamic methods are complementary, as they view the system for different viewpoints. We note that our analysis enables us to predict vibrational frequencies and we also report Natural Population Analyses that can be used for interpretation of the numerical results obtained.

The scope of the present work is to investigate the consequences of treating explicitly a second hydration sphere by QM methods, and to compare with experiment where possible. We make a few simplifying hypotheses and assumptions. First, we concentrate our attention on a limited number of observables: molecular structure (in particular, bond distances), Raman and IR vibrational frequencies and charge transfer. These parameters are strongly correlated. Precise experimental values of the vibrational frequencies are available for the uranyl ion in aqueous solution. We do not attempt here a definitive theoretical study of the energetics of solvation, for two reasons: first, the approach that we have adopted is not particularly suitable for this purpose, as will become clear, and second, the experimental data available are so imprecise that no useful theory–experiment comparison can be undertaken at present.

Second, the system that we study is mostly limited to a partial second solvation shell, though we also have some partial results for the influence of a third shell. This partial second shell is limited to water molecules that are hydrogen-bonded to those in the first shell: two molecules in the second shell for each one in the first. It seems plausible to suppose that charge transfer is mostly mediated through hydrogen bonds, and we therefore suppose that additional water molecules may be neglected so far as this parameter is concerned. It is surely an approximation to suppose that all molecules in the second hydration shell are H-bonded, and so one might conclude that this approach must overestimate the effects of charge transfer from the second shell. In fact, thermal agitation both increases and decreases internuclear distances, and, more importantly, it moves molecules in an angular sense away from positions that are optimal for H-bonding and charge transfer, so we can draw no firm conclusions about the sign of our likely error here. We have estimated limits for the under-estimation of charge transfer caused by the absence of third and subsequent hydration shells.

Third, we have imposed idealized symmetries on our models, such as  $D_{4h}$  or  $D_5$ . Subsequent vibrational analysis reveals some very low imaginary vibrational frequencies that correspond to rotations of water molecules. These instabilities are simply consequences of our simplified models that (mostly) ignore hydration beyond the second sphere. Within these limitations, we believe that our calculations establish beyond doubt that the effects of a second hydration shell are quite large on the parameters which interest us here. We note that we have not detected any inconsistencies for any of the quantities of principal importance to us (bond distances, charge transfer and vibrational frequencies) due to changes in the symmetry imposed.

## 2. Computational details

All the calculations were performed with the Gaussian 98 package [15]. In most cases, we used the hybrid B3LYP version of density functional theory [16]. It has pre-

viously been shown that this hybrid method gives reliable results, when compared to fully relativistic 4-component methods, at low computational cost [17]. We adopted a “small-core” pseudopotential for uranium that describes 60 electrons, with the remaining 32 semi-core and valence electrons (5s, 5p, 5d, 5f, 6s, 6p, 6d and 7s) treated explicitly [18]. The associated [10s, 11p, 9d, 8f] basis was flexibly contracted to (8s, 8p, 6d, 5f) for  $U^{4+}$ , as described in [17]. For oxygen, we used the pseudopotential and basis set described in [19]; the basis is of “double-zeta plus diffuse plus polarization” quality ( $\xi_{3d} = 0.73$ ). A standard double-zeta basis was used for hydrogen [20].

A few test calculations were performed under different conditions. In some, a polarization function ( $\xi_{2p} = 0.90$ ) was added to the hydrogen basis. In others, the PW91 exchange and correlation functionals were adopted [21].

### 3. Results

#### 3.1. Notation adopted for the structures considered

All the structures considered in this work are identified and characterized in the text with the following notation:  $U/x/y/sym/ind/z$ .  $U$  stands for the uranyl ion;  $x$ ,  $y$  and  $z$  are the number of water molecules in the first, second and third hydrogen spheres, respectively, those in shell  $(n + 1)$  being hydrogen-bonded to those in shell  $n$ .  $Sym$  is the point-group symmetry label.  $Ind$  is an optional indicator to describe the structure:  $ind$  equals “o” if each plane containing a water molecule in the second sphere is orthogonal to the plane containing the water molecule of the first sphere to which it is hydrogen-bonded, and  $ind$  equals “p” if these planes are parallel. (Note that this indicator is not appropriate in all cases, for example if the overall symmetry is  $D_5$ .) We also describe structures of the type  $U/x/PCM$ , where the continuum model has been adopted. The  $U/5/10/D_5h/p$  structure is represented in Fig. 1 (compared with the MOLEKEL program) [22,23]. A summary

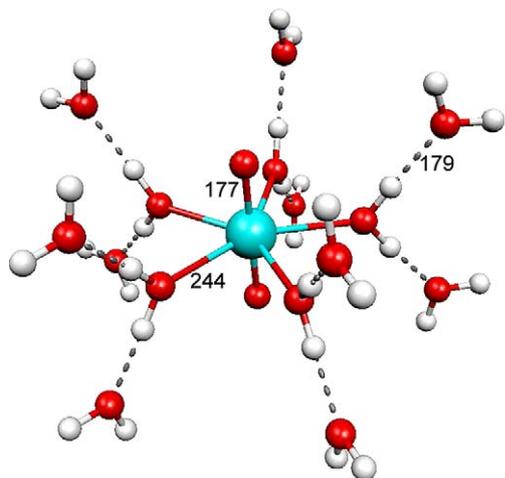


Fig. 1. Perspective view of a  $U/5/10$  structure (S8). Point group is  $D_{5h}$ . Distances are indicated in pm.

of the results obtained for all the structures considered is presented in Table 1.

#### 3.2. Overview of similar structures

For most of the systems studied in this work, we report results for different symmetries. This provides one way of checking the consistency of our results. It is important to understand that in most cases we are modelling only a partial second sphere; in other words, we do not pretend that our model is completely realistic, but rather that it is representative of possible solvation models. It is also important to realize that many different structures can presumably coexist in solution.

We remark first that the calculated uranyl bond lengths are increased appreciably by coordination in the first hydration sphere, as already noted by other workers [1,8,10]; we find increases of 4.4 or 4.7 pm for coordination of four or five water molecules. The orientation of the water molecules in the second sphere has only a small influence on the properties of the uranyl group. Within a given group, such as  $U/5/0$ ,  $U/4/8$  or  $U/5/10$ , the differences in uranyl bond lengths are typically only around 0.4 pm, and never more than 0.9 pm. The orthogonal orientation of these second-sphere molecules is slightly more favourable than the parallel, for example by nearly 10 kJ/mol for the  $U/4/8/o$  and  $U/4/8/p$  comparison; when the symmetry is lowered from  $D_{4h}$  to  $D_4$ , the resulting structure S7 turns out to be a true minimum. The properties of the uranyl group in this structure (bond length and symmetric stretching frequency) are intermediate between those of the structures with “o” (S6) and “p” (S5) conformations.

Although the  $U/4/0$  structure with  $D_{4h}$  symmetry (S2) is a true minimum, in which the water molecules are perpendicular to the equatorial plane, the  $U/5/0$  species adopts a geometry with only  $D_5$  symmetry (S4); each water molecule is twisted about the  $U-O$  direction by about  $21^\circ$ , leading to a small energy gain of 3 kJ/mol, as first shown in [24]. This tendency is strongly reinforced by the presence of the second hydration sphere, as the energy difference between  $U/5/10/D_5$  and  $U/5/10/D_{5h}$  is as large as 31 kJ/mol. Since the dominant coordination number has been shown experimentally to be 5 [25,26], the  $U/5/10$  complexes are the most realistic amongst those we have studied. The Raman (symmetric-stretch) vibrational frequency for the three structures we have considered in this group varies between 895 (S8) and 914 (S9)  $cm^{-1}$ , with the most stable structure S10 roughly in the middle of the range at 902  $cm^{-1}$ . Since this frequency difference arises just from the rotations of water molecules in the second sphere, we infer that this range indicates the accuracy that can be achieved by our type of model in which simplifying assumptions are made about the orientations of the second hydration sphere. The experimental width of the Raman band is about 25  $cm^{-1}$  [27], presumably because several different structures co-exist in solution. When considering the  $U/4/8$  and  $U/5/10$  structures together, the difference between the

Table 1  
Summary of modelled structures

Name	Hydration structure in sphere			Apical link	Point group	Distances (pm)		NPA charges (milli-electron)		Raman frequencies $\nu_1$
	1st	2nd	3rd			dUOyl	dUOH	qU	qOyl	
S1	0	0			$D_{iH}$	170.50		3302	−651	1039
S2	4	0			$D_{4H}$	174.93	243.69	3100	−782	953
S3	5	0			$D_{5H}$	175.29	250.09	3100	−808	944
S4	5	0			$D_5$	175.20	250.16	3103	−805	945
S5	4	8			$D_{4H} p$	177.28	236.25	3065	−852	902
S6	4	8			$D_{4H} o$	176.51	238.04	3069	−831	918
S7	4	8			$D_4$	176.80	237.21	3069	−840	912
S8	5	10			$D_{5H} p$	177.49	244.01	3078	−875	895
S9	5	10			$D_{5H} o$	176.65	245.96	3088	−853	914
S10	5	10			$D_5$	177.14	244.25	3088	−868	902
S11	5	10			$C_1$	177.49	244.01 <sup>a</sup>	3079	−876	900
S12	5	10		Yes	$C_S$	178.51	242.43 <sup>a</sup>	3112	−916	875
S13	5	10		Yes	$C_2$	178.70	242.44 <sup>a</sup>	n.a.	n.a.	876
S14	4	8	16		$D_{4H}$	177.43	235.75	n.a.	n.a.	899
S15	4	D-PCM			$D_{4H}$	176.10	237.85	3093	−822	929
S16	4	C-PCM			$D_{4H}$	176.13	237.69	3094	−821	928
S17	5	D-PCM			$D_{5H}$	176.52	244.40	3088	−847	917
S18	5	C-PCM			$D_{5H}$	176.52	244.05	3087	−845	917
[25]						176.6	242.0			
[35]						176	241			
[27]										870

<sup>a</sup> Indicates average distances.

highest and lowest Raman frequency is  $23 \text{ cm}^{-1}$  (structures S6 and S8). We conclude that none of our 2-sphere structures can be excluded on the basis of the Raman frequency.

### 3.3. Uranyl coordination number and water distance

Experiments show that the average number of water molecules coordinated to the uranyl ion in the equatorial plane is between 4 and 5, but closer to 5 [25]. Various computational predictions have been reported [1,10,12,28–32]. There is general agreement that the most favoured coordination number is 5 in the gas phase, but with only a small energy difference compared to coordination of six water molecules, and that five is also preferred in the liquid phase, by a greater energetic margin. The quality of the calculated results is therefore improved when attempts are made to describe hydration. However, a very recent publication states that five and six-coordination are equally preferred [10].

Calculations for systems limited to the first hydration sphere typically lead to uranium–water distances that are substantially overestimated, by some 7–10 pm. This distance has recently been reported to be 242.0(1) pm by X-ray diffraction [25], confirming previous results [33]. Similar values were obtained by EXAFS studies [34–36]. Our prediction here for the U/5/0 species is 250.1 pm, and other authors have obtained fairly similar results with different theoretical methods [1,10].

Comparing our results for U/4/0 with those for U/4/8, or for U/5/0 and U/5/10, we find a shortening of the U–water distance due to the second hydration sphere of 8 or 6 pm, respectively; the resulting distances of 236 pm for U/4/8 or 244 pm for U/5/10 bracket the most recent and

most precise experimental result of 242.0(1) pm [25]. Since this X-ray experiment reported that between 6% and 21% of the uranyl ions in solution are coordinated to only four water molecules in the primary sphere, the appropriate weighted average of our predicted distances is remarkably close to the experimental value. We note that the use of a CM model to describe hydration can also lead to U–water distances that are close to the experimental value (244 pm for U/5/CPM/ $D_{5H}$ , see Table 1). However, variable results have been reported by other workers: like us, Spencer and co-workers found that a CM model produces a shortening of the U–water distance, by 5 pm to 250 pm [28], but according to Fuchs and co-workers, the adoption of a CM model apparently leads to a lengthening of the U–water distance, from 253 to 264 pm [8].

### 3.4. Apical links

We have considered whether water molecules can coordinate by hydrogen bonding to the apical (“yl”) oxygen atoms of the uranyl ion in aqueous solution. This situation is present in structures S12 and S13 (see Fig. 2). The optimized distance between the yl oxygen and hydrogen is 192 pm, which is typical for O···H bonds. The potential importance of such apical links has already been noted in [11]. Such apical coordination is not favoured to either an isolated uranyl ion or to a uranyl with only first-sphere hydration, and this reluctance is easily rationalized by a simple electrostatic argument [11]. But the presence of a second hydration sphere opens up the possibility of an extended H-bonding network, in which water molecules can simultaneously be H-bonded to an yl oxygen and to

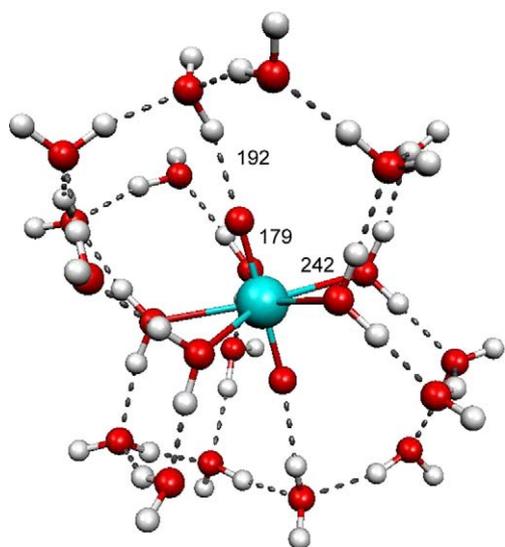


Fig. 2. Perspective view of an U/5/10/Apical structure (S13). Point group is  $C_2$ . Comparison with S8 indicates that the formation of each apical link includes three water molecules. Distances are indicated in pm.

hydrogen atoms of water molecules in the second sphere. There are surely many ways in which such a network can be established. In structure S12 (not shown), which contains two apically coordinated water molecules, there are *no fewer than four* extra H-bonds to the second sphere per apical water. As a result of these extra H bonds, the local symmetry of the first coordination sphere is lowered and the total binding energy of these extra water molecules is substantial. But the formation of these additional H bonds and the subsequent geometrical rearrangement means that it is not possible to provide a meaningful value for the energy of the apical links. We also conclude that the maintenance of local high symmetry around the uranyl ion in aqueous solution is unlikely. The influence of these apical bonds on the vibrational frequencies of the uranyl ion is considered in Section 3.8.

### 3.5. Uranyl bond length

The U/4/8 (S5–S7) and U/5/10 (S8–S11) structures show an average uranyl bond length close to 177 pm, which agrees well with the experimental value of 176.6(1) pm [25]. The range within a group of the same stoichiometry is less than 1 pm, and the difference between the averages of the two groups is smaller than the range within a group. When our models are extended to allow for the possibility of apical binding of water molecules (S12 and S13), the calculated uranyl bond length increases slightly, to about 178.5 pm, which differs from experiment by no more than 1%.

### 3.6. Second-sphere structure

The radial distribution function obtained by X-ray diffraction shows a broad peak at 446 pm, which can be attributed to the distance between U and the oxygen atoms

in the second hydration sphere [25]. This observation indicates that there is some definite structure in the second sphere, although, as we have already noted, our models surely overestimate this degree of structuration. We find U–O (second sphere) distances in our various structures that are consistently close to 450 pm.

### 3.7. Hydrogen bonds

The calculated hydrogen-bond distances between the first and second hydration spheres are smaller than the established value for bulk water (187 pm at 0 °C [37]), due to the vicinity of the cation. They vary appreciably from one structure another. For the U/4/8 and U/5/10 systems, the H-bond lengths are 170 and 179 pm, respectively, but the distance between the second and third sphere increases to 191 pm. Since the strength of H-bonds varies inversely with their length, it is natural to infer that those linking the first and second hydration spheres are particularly strong. But we note that according to a model potential developed recently for the description of uranyl–water complexes, the dominant interaction for second-sphere water molecules is in fact with the uranyl cation, or more particularly with the U atom [11]; this interaction is indeed remarkably strong, at about 60 kJ/mol.

### 3.8. Charge transfer and frequencies

We aim to estimate the Raman- and IR-active uranyl vibrational stretching frequencies ( $\nu_1$  and  $\nu_3$ ). These two frequencies are highly correlated, because the off-diagonal (stretch–stretch) interaction force constant that links the two U–O bonds is close to zero [38]. The ratio  $\nu_3/\nu_1$  is constant to within much less than 1% for all our results, so in the following we may safely limit our analysis to  $\nu_1$ .

Charge transfer from water to the uranyl ion in aqueous solution is observed experimentally, although the experimental results alone do not enable this transfer to be quantified very precisely [25]. Theoretical studies of hydration are consistent with this result, and show considerable charge transfer from the first hydration shell to uranyl, mostly to the “yl” oxygens [36]. Our results in Table 1 show that this transfer is amplified by the addition of a second hydration sphere: the five water molecules in the first hydration sphere of the complex U/5/0/D<sub>5</sub> transfer a total of 0.51 electrons to the uranyl ion (0.20 to U and 0.15 to each yl oxygen), while the ten additional water molecules in the second hydration sphere of the complex U/5/10/D<sub>5</sub> transfer a further 0.14 electrons, almost entirely to the yl oxygens (0.06 electrons to each). The additional charge transfer from the second hydration sphere is thus far from negligible, as it amounts to some 28% of that produced by the primary hydration sphere. It is interesting to compare the charges on the yl oxygens in these hydrated complexes with those calculated for the oxygen atom in an isolated water molecule; the values are not all that different, at  $-0.916e$  for the U/5/10 complex with two apical links

and  $-0.968e$  for water. As the charge on oxygen in an isolated uranyl ion is only  $-0.651e$ , it is clear that the effects of hydration on the chemical properties of uranyl will be substantial: any modeling that ignores charge transfer seems doomed to failure.

The charge transfers are compared in Fig. 3 with the predicted Raman-active stretching frequency for each structure (we use “natural” (NPA) charges [39,40], since Mulliken-type charges are highly sensitive to the details of the basis used, particularly when, as here, the basis contains diffuse functions, whereas the natural charges are empirically found to be quite robust towards details of the basis). The reference point for the charges is the isolated uranyl ion, and the reference charges in this ion (see Table 1 for details) are subtracted from all the values in Fig. 3. We plot the charges transferred to U and to each uranyl oxygen. In order of decreasing Raman frequency, we find the isolated uranyl ion, the single-hydration-sphere structures, the continuum models and finally the structures with two explicit hydration spheres. It is clear that the charge on uranium is essentially saturated by the addition of a single sphere, whereas the charge on the uranyl oxygens is very strongly correlated with the Raman-active frequency. In Fig. 4, we plot the relationship between the uranyl bond length and the Raman-active vibrational frequency in the structures we have studied: these correlations between these quantities is extremely strong. A (non-linear) correlation between the U–O force constant and the U–O bond distance has already been noted, which appears to be independent of the theoretical method used [38]. We conclude from the data in Figs. 3 and 4 that the U–O vibrational frequencies, the natural charge transferred to the uranyl oxygens and the U–O bond length in the uranyl ion are all highly correlated in the systems we have studied in this work.

The data in Fig. 4 show that a single hydration sphere around U reduces the Raman-active vibrational frequency

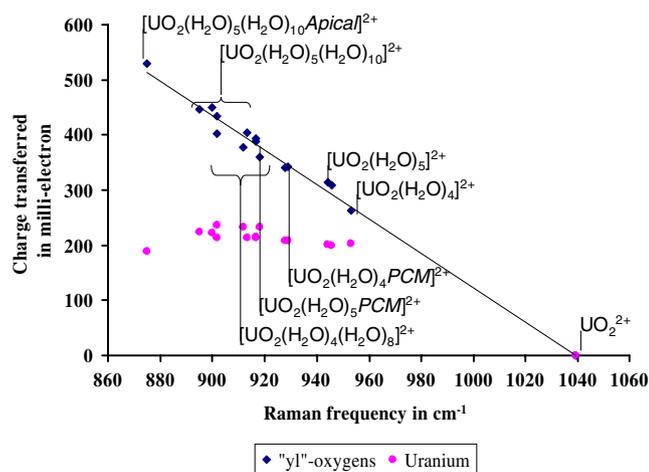


Fig. 3. NPA charge transferred to the uranyl atom and to the “yl” oxygen atom upon complexation versus Raman frequency.  $R^2 = 0.986$ , and the slope corresponds to  $0.64 \text{ cm}^{-1}$  per milli-electron transferred.

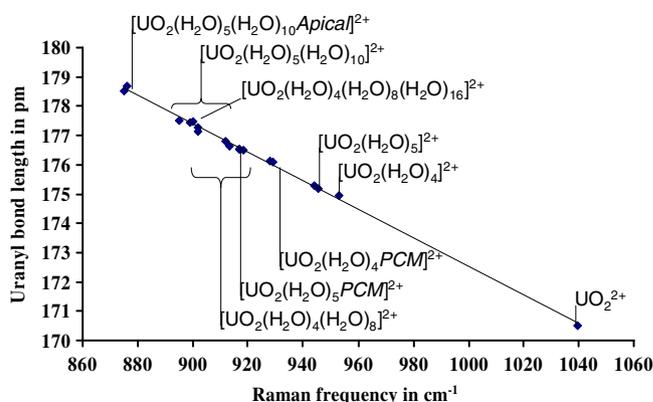


Fig. 4. Uranyl bond length versus Raman frequency.  $R^2 = 0.997$ , and the slope corresponds to  $20 \text{ cm}^{-1}$  per pm.

by some  $90 \text{ cm}^{-1}$ , that the addition of a second sphere leads to an additional lowering of  $45 \text{ cm}^{-1}$  and that the presence of apical links yields a further drop of  $25 \text{ cm}^{-1}$ . We note that the two-sphere structures with apical links yield frequencies that are close to the experimental value of  $870 \text{ cm}^{-1}$  (see Table 1). This observation reinforces our suggestion made in Section 3.4 that apical links are present in aqueous solution, and that their influence is non-negligible. Detailed inspection of Table 1 shows that the distributions of frequencies for the four- and five-coordinated structures overlap, depending on the orientations assumed for the water molecules in the second sphere. If these second-sphere molecules adopt “parallel” conformations, charge transfer to the uranyl ion is more effective than for the “orthogonal” case, leading to lower vibrational frequencies, following the correlations discussed above. Structures with lower symmetry ( $D_4$  or  $D_5$ , structures S7 and S10) have intermediate charge transfer and vibrational frequencies.

Since we have adopted a simplified, incomplete second hydration-sphere to model the hydrated uranyl ion, we therefore need to examine the importance of the water molecules that are missing from the second sphere and of the surrounding medium. How many extra water molecules should be present in the second sphere? This question can be answered in two ways. First, we consider simply the density of bulk water: within a sphere whose radius is  $500 \text{ pm}$ , there are 17 water molecules, but the uranyl ion itself has a finite volume, so 17 is an upper bound. Second, we learn from a molecular-dynamics simulation of the hydrated uranyl ion [41] that there are typically 20 oxygen atoms (from water molecules) within  $500 \text{ pm}$  of the U atom. The number of oxygen atoms in the vicinity of uranyl (20) exceeds the number derived from the density of water (17) because the highly charged uranyl ion both attracts the water molecules towards it and imposes a preferential orientation to them. The molecular-dynamics derived estimate is more refined and is presumably the more reliable. Now our model U/5/10 complex contains 15 water molecules, all within  $500 \text{ pm}$  of U, so we estimate that this model

“misses” no more than five extra water molecules. From the discussion above in Section 3.8, we infer that the structural effect of these extra molecules will be related to the additional charge transfer that they produce. We know that charge transfer implies a chemical link, and that there will be no chemical link from non-H-bonded water molecules. We estimate the magnitude of the additional charge transfer from a further calculation. We consider a U/4/8 complex to which we add four extra water molecules to the equatorial plane. These molecules are fixed at 450 pm from the U atom (the U–O<sub>w</sub> distance for molecules in the second sphere) and the remaining geometrical parameters are optimized. We discover that each of these additional “extra” molecules increases the charge transfer by only two milli-electrons, whereas in the U/5/10 structure the total charge transfer is 650 milli-electrons. We conclude that within the simplifications imposed by the models we use here, any “extra” water molecules in the second hydration sphere may safely be neglected.

We also need to estimate the influence of water molecules in the third and subsequent hydration shells. For this purpose, we suppose that the third shell is perfectly ordered. Starting from the structure S5 (U/4/8/D<sub>4h</sub>/p), we add 16 further water molecules in a third sphere, and optimize the geometry in D<sub>4h</sub> symmetry, to give structure S14. Rather than undertake an explicit calculation of the vibrational frequencies for this species, we rely on the correlation described above between the uranyl bond length and the Raman-active frequency, and discover that the frequency shift is small, only about 5 cm<sup>-1</sup>. This quantity is small compared both to the shift induced by the second sphere (45 cm<sup>-1</sup>) and to the experimental bandwidth (25 cm<sup>-1</sup>). We conclude that it is negligible compared to the other approximations of our models.

### 3.9. Comparison with continuum models

We have undertaken comparisons with CM models (also known as Apparent Surface Charge or ASC models). Both the D-PCM and C-PCM methods were tested, using the Gaussian default values for medium and solute parameters. Four series of calculations were undertaken: with four or five explicit water molecules in the first sphere, and with the D- and C-PCM methods, with full geometry optimization. We examine the optimized uranyl bond lengths, and infer the Raman-active vibrational frequencies from them.

We find no difference between D- and C-PCM for these systems. Comparing the U/4/0/D<sub>4h</sub> or U/5/0/D<sub>5h</sub> with U/4/PCM or U/5/PCM structures, we find decreases in the vibrational frequency for the latter of about 25 cm<sup>-1</sup>, which is only a little more than half the shift found by explicit inclusion of the second hydration sphere (compare, for example, U/4/0/D<sub>4h</sub> with U/4/8/D<sub>4h</sub>/p, see Table 1). The discrepancy between U/5/PCM and U/5/10/apical is even larger (see Table 1). This reduced frequency shift is well correlated with a reduced charge transfer, following the reasoning in Section 3.8 above.

Cao and Balasubramanian have recently described an extensive computational study of hydrated actinyl ions [10]. B3LYP and MP2 methods were used, in conjunction with a CM approach to represent solvent beyond the first hydration sphere. In general, the data they report are similar to ours: for example, they obtain the same B3LYP value for the symmetric-stretching frequency in the gas-phase U/5/0 complex as we do (945 cm<sup>-1</sup>), and the reduction produced by a CM model of 30 cm<sup>-1</sup> is similar to ours (25 cm<sup>-1</sup>). However, their resulting liquid-phase value of 915 cm<sup>-1</sup> agrees only moderately with the experimental value of 870 cm<sup>-1</sup>, though their MP2 result of 885 cm<sup>-1</sup> is more satisfactory.

### 3.10. Extra calculations

We have performed a few extra calculations, to show that the conclusions we may draw from this work are not sensitive to details of our computational methodology. We have added p-type polarization functions to the hydrogen basis for tests of U/4 and U/4/8. No significant changes were observed for the quantities of greatest interest to us here (the geometry around the U atom and the vibrational frequencies of the uranyl group).

We have also investigated the effect of replacing the B3LYP version of DFT by the PW91 correlation and exchange functionals [21]. Calculations on U/4 and U/4/8 show an increase in the uranyl bond length of 5 and 8 pm, respectively, similar to the B3LYP increases of 4 and 7 pm. The total charge transfers to the two “yl” oxygens in U/4/8 structures at the PW91 and the B3LYP level are, respectively, 428 and 402 milli-electrons, respectively. For the  $\nu_1$  vibrational frequency, the absolute values are lower with PW91 than with B3LYP, as the uranyl bonds are longer, but the changes produced by hydration are very similar in the two cases. The ratio of that frequency in U and U/4 is 1.08 for both PW91 and B3LYP, while the ratio between U and U/4/8 is 1.16 for PW91 and 1.14 for B3LYP. We may summarize by noting that the two versions of DFT produce results that are completely consistent.

## 4. Conclusions

We have estimated the influence of hydration on geometry and the Raman- and IR-active vibrational frequencies of the uranyl ion. We have shown that explicit inclusion of the second hydration sphere with QM models reduces the Raman frequency by about 40–45 cm<sup>-1</sup>, whereas CM models added to a system containing an explicit first sphere imply a decrease of only about 25 cm<sup>-1</sup>. We have also shown that consideration must be given to apical coordination of water molecules to the “yl” oxygen atoms for uranyl, as explicit inclusion of such interactions leads to non-negligible changes in the vibrational frequencies of the uranyl ion. These findings may explain some of the problems encountered in recent studies of aquo/fluoro

complexes of the uranyl ion, in which the predicted U–F distance did not match very well the value obtained by EXAFS in aqueous solution [36].

The method we have proposed to describe the uranyl ion in aqueous solution, although it is approximate, yields predictions for the structural and vibrational data that agree almost quantitatively with *all* the experimental data available. The influence of the second hydration sphere is fairly large, though subsequent shells seem to have relatively little influence. It appears that complex networks of hydrogen-bonded water molecules interact with the apical or “yl” oxygen atoms. A complete description of these interactions will not be easy.

We have also shown that the charge transferred to the “yl” oxygen atoms, as measured by the NPA method, is highly correlated with the shift in vibrational stretching frequencies of the uranyl ion. This charge transfer is very highly correlated with the uranyl bond length. Charge transfer to the “yl” oxygen atoms increases when the second hydration sphere is modelled explicitly, but the charge on the uranium atom is affected only slightly by the second sphere.

We believe that our “explicit partial second sphere” model may prove useful in the future for studies of uranyl complexes with other ligands in aqueous solution. Work is in progress along these lines.

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