Hydration of UO_2^{2+} and PuO_2^{2+}

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We study the hydration of the actinyl cations, uranyl UO_2^{2+} and plutonyl PuO_2^{2+}, by performing Kohn−Sham Density Functional Theory calculations using a new quantum chemistry code—MAGIC. The calculations have been performed on the separate uranyl and plutonyl species, and on the complexes $AcO_2^{2+} \cdot nH_2O$ (Ac = U, Pu and n = 4, 5, and 6), in the gas and aqueous phases. The liquid-state environmental effects are included via a simple cavity model and by using the self-consistent reaction field method. The calculations find that the solvent effects are crucial. By this, we mean that a simple cavity model, alone, will be incapable of giving insight into the chemical behavior of such molecules. The short-ranged interactions between the actinyls and their closest water molecules are very strong and involve an appreciable amount of charge transfer, an effect that cannot be included in cavity models. The actinyls form strongly bound complexes with the surrounding water molecules, with n = 5 being the most stable. Thus, the short-range solvent effects are important. The binding energies of the complexes are very large, and in the gas phase they are about twice as large as in the aqueous phase. Thus, the bulk solvent effects are also important. Any reactivity of the actinyls with other species will thus be impeded by the existence of such strongly bound complexes, and the solvent will play an *active* role in such phenomena. Regarding the chemical behavior of the actinyls in aqueous solution, our studies provide preliminary evidence that there will be no qualitative and very little quantitative difference between the uranium and plutonium species.

1. Introduction

One of the chemical reactions of major importance in the nuclear industry is[1]

$$UO_2^{2+}(aq) + 2NO_3^-(aq) + 2TBP(org) \rightleftharpoons$$
$$UO_2(NO_3)_2(TBP)_2(org) \quad (1)$$

This equation, along with its plutonium counterpart, describes one of the reactions involved in the process of separating the reusable uranium and plutonium from the highly radioactive fission products contained in spent nuclear fuel. In the process, the spent nuclear fuel is initially dissolved in aqueous nitric acid, resulting in the formation of UO_2^{2+}, PuO_2^{2+} and NO_3^- ions in an aqueous solution, along with the fission by-products of the nuclear reactions that take place in the reactor. The latter of these is the waste that needs to be separated. Solvent extraction is then used to isolate the uranyl and plutonyl from the waste. Typically, tri-*n*-butyl phosphate(TBP) diluted in an organic solvent (e.g., odor-less kerosene(OD)) is added to the aqueous solution. The TBP then binds to the uranyl and plutonyl, the idea being that these parts are then confined to the organic phase while the waste fission products remain in the aqueous solution. The two solutions can then be separated due to their immiscibility. One would then like to understand this process in order to develop more efficient chemical processes for the solvent extraction.

In the current article, we study the hydration of the UO_2^{2+} and PuO_2^{2+} species as a first step in understanding the above reaction. The behavior of UO_2^{2+} in aqueous solution has been studied experimentally by several groups. In close connection with the above system, ligand exchange reactions have been studied for uranyl−fluoride complexes.[2] Also, the complexation of UO_2^{2+} with various crown ethers has also been studied experimentally[3−6] and by the use of molecular mechanics simulations.[7] In these systems, the UO_2^{2+} and the crown ether form an inclusion complex in nonaqueous solutions while, in water, the crown ether is bound to the uranyl cation via first coordination shell water molecules; i.e., the water does not act simply as a solvent but, rather, takes an *active* role in the complex formation. Since the aqueous solvent seems to make such an essential contribution to the behavior of the systems described above, we feel that a preliminary study of the hydration of UO_2^{2+} is essential in order to understand more complex chemical phenomena such as those mentioned. The question of the coordination properties of uranium also clearly depends on the environment that surrounds the uranyl. Coordination numbers up to z = 8 can be observed in uranium complexes, depending on which ligands bind to the actinide. Molecular mechanics studies of complexes of UO_2^{2+} and the calix-6-arene ligands in aqueous solution have observed that the ligand deforms sufficiently such that only five of the six oxygens on the ligand bind to the cation, thus giving a uranium coordination of z = 7.[8] The observation of the uranyl and 18C6 complex in aqueous solution again suggests that the uranium

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has a coordination number of 7—the two oxygens in the uranyl molecule plus the oxygens of five water molecules, where these five additional oxygens lie in the plane perpendicular to the uranyl. The uranyl and 18C6 complex in nonaqueous solution has a coordination of 8, as the six oxygens of the crown ether bind to the uranium. When uranyl nitrate forms in water, two nitrate groups act as bidentate ligands and two additional water molecules also bind to the uranium, also suggesting a coordination of $z = 8$. When one discusses the coordination, one is always concerned with the binding of *equatorial* ligands to the uranium, i.e., ligands that bind in the plane perpendicular to the axis of the uranyl. The binding of various equatorial ligands to uranyl and plutonyl in solution is clearly important in the overall reactivity of such compounds. The solvent also plays an important role, and it is what we have studied here.

In the present article, as well as in some previous papers,[9,10] we present some preliminary calculations using the MAGIC program, a new quantum chemistry code in continuous development by the authors. MAGIC has been developed specifically to have the capabilities of performing calculations on large, heavy-atom systems. Such calculations are based on Kohn–Sham density functional theory (DFT) with the inclusion of relativistic and liquid-state effects. An article containing a description of the full capabilities of MAGIC is currently in preparation.[11] If one looks at the literature, the number of ab initio studies of actinide systems is limited. Previous studies are mainly concerned with the comparison between relativistic and non-relativistic quantum mechanical calculations of the electronic structure and geometry of small actinide molecules such as UF_6[10] and UO_2^{2+}.[12] Such studies are essential in order to develop the standard gas-phase quantum chemistry techniques to include relativistic effects—effects which are vital when one wishes to study systems that include heavy atoms such as the actinides. Studies that address chemical problems such as those described above are sparse, a recent example which is of relevance to the current study concerns the complexes of UO_2^{2+} with phosphoryl-containing ligands.[13]

In this publication, we consider the hydration of the two species UO_2^{2+} and PuO_2^{2+} as a first step in understanding chemical problems such as that outlined above, as well as assessing the performance of the current capabilities of the MAGIC code regarding the inclusion of liquid-state effects into standard quantum chemical calculations.

2. The MAGIC Code

The MAGIC code is designed with a view toward performing calculations on large, heavy-atom systems. In this section, we outline some of the main features of the program, a more detailed description being in preparation.[11] MAGIC can calculate molecular properties within the Kohn–Sham density functional theory formulation of non-relativistic quantum mechanics. Relativistic corrections can be included via the Douglas–Kroll or CPD methods, or by simply representing the core of the heavy atoms by relativistic effective core potentials (ECPs). The current article is not primarily concerned with a detailed discussion and comparison of such methods, and all calculations presented herein include relativity via the ECP method. Articles written by the authors on aspects of relativistic effects in MAGIC can be found in the literature.[9,10] Due to the heavy computational element required in performing calculations on large, heavy-atom systems, MAGIC is written in a particularly efficient manner to reduce the memory requirements. In particular, the coulomb contribution to the electronic energy is calculated with the use of auxiliary basis sets in order to reduce

the scaling properties from N^4 to N^3, N being the number of basis functions. All two-electron integrals are then calculated directly as and when they are needed. The exchange-correlation part of the calculation is calculated via numerical quadrature, where the local density approximation(LDA) with or without Becke's gradient correction term (B-)[14] can be included for the exchange energy, while correlation energies are calculated using either the functionals of Vosko, Wilk, and Nusair(VWN)[15] or Lee, Yang, and Parr(LYP).[16] Full analytic first derivatives of the energy can be calculated in order to allow geometry optimizations and simple property analyses can be performed, namely calculation of dipole and quadrupole moments as well as a Mulliken charge analysis.

2.1. Liquid Effects. As well as the above brief summary of its capabilities, MAGIC also includes a simple model for calculating the effects of a liquid environment on the electronic structure of a solute molecule. The model used is based on the concept of the reaction field, first introduced by Onsager in 1936.[17] The specific mathematical formalism of this concept that is implemented in MAGIC is that of the ellipsoidal cavity model developed in the group of Rivail.[18] The model is summarized below.

The molecule under consideration is placed inside an ellipsoidal cavity embedded in an infinite dielectric continuum. This dielectric continuum represents the bulk of the liquid. Thus, rather than explicitly including all the motions of the surrounding liquid molecules, these motions are pre-averaged and then the theory of dielectric continua is used to calculate the response of the liquid, in an average way, to fluctuations in the charge distribution of the molecule under study. Therefore, as the dielectric is polarized by the field of the solute molecule, it creates an electric field which then *reacts* back on the solute molecule. This is Onsager's reaction field concept and it can be thought of as a mean-field theory for the effect of the presence of the surrounding liquid on the molecule contained in the cavity.

The frequency-dependent dielectric constant of the continuum is $\epsilon(\omega)$, while that inside the cavity is the dielectric constant of free space, $\epsilon_0 = 1$. The frequency dependence arises simply from the fact that any dielectric medium has a finite response time to any changes in electric field. Thus, in order to calculate the vibrational frequencies, for example, this response of the dielectric medium will be important since the electric field due to the vibrating molecule will be constantly changing. The response of the dielectric is also important when cavity models are used to study non-equilibrium effects in reaction processes.[19] Since, in the current article, we shall not be calculating dynamic effects, the static dielectric constant is employed, i.e., the dielectric constant is assumed to be frequency independent and is given by the static (zero frequency) dielectric constant, $\epsilon(\omega \rightarrow 0) = \epsilon$.

The probability density of the N-electron system under consideration is considered as a continuous classical charge distribution, $\rho(\mathbf{r})$. For a cavity that is ellipsoidal, with its semiaxes $A \leq B \leq C$, the interaction energy, calculated from interaction between the classical charge distribution $\rho(\mathbf{r})$ inside the cavity and the infinite dielectric continuum, can be expressed as

$$H' = \frac{1}{2} \sum_{l=0}^{\infty} \sum_{m=0}^{2l} \Gamma_{lm} \langle Q_{lm} \rangle^2 \tag{2}$$

where the Γ_{lm} are the reaction field factors and the Q_{lm} are closely related to the moments of the charge distribution within

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the cavity. The former of these depends only upon the geometry of the cavity, i.e., *A*, *B*, and *C*, along with the value for the dielectric constant, ϵ. The dimensions of the ellipsoid are calculated from the van der Waals radii for each atom in the molecule and the molecular geometry, precisely in the manner outlined in ref 18. The $\langle Q_{lm} \rangle$ are related to the expectation values of the multipole moments of the charge distribution of the solute molecule and the full calculation of such terms is given by Rivail and Terryn.[20] Currently, in MAGIC, this series expansion is truncated after the term $l = 2$, i.e., multipoles up to and including the quadrupole are present in the calculation.

One may argue that the ellipsoidal shape of the cavity and the truncation of the expansion at $l = 2$ are two major deficiencies in the model, especially since this particular model has been developed in the literature to have a more general cavity shape and expansion up to $l = 7$.[21] We have chosen the above version of the model because of the type of calculation that our code has been designed for, namely, large heavy-atom complexes. Such large complexes will typically be quite ellipsoidal or even spherical in shape and will probably be of very low symmetry, i.e., they will not have any dominant high-order multipoles. Thus the shape of cavity and the truncation at the quadrupole seem like good approximations.

The expression in eq 2 calculates a purely electrostatic contribution to the energy of solvation. From this term, a contribution to the atomic-orbital Fock matrix can be calculated, so that, rather than calculating the above interaction energy using the gas-phase density, the self-consistent field calculation is performed in the presence of the liquid and thus, in general, $\rho_{liq}(\mathbf{r}) \neq \rho_{gas}(\mathbf{r})$. Therefore, the calculation also includes an electronic polarization contribution. With the addition of analytical first derivatives of eq 2 with respect to the nuclear coordinates, geometry optimizations can also be performed in the cavity, thus allowing for nuclear polarization effects as well. Two contributions that have been omitted from the calculation of the solvation energy are the dispersion and cavitation terms. While such terms are important for the calculation of absolute free energies of solvation, they have little effect on the optimized geometry of the solute.[21]

The model described above is clearly a highly simplified representation of the surrounding liquid environment, and one would expect that it would not be suitable in every case. The model will work well when the interactions between the solute and the surrounding solvent molecules are not particularly strong, i.e., when there is no charge transfer between solute and solvent or any sort of bonding under the conditions of the study. In such a case the solvent is *passive* and the presence of the surrounding liquid environment simply serves to perturb the electronic structure of the solute and, therefore, its potential energy surface. Thus, properties of the molecule, such as its geometry, vibrational frequencies, and the height of energy barriers to isomerization, etc., will be affected by such a passive solvent. The cavity model will break down when the solvent becomes an *active* solvent. Here, the interactions between solute and solvent molecules are very strong, and complex formation can result. Thus, a number of solvent molecules will take on an active role in any chemical reaction. To calculate the properties of such systems then requires the use of supermolecule-type calculations, where some of the surrounding water molecules are explicitly included in the DFT calculation. The model can then be used by placing the whole complex inside the cavity. In this sense, the cavity model represents the long-range interaction of the bulk of the liquid with the solute but if the short-range interactions become important, this model falls down.

TABLE 1: Optimized Actinide−Oxygen Bond Length, Quadupole Moment, and Mulliken Charges for Uranyl and Plutonyl in the Gas and Liquid Phases

		R_{Ac-O} (Å)	Q_{xx}	q_{Ac}	q_O
UO_2^{2+}	gas	1.7461	−3.5880	2.0328	−0.0164
	liquid	1.7477	−5.7123	2.1984	−0.0992
PuO_2^{2+}	gas	1.7672	−0.7516	1.9266	0.0367
	liquid	1.7568	−3.9795	2.0996	−0.0498

2.2. Calculation Specifications. The calculations in this paper concern hydration of the two species UO_2^{2+} and PuO_2^{2+}. Calculations are performed in the gas and liquid phases for the single uranyl/plutonyl molecule as well as with the first solvation shell of water molecules. For the liquid-phase calculations a dielectric constant of $\epsilon = 78.5$ was taken. We perform restricted Kohn−Sham DFT calculations at the BLYP level of exchange and correlation. DZP basis functions are included on all atoms apart from the two actinide elements. These are represented using the ECP basis of Hay.[22,23] Each ECP is represented by a platinum core leaving 14 and 16 valence electrons for the uranium and plutonium, respectively.

One could argue that, in order to study the hydration of such cations, one must go beyond first-shell coordination−water molecules that are hydrogen-bonded to the oxygens of the cations as well as second-shell solvation water molecules may be important. We do not include these explicit water molecules for numerous reasons. Firstly, the effects on the energetics of the system induced by including hydrogen-bonded apical water molecules will be negligible as this is a much weaker interaction than that between the actinide center and the equatorial water molecules. Secondly, the inclusion of second-shell hydration would involve between 15 and 20 explicit water molecules. Such a calculation would then become a complicated conformational problem that would most effectively be treated by simulation techniques. Finally, in this article we are primarily interested in the formation of actinyl complexes in solution. As stated in the introduction, the ligands that form complexes with such cations are *equatorial* ligands and, thus, these ligands are of primary interest. Much of the experimental data addressing these cations involves an aqueous environment and in this initial study, the ligands are the water molecules themselves. We are concerned with the stability of such complexes as the stability will clearly affect the formation of other actinyl complexes in aqueous solution. Thus, in our calculations, we explicitly include the equatorial water molecules in the quantum chemical part of the calculation and the rest of the liquid is treated by using the cavity model described above.

3. Results and Discussion

3.1. UO_2^{2+} and PuO_2^{2+}. The results for the uranyl and plutonyl species are shown in Table 1. In all cases, the geometry is linear. The quantities shown are the optimized actinide−oxygen bond length, the quadrupole moment, and the Mulliken charge populations. It should be noted that, since we have linear molecules (aligned along the *x*-axis) with the actinide at the origin, the quadrupole tensor is diagonal. Also, due to the symmetry, the components $Q_{yy} = Q_{zz}$ and, since the quadrupole tensor is traceless, i.e., $Q_{xx} + Q_{yy} + Q_{zz} = 0$, there is only one independent element of the quadrupole tensor, given here as Q_{xx}.

One can compare our value of the U−O bond length in the gas phase to previous quantum chemical results. Our result of 1.75 Å compares well with current figures in the literature. Van Wezenbeek et al.[12] have calculated a bond distance of 1.70 Å for relativistic Hartree−Fock−Slater calculations while Craw

et al.[24] calculate 1.663 Å for Hartree−Fock and CASSCF, 1.783 Å for MP2, 1.7 Å for CISD, and 1.779 Å for BLYP. Pyykkö[25] has calculated 1.648 Å at the Hartree−Fock level, and Cornehl et al.[26] calculate 1.697 Å at the CCSD level. Since all these calculation, including ours, are done at different levels and use different basis sets, we have no figure to directly compare to.

One noticeable feature of these results is in the calculation of bond lengths. For the uranyl case, the molecule in the liquid phase has an increased bond length of 0.0016 Å, while the change in going from the gas to aqueous phase for the plutonyl molecule is a *decrease* of 0.0104 Å. One can give a possible rationalization of these results by examining the model we have used for the calculations, i.e., by examining the Kohn−Sham orbitals for each calculation. For the uranyl cation one can compare the orbitals from the gas- and liquid-phase calculations. These orbitals are qualitatively identical, i.e., the symmetries and bonding/antibonding characteristics are the same and there is no swapping of the (energetic) ordering of the orbitals. Thus, the cavity has a small quantitative effect on the orbitals but has no qualitative effect. In the plutonyl case, again the orbitals are qualitatively the same with regard to the symmetry, i.e., each orbital in the gas-phase calculation has its counterpart in the liquid calculation, but, in the liquid calculation, the ordering of the orbitals has changed, with one of the orbitals being shifted two places. This particular orbital has a lower *relative* energy in the aqueous phase than the gas phase. On examining this orbital, one sees that it is of bonding character and is constituted of p_x-orbitals on the oxygens and f-orbitals on the plutonium, noting that the molecule is aligned along the *x*-axis. Thus, the shifting of this orbital to lower energy favors a more strongly bonded molecule, thus the bond length shortens. It is also interesting to notice that, when comparing the gas-phase (or aqueous phase) uranyl and plutonyl molecules, the orbital characteristics are again identical (but with a slightly different ordering) and the two additional electrons that the plutonyl molecule has simply sit in a non-bonding f-orbital on the plutonyl atom. Thus, since these two molecules are cations, and we can expect them to be electron acceptors rather than donors, when they interact with other molecules, for example the surrounding water molecules when in the aqueous phase, we might expect that there will often be very little difference between their respective chemical behaviors. We will see in the next section that this is indeed the case.

3.2. $UO_2^{2+}\cdot nH_2O$ and $PuO_2^{2+}\cdot nH_2O$. We have also performed calculations on these complexes, in the gas and liquid phases, with $n = 4$, 5, and 6. The geometry of each complex is a bipyramid-type structure. The oxygen atoms of the water molecules lie in the plane perpendicular to the actinyl molecule, while the actual water molecules lie in the plane parallel to the actinyl. The complex with $n = 5$ is shown in Figure 1. For $n = 4$ and 6, the water oxygens form a square and hexagon, respectively. The geometry of the actinyl was taken from the optimized geometry of the relevant calculation in section 3.1, i.e., the uranyl−oxygen bond distance for gas-phase calculations on the uranium complex was taken as 1.7461 Å, or 1.7477 Å for liquid-phase calculations. The geometry of each water molecule was taken to be the same, using a bond length of 1.0266 Å and a bond angle of 115°. This choice of geometry for the water molecules may seem unusual and was taken from a calculated geometry for the water molecules in the $UO_2(NO_3)_2\cdot(H_2O)_2$ complex.[24] This geometry was obtained from an optimized calculation with a double-ζ basis, whereas we use DZP. We expect that this will make little difference to our results as we are primarily concerned with differenced, rather than
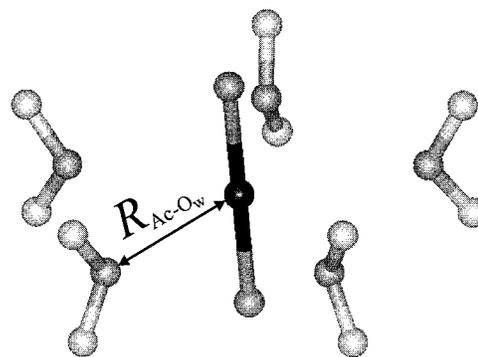
Figure 1. The pentagonal bipyramid geometry of $AcO_2^{2+}\cdot 5H_2O$ (Ac = U, Pu).

absolute, quantities. This assumption is supported by the results which have good agreement with experiment. All these geometries have been kept constant throughout the calculations, leaving the only variable distance as that between the actinide atom and the oxygens of the water molecules, R_{Ac-O_w}, as indicated in Figure 1. We believe that this is the degree of freedom that will be of most importance in the study of the stability of these complexes.

We calculate the dissociation energy of the complexes. We have defined this as the difference between the energy of the complex at its minimum energy and that of its molecular components, i.e.,

$$\Delta E = E_{complex} - (E_{actinyl} + nE_{water}) \qquad (3)$$

In the gas phase, this can also be clearly defined by the expression $\Delta E = E_{min} - E(R_{Ac-O} \rightarrow \infty)$. In the liquid state, however, such a definition becomes meaningless since, as R_{Ac-O_w} becomes large, other water molecules will clearly fill the voids created by stretching R_{Ac-O_w}. What we have calculated here, is of the form of eq 3, where the three energies on the right-hand side of that equation are all calculated for each particular system *in its own cavity*. Thus, the dissociation energy calculated for the liquid-state studies can be defined as the difference in energy between the liquid consisting of bound complexes and the liquid consisting of unbound molecules. This dissociation energy will be relevant for any reactions that happen in the liquid phase, i.e., this energy will be related to the barrier that needs to be overcome to replace the first-shell water molecules with some other (probably anionic) ligands, e.g., in the formation of nitrate complexes. Figure 2 shows the variation of the dissociation energy of the $UO_2^{2+}\cdot nH_2O$ complex, in the (a) gas and (b) liquid phases, with the uranium−water oxygen bond distance, R_{U-O_w}. Figure 3 shows the equivalent for the plutonium complex. Each plot shows 3 curves, each representing $n = 4$, 5, and 6.
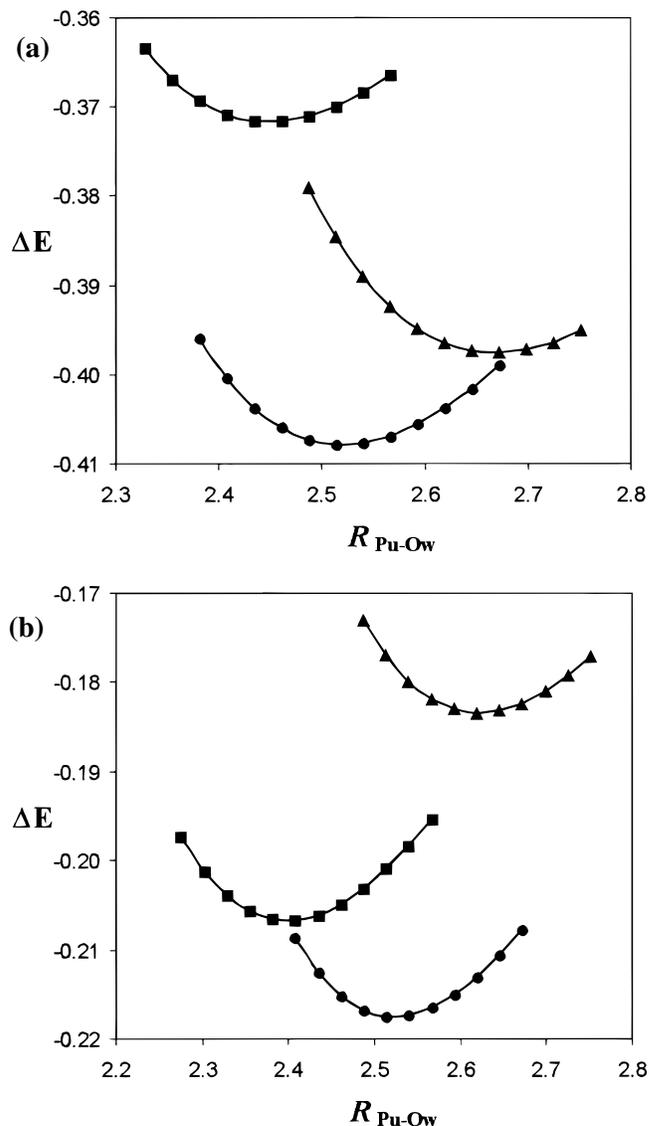
When calculating the energetics of such systems using quantum chemical techniques, one has to consider the basis-set superposition error (BSSE). We have calculated this for the gas-phase uranyl−water complex. The BSSE accounts for approximately 5% of the total dissociation energies. After correcting for the BSSE, there is clearly a small quantitative change involved but there is strictly no qualitative change. The BSSE cannot be calculated in the liquid-phase calculations. This is due to the fact that the isolated components of the complex are treated in a cavity constructed to fit the particular size of that molecule. Thus, if one was to include the basis functions of the surrounding water molecules in the calculation of the uranyl cation in its own cavity, these basis functions would actually be positioned outside of the cavity and in the continuum.

(a)

(a)

(b)

(b)
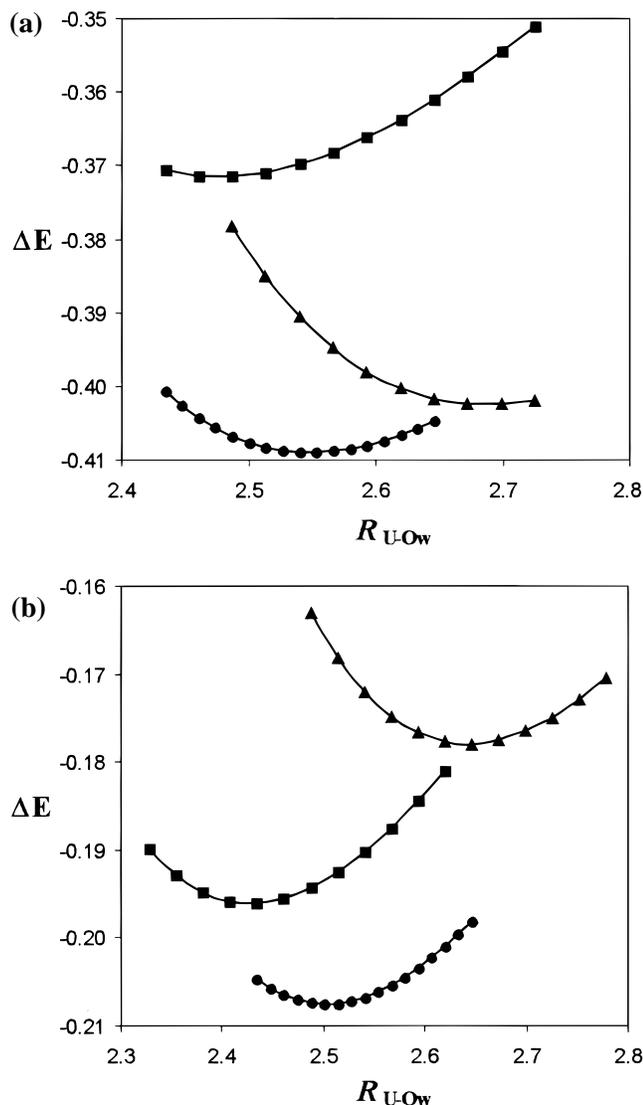
Figure 2. The dissociation energies, ΔE, as a function of the uranium−water oxygen distance, $R_{U\_O_w}$, of the $UO_2^{2+} \cdot nH_2O$ complex in (a) the gas phase and (b) the liquid phase. Energies are in Hartree, distances in Å, and the three curves represent $n = 4$ (squares), $n = 5$ (circles), and $n = 6$ (triangles).

Figure 3. The dissociation energies, ΔE, as a function of the plutonium−water oxygen distance, R_{Pu-O_w}, of the $PuO_2^{2+} \cdot nH_2O$ complex in (a) the gas phase and (b) the liquid phase. Energies are in Hartree, distances in Å, and the three curves represent $n = 4$ (squares), $n = 5$ (circles), and $n = 6$ (triangles).

It would make no sense to perform such a calculation as the mathematics relies on the fact that the charge distribution of the solute remains in the cavity. Given the fact that the BSSE does not noticeably affect the results for the gas-phase calculations, we also expect that the liquid calculations are qualitatively and quantitatively accurate (as far as any sort of BSSE-type correction is concerned). Also, given the qualitative and quantitative similarity between the uranyl and plutonyl complex calculations, we also assume that the BSSE will have little effect on the plutonyl results. Thus, as the BSSE has a negligible quantitative effect in all cases, the results presented have not been corrected for such insignificant errors.

 When examining these curves, one can immediately see that the qualitative behavior for the uranium and plutonium cases are identical. Tables 2 and 3 contain various quantities for the two complexes in the gas and liquid phases−the dissociation energy, ΔE, the optimized distance, $R_{Ac\_O_w}$, and then a Mulliken charge analysis for each complex. The charges are given by q with the subscripts being obvious labels for the particular centers involved in each calculation. All units are in atomic units apart from the distances, which are in angstroms. One can see that

TABLE 2: Calculated Quantities for the $UO_2^{2+} \cdot nH_2O$ Complex[a]

| | $UO_2^{2+} \cdot nH_2O$ | | | | | |
| | gas | | | liquid | | |
	$n = 4$	$n = 5$	$n = 6$	$n = 4$	$n = 5$	$n = 6$
ΔE	−0.3715	−0.4089	−0.4025	−0.1960	−0.2075	−0.1780
R_{U-O_w} (Å)	2.479	2.550	2.687	2.428	2.502	2.643
q_U	1.411	1.361	1.350	1.405	1.342	1.327
q_O	−0.211	−0.223	−0.225	−0.248	−0.248	−0.239
$q_{UO_2^{2+}}$	0.989	0.915	0.900	0.909	0.846	0.849
q_{O_w}	−0.604	−0.606	−0.601	−0.595	−0.601	−0.597
q_H	0.428	0.412	0.392	0.434	0.416	0.394
q_{H_2O}	0.252	0.218	0.183	0.273	0.231	0.191

 [a] All quantities are defined in the text.

the dissociation energies are almost quantitatively the same as well and, as one might expect, the distance $R_{Ac\_O_w}$ increases with n. If one writes ΔE_n as the dissociation energy for a particular number of water molecules, the behavior of the uranium and plutonium complexes is the same, i.e., in the gas phase $\Delta E_5 < \Delta E_6 < \Delta E_4$ while $\Delta E_5 < \Delta E_4 < \Delta E_6$ in the liquid

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TABLE 3: Calculated Quantities for the $PuO_2^{2+} \cdot nH_2O$ Complex

	$PuO_2^{2+} \cdot nH_2O$					
	gas			liquid		
	$n = 4$	$n = 5$	$n = 6$	$n = 4$	$n = 5$	$n = 6$
ΔE	−0.3716	−0.4079	−0.3976	−0.2067	−0.2175	−0.1834
R_{Pu-O_w} (Å)	2.451	2.522	2.671	2.399	2.523	2.624
q_{Pu}	1.303	1.241	1.223	1.289	1.215	1.191
q_O	−0.188	−0.198	−0.198	−0.221	−0.218	−0.206
$q_{PuO_2^{2+}}$	0.927	0.845	0.827	0.847	0.779	0.779
q_{O_w}	−0.590	−0.596	−0.589	−0.580	−0.590	−0.586
q_H	0.429	0.413	0.393	0.434	0.416	0.395
q_{H_2O}	0.268	0.230	0.197	0.288	0.242	0.204

phase, in both cases the complex with $n = 5$ being the most strongly bound, indicating a coordination number of $z = 7$ for the actinide atoms. For the uranium compound, the bond distances for $n = 5$ are given by 2.55 Å in the gas phase and 2.50 Å in water. These distances are consistent with molecular mechanics simulations[7] and with the experimental length of 2.42 Å for complexes of $UO_2(OH)_5(ClO_4)$ with 18C6 in the solid state[6] and on complexes of uranyl perchlorate in aqueous solution.[5]

In comparing the results for the dissociation energy of each complex, one sees that the energies in the gaseous phase are about twice those in the aqueous phase. These energies that we have calculated should not be confused with experimentally measured thermodynamic quantities. The dissociation energy calculated in the gas phase is directly related to the experimental enthalpy of formation of the ionn-water complex in the gas phase, but the dissociation energy that we have calculated in the liquid phase has no relation of the enthalpy of bulk hydration. From the book of Marcus,[27] one can compare the enthalpies of formation of cation−water complexes in the gas phase and enthalpies of bulk hydration. The second is always larger than the first. The enthalpy of bulk hydration of the uranyl 2+ cation is taken from experiment to be 0.52 au. This can be expected to be larger than the enthalpy of formation of the most stable UO_2^{2+}−water gas-phase complex by anything up to 40%.[28] As the later of these quantities has not been measured experimentally, we can compare it to our calculated value of approximately 0.41 au, thus showing that our calculations seem to be calculating energetics that are consistent with experimental trends regarding other cations. As stated previously, the dissociation energy that we have calculated in our liquid-phase calculations is related to the unbinding of the complex *while still in solution* and is not to be mistaken for the enthalpy of bulk hydration of the actinyl cations. One conclusion to draw here is that, if one studies processes in solution by the use of standard gas-phase quantum chemistry techniques, the energetics could easily be erroneous by a factor of 2. This seems consistent with what one might expect−the fact that a complex in solution is probably more weakly bound than the same complex in the gas phase, a clear effect of the interaction with the surrounding liquid environment. Thus, even though the coordination of the cations, i.e., five water molecules, is given correctly in both the gas- and liquid-phase calculations, the clear quantitative difference in the energetics, brought about by building the physics of the liquid state into the calculation (albeit in a highly simplified manner), will be very important.

The interactions that govern the structure of the studied complexes are strong but relatively simple. There are two main competing energies within each complex. The first is that of the strong ion−dipole interaction between the actinyl cation and each water molecule. In the liquid phase, this interaction is responsible for the alignment of the water molecules nearest to the cation and is attractive. The second is the interaction between neighboring water molecules in the complex. As the distance R_{Ac-O_w} decreases due to the ion−dipole attraction, the distance between the oxygens of neighboring water molecules will also decrease. Eventually, the electronic charge distributions of the waters will overlap causing a repulsion. It is the balance of these two energies that forms the complexes with, in these cases, an optimum water coordination of $n = 5$.

We employ a simple Mulliken population analysis to give us a general qualitative impression of how the charge is partitioned within the system. When one examines the Mulliken analysis in Tables 2 and 3, the first conclusion to draw is that there is an appreciable amount of charge transfer between the first coordination shell of water molecules and the actinide. This presents a problem for molecular mechanics parameterizations. One can never unambiguously define parameters for such systems, such as the molecular mechanics charges on each center, as these charges will undoubtedly depend on the particular environment of the actinyl. In ref 7, the authors perform simulations for a range of charge parameter of $3 \leq q_U \leq 6$ (corresponding to $-0.5 \geq q_O \geq -2$) where they state that the extreme parameters of this range are "a priori unsatisfactory". In the calculations presented herein, for the uranyl and plutonyl complexes in water, the charge on the actinide center is found to be less than 1.42 in all cases, which is even outside of the parameter range considered in ref 7. As the actinyl−water oxygen bond distance increases, the charge on the actinide increases monotonically toward its asymptotic value of $q_U \approx 2$. Another interesting point to notice about the charge analyses is the charges on the hydrogens of the water molecules. These centers will be primarily responsible for hydrogen bonding of these complexes to the rest of the liquid. Again the figures show that these values are the same for the uranium and plutonium complexes, thus providing more evidence that the uranyl and plutonyl species should have very similar behavior in aqueous solution.

Our calculations of the binding energies of the uranyl and plutonyl complexes in water conclude that $n = 5$ is the most stable complex. This is, of course, true energetically speaking. Given that this study is essentially one of the liquid phase, it is the minimum *free* energy of such a calculation that will stabilize the complexes. Thus, one may ask the question of whether or not entropic effects are important. In the liquid calculations presented, a simple cavity model was used. The contribution to the free energy of solvation that this model offers is the electrostatic contribution. It is assumed that entropy effects within the liquid will not play an important role and, as such, they are not included in the model. Thus, the energies that such a model gives will be more related to the actual internal energy U of the system, rather than its free energy $F = U + TS$. However, looking at the magnitude of the figures produced by the calculation gives us immediately the answer we require. For the complex $UO_2^{2+} \cdot 5H_2O$, the binding energy in solution was calculated (using the cavity model) to be 0.2075 Hartree or about 130 kcal mol^{-1}. Compared to the thermal energy at room temperature, i.e., $kT \approx 0.6$ kcal mol^{-1}, this is enormous and will certainly be bound. Also, one can consider the atomization of the uranyl cation itself, which we have calculated to be 0.1382 Hartree (86.71 kcal mol^{-1}). Thus, the water molecules are more strongly bound to the uranyl than the actual binding energy of the uranyl itself. Since this molecule clearly exists in an aqueous environment, we conclude that the complexes discussed in this article must be bound in the actual experiments and entropy

plays little part in the answer of such questions. This is clearly in accord with experiments on the uranium complexes, but since experiments on the plutonium complexes are extremely sparse, we can conclude that the same type of complexes will exist in plutonium solutions as those that are observed in uranium solutions.

4. Summary

We have studied the hydration of the uranyl and plutonyl cations. For these systems, the solvent plays a vital role. Since the interactions between the cation and the solvent molecules in its immediate vicinity are very strong and involve appreciable amounts of charge transfer, these solvent molecules behave like actual binding equatorial ligands.

When performing quantum chemical calculations with the inclusion of a simple cavity model to assimilate a liquid environment, such a cavity model will only account for the effects of a bulk liquid environment and will not be capable of describing strong, short-ranged interactions between solute and solvent. To gain any sort of insight into the behavior of systems where such interactions are important, explicit water molecules *must* be included in a supermolecule type calculation. The systems that we have studied here fall into this category. The calculations reported are among the first that use the new MAGIC code—a code developed especially to perform DFT calculations on large, heavy-atom systems. Since much of the reactivity studies of the actinyls take place in aqueous solution, a study of the hydration of these species seemed appropriate. Qualitatively, the results are consistent with experiments, giving actinyl–water complexes with five water molecules the most stability. This has been observed in experiments on solid- and liquid-state complexes. The actinyl–water oxygen bond distance that we have calculated is also close to that observed experimentally. Also, our calculations have shown very little difference between the behavior of the uranium and plutonium complexes. Since experiments on plutonium complexes are particularly rare, we have no experimental corroboration of this.

The ligand-binding chemistry of these cations is concerned with equatorial ligands. When these cations are hydrated, complex formation between the cation and some solvent molecules results. The stability of the actinyl–water complexes will clearly be of great importance in such matters. The calculations that we have presented show that these complexes are very strongly bound. The binding energies of the complexes in solution are approximately calculated as -0.21 and -0.22 au for the uranium and plutonium complexes, respectively. This is related to the barrier that will have to be overcome for other ligands to bind to the cations and is clearly important in solvent extraction processes. This value is roughly doubled for the complexes in the gas phase. Thus, if one wishes to study the ligand-binding properties of such cations in solution, gas-phase quantum chemistry is capable of giving large deviations in the energy barriers involved and, thus, solution models must be employed. Thus, in the hydration of these systems, our calculations have shown that both the short-range and the bulk solvent effects are very important. The study presented here is probably the first to treat these systems quantum mechanically as well as including the important solvent effects.

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