Theoretical studies of $\text{UO}_2(\text{OH})(\text{H}_2\text{O})_n^+$, $\text{UO}_2(\text{OH})_2(\text{H}_2\text{O})_n$, $\text{NpO}_2(\text{OH})(\text{H}_2\text{O})_n^+$, and $\text{PuO}_2(\text{OH})(\text{H}_2\text{O})_n^+$ ($n \leq 2$) complexes in aqueous solution

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Extensive ab initio calculations have been carried out to study equilibrium structures, vibrational frequencies, and the nature of chemical bonds of hydrated $\text{UO}_2(\text{OH})^+$, $\text{UO}_2(\text{OH})_2$, $\text{NpO}_2(\text{OH})$, and $\text{PuO}_2(\text{OH})^+$ complexes that contain up to 21 water molecules both in first and second hydration spheres in both aqueous solution and the gas phase. The structures have been further optimized by considering long-range solvent effects through a polarizable continuum dielectric model. The hydrolysis reaction Gibbs free energy of $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ is computed to be 8.11 kcal/mol at the MP2 level in good agreement with experiments. Our results reveal that it is necessary to include water molecules bound to the complex in the first hydration sphere for proper treatment of the hydrated complex and the dielectric cavity although water molecules in the second hydration sphere do not change the coordination complex. Structural reoptimization of the complex in a dielectric cavity seems inevitable to seek subtle structural variations in the solvent and to correlate with the observed spectra and thermodynamic properties in the aqueous environment. Our computations reveal dramatically different equilibrium structures in the gas phase and solution and also confirm the observed facile exchanges between the complex and bulk solvent. Complete active space multiconfiguration self-consistent field followed by multireference singles+doubles CI (MRSDCI) computations on smaller complexes confirm predominantly single-configurational nature of these species and the validity of B3LYP and MP2 techniques for these complexes in their ground states.


I. INTRODUCTION

Actinide complexes have been the topic of numerous experimental and theoretical studies due to their importance in the environmental migration of high-level nuclear wastes and fundamental interest concerning the nature of bonding and spectra of actinide species. These studies are critical to the understanding of the migration of actinides and sorption complexes formed by actinides in geochemical and biological environments. The actinide ions from high-level wastes seem to migrate by solubility in ground water or through other mechanisms such as sorption onto mobile colloidal species. On the other hand, sorption onto geological minerals could prevent migration and thus is considerable interest in the study of interplay between sorption and migration of actinide complexes with species in ground water under aqueous environmental conditions. Species present in aqueous solution and their thermodynamic properties of redox reactions, hydrolysis, and complexation reactions with a number of geochemical species have been the focus of major attention.

In aqueous solution, actinyl ions coordinate with water molecules or hydroxide ligands, and the number of each ligand varies with the pH. Five water ligands are coordinated in acidic solution, a mixture of water and hydroxide ligands in neutral solution, and four or five hydroxide ligands in highly alkaline solution. Actinyl complexes in aqueous solution, particularly those at low pH, have been studied experimentally$^1$–$^{13}$ and theoretically.$^{13}$–$^{23}$ The actinyl ions exist in different oxidation states in the environment but $\text{UO}_2^{2+}$, $\text{NpO}_2^{2+}$, and $\text{PuO}_2^{2+}$ are the most abundant and thus the complexes formed by these species under different pH conditions are of considerable interest. In particular at higher pH values these species form hydroxide complexes and thus their hydrolysis in solution is of particular interest. Moreover we have chosen a particular set of hydroxide complexes with water molecules in the first hydration sphere so as to complete the first coordination sphere. Then we also tested the effect of the water molecules in the second hydration sphere especially on the geometry of the complex by explicit quantum chemical treatment of actinyl hydroxide complex with 20 water molecules. The choice of the particular number of water molecules was influenced by the number of molecules needed to complete the first and second hydration spheres of the complexes considered here. These complexes present a considerable challenge$^{24}$–$^{38}$ for quantum chemical calculations, due to relativistic effects including the spin-orbit interaction as well as many-electron correlation energy. As demonstrated from the past work$^{24}$–$^{38}$ on the coordination
complexes with uranyl, there are difficulties in treating these complexes especially in solution. Clark et al.\textsuperscript{14} investigated the uranyl ion at higher pH conditions and interpreted their results on the basis of a mixture of four and five hydroxide ligands coordinated to the uranyl ion. This was later questioned by Wahlgren et al.\textsuperscript{11} who performed similar experiments but concluded that only a tetrahydroxide compound was present in solution. More recent computational studies\textsuperscript{22} also found the tetrahydroxide compound to be more stable than one with five hydroxides. In addition, Hay et al.\textsuperscript{15} computed the Gibbs free energies of hydrolysis reactions of uranyl in both the gas phase and aqueous solution and considered the energetics of the process of deprotonating one of the water molecules in the first solvation shell. They have shown that the hydrolysis reaction is exothermic in the gas phase but endothermic in aqueous solution. The influence of atomic radii in PCM models has been discussed recently in a number of works.\textsuperscript{36,39} They concluded that while their results for actinide may be reflective of the overall absolute errors in combination of electronic structure and solvation models, calculations of this type should be able to predict relative energies among a series of molecules. Tsushima et al.\textsuperscript{17} have shown that both temperature and pressure significantly changed the equilibrium constants of actinyl hydrolysis reactions. Molecular dynamics calculations were carried out in order to investigate the hydration structure of uranyl in aqueous solution by these authors. Druchok et al.\textsuperscript{21} demonstrated the existence of five ligands in the uranyl first hydration shell, and that the pentacoordinated complex possesses a bi-pyramidal structure. Charge redistribution effects resulted in ligands of four water molecules and a hydroxyl that was found closer to uranium than the other ligands.

As discussed by Tsushima and Reich,\textsuperscript{16} past theoretical studies computed the solvation properties by combining thermodynamic Gibbs free energies in the gas phase with a dielectric continuum model to treat solution effects; in such studies the PCM energy gives only an approximate value in the case when the gas-phase structure is used in solution without further optimization. This shows that computing the properties of these complexes requires far more sophisticated treatments. In the present study we considered explicit geometry optimization of water molecules not only in the first hydration sphere of the complex but also the second hydration sphere, thus treating the actinide complexes in a fully ab initio quantum chemical treatment that included up to 21 water molecules. In a recent paper,\textsuperscript{40} we reported that bulk solvent effects are important and have effects on the structures of hydrated actinyls, especially An–OH\textsubscript{2} bonds. Therefore, the structural reoptimization in a cavity is critical to accurate computations of spectra, structures, and energetics of these species. Moreover, there is less information available on the structural, electronic, and frequency properties of neptunyl and plutonyl hydroxide complexes. In this work, extensive ab initio calculations have been carried out to study the equilibrium structure, vibrational frequencies, and bonding characteristics of various hydrated actinyl hydrolysis complexes. For comparison, geometries of the complexes were optimized at the DFT/B3LYP and MP2 levels, respectively. In addition the geometries of complexes with up to 21 water molecules both in the first and second hydration spheres were optimized quantum chemically both in the gas phase for all complexes and in solution for the uranyl complex. Bulk effects were taken into account on geometries, spectra, and energies.

II. COMPUTATIONAL METHOD

Equilibrium geometries in the gas phase were optimized using the DFT,\textsuperscript{41} second order Moller-Plesset perturbation (MP2),\textsuperscript{42} and coupled cluster singles-t-doubles (CCSD) approaches. The DFT approach utilized Becke’s three-parameter functional\textsuperscript{43} with the local correlation part of Vosko et al.\textsuperscript{44} and the nonlocal part of Lee et al.\textsuperscript{45} (abbreviated as B3LYP). The B3LYP computations were carried out using spin unrestricted methods and likewise the MP2 and CCSD computations were all based on spin unrestricted Hartree–Fock orbitals. The uranyl complexes were all in singlet states while the plutoxy and neptunyl complexes exhibited 5f\textsuperscript{2} triplet states. All the calculations were carried out using relativistic effective core potentials (RECPs), which represent the effect of the 78 core electrons of uranium, neptunium, and plutonium.\textsuperscript{46} In a previous study,\textsuperscript{28} we made extensive comparisons of these RECPs with small-core RECPs that included more electrons explicitly in the calculations. However, our computed properties exhibit very little differences between the two RECPs and thus we included 78 electrons in the core explicitly for all of the actinides considered in this study. Moreover in the present study we made explicit comparisons of the 78-electron RECPs with 60-electron Stuttgart RECPs. The 6s and 6p outer core electrons, as well as the valence 5f, 6d, and 7s electrons, are explicitly treated using contracted Gaussian basis sets, i.e., [3s3p3d2f] for U, [5s3p3d2f] for Np, and [4s4p3d3f] for Pu.\textsuperscript{46} For oxygen, RECPs were employed retaining the outer 2s, and 2p shells in the valence space.\textsuperscript{47} The corresponding basis set for the element, taken from Pacios and Christiansen,\textsuperscript{47} was augmented with a six component 3d Gaussian function (\(a_0=0.85\)) adopted from Dunning and Hay.\textsuperscript{48} Duijneveldt’s\textsuperscript{49} hydrogen basis set was used for the hydrogen atoms augmented by a set of polarization functions. The basis sets have been previously tested and utilized for the uranyl complexes successfully.\textsuperscript{40,50–52}

The RECPs employed here for most of the computations included 78 electrons in the core with 6s\textsuperscript{2}6p\textsuperscript{6}5d\textsuperscript{6}6s\textsuperscript{7}7s\textsuperscript{2} shells in the valence space. These ECPs are characterized as large-core RECPs as they include more electrons in the core. In order to gauge the accuracy of these RECPs, we carried out computations that used small core ECPs that comprised of 60 electrons in the core and remaining electrons in the valence space referred to as Stuttgart 60-electron RECPs. Moreover, we carried out a similar comparative study on \([\text{UO}_2(\text{H}_2\text{O})_n]^{2+}\) complexes in our earlier study.\textsuperscript{40} For the \([\text{UO}_2(\text{OH})]^+\) complex 78e RECPs gave average U=O distance of 1.728 Å compared to 1.741 Å obtained using 60e Stuttgart ECPs. The U–OH\textsubscript{2} distance was computed as 2.033 Å compared to 2.012 Å obtained using 60e Stuttgart ECPs. On the basis of these two studies, we found that the results of
78-electron RECPs are quite satisfactory and thus we uniformly used 78-electron RECPs for the species considered here.

We employed the complete active space multiconfiguration self-consistent field methods (CASSCF) followed by multireference singles+doubles configuration interaction computations schemes in order to assess the efficacy and accuracy of the MP2 and DFT/B3LYP techniques. The CASSCF/MRSDCI techniques were used for the triplet ground electronic states of PuO$_2$(OH)$_2$ complex as such calculations are feasible on smaller complexes. Our CASSCF method included the Pu(5f), Pu(7s) orbitals in the active space while the Pu(6s) and Pu(6p) orbitals are inactive in that no excitations were allowed from these orbitals. For oxygen the 2$p$ orbitals were kept active while the H(1$s$) orbitals were kept active. The CASSCF method included a full CI obtained by distributing all these electrons among the active orbitals. The MRSDCI computations included single + double excitations from all reference configurations in the CASSCF with coefficients greater than 0.07. The CASSCF demonstrates that the leading configuration for the triplet ground state of PuO$_2$(OH)$_2$H$_2$O has a coefficient of 0.9714 and this leading configuration is the same as the one in the DFT/B3LYP, MP2, and CCSD methods for the ground state of this complex thus confirming the validity of single-reference based methods for the treatment of these complexes arising from PuO$_2$$^{2+}$, NpO$_2$$^{2+}$, and UO$_2$$^{2+}$. The second leading configuration for the triplet state has six open shells with a coefficient of 0.1065. We also considered spin-orbit effects by employing a relativistic configuration interaction (RCI) method and also by scaling the spin-orbit effects obtained earlier by Matsika and Pitzer$^{53}$ for the uranyl and neptunyl ions by a factor of $Z^2$ for PuO$_2$$^{2+}$ complexes. The two techniques provide satisfactory treatments for the spin-orbit effects as indeed the NpO$_2$$^{2+}$ complexes and PuO$_2$$^{2+}$ complexes both retain the $5f^2$ (triplet) character for all the complexes. As expected for Pu-complexes of these kinds, the $5f^2$ shell acts like a semicore in the ground triplet states and thus spin-orbit effects obtained for these complexes using both techniques are valid. We note that spin-orbit effects have also been considered earlier for the actinyl ions using the CI formalism by Hay et al.$^{15}$ We used these values to estimate the spin-orbit effects. Our RCI computations for the PuO$_2$(OH)$_2$H$_2$O$^+$ complexes were carried out by including all reference configurations arising by distributing the two $5f$ electrons in all possible ways compatible with the double group. We then allowed single and double excitations from these reference configurations in the RCI.

The effect of solvent (water) was further studied at the DFT/B3LYP and the MP2 levels using the self-consistent reaction field models considering the solvent to be a dielectric continuum. Integral equation formalism PCM model (IEFPCM)$^{54-57}$ was used for this purpose. The geometries were fully reoptimized using these models to seek their structures in aqueous solution. In the IEFPCM model, the solute is immersed in a shape-adapted cavity defined by interlocking spheres centered on each solute atom or group and with standard united atomic topological model radii.$^{58}$ We also carried out vibrational frequency calculations to characterize the stationary points and estimate zero-point vibrational and entropy contributions to Gibbs free energies by using a standard mechanical formula$^{58}$ in the gas and solvation phases. We also note that there are other solvation models$^{59-63}$ and other functionals but the ones used here work satisfactorily as demonstrated with other methods such as CASSCF/MRSDCI methods.

The Gibbs free energy of hydrolysis reaction of a complex AnO$_2$(H$_2$O)$_n$$^{Z+}$ was estimated as $\Delta G_{\text{solv}} = \Delta G_{\text{gas}} + \Delta G_{\text{solv}}(\text{AnO}_2(H_2O)_{n-1}(OH)^{Z+}) + \Delta G_{\text{solv}}(H_2O^+) - \Delta G_{\text{soln}}(\text{AnO}_2(H_2O)_{n}^{Z+}) - \Delta G_{\text{solv}}(H_2O)$. Where $\Delta G_{\text{gas}}$ and $\Delta G_{\text{solv}}$ are Gibbs free energies of hydrolysis reactions in the gas phase and aqueous solution, and others are solvation Gibbs free energies. All of the thermochernistry computations were performed at standard conditions, that is, T = 298.15 K and P = 1 atmosphere. For solvation Gibbs free energies of H$_3$O$^+$ and H$_2$O, we used experimental values of −6.3 kcal/mol for H$_2$O (Ref. 64) and −102 kcal/mol for H$_3$O$^+$.$^{55}$

AnO$_2$(H$_2$O)$_n$$^{Z+}$ + H$_2$O → AnO$_2$(H$_2$O)$_{n-1}$(OH)$^{Z+}$ + H$_3$O$^+$.

All the calculations were carried out using the GAUSSIAN 03 package of codes.$^{58}$ Geometry optimization and frequency calculations at the CCSD level were performed on Lawrence Livermore’s ASCII machine which consists of 992 IBM SP4 processors.

III. RESULTS AND DISCUSSIONS

A. Structural and electronic properties

The geometries of UO$_2$(OH)(H$_2$O)$_4$$^+$, PuO$_2$(OH)$\times$(H$_2$O)$_4$$^+$, NpO$_2$(OH)(H$_2$O)$_4$, and UO$_2$(OH)$_2$(H$_2$O)$_4$ have been studied both in the gas phase and in aqueous solution. The structures were initially optimized in the gas phase and then reoptimized in aqueous solution at both DFT/B3LYP and MP2 levels. We treated water molecules beyond the first hydration sphere in two different ways. The first method treated them as a polarized dielectric continuum of aqueous environment at ambient conditions 25 °C with a dielectric constant of 78.39. In the second method we treated the water molecules in the second hydration sphere quantum chemically by explicit geometry optimization of a cluster of a complex comprised of water molecules both in the first and second hydration spheres. As we discuss subsequently, the geometries and other properties of the complex are nearly the same in both methods of optimization thus confirming the PCM model for water molecules in the second and outer hydration spheres. The structural parameters obtained through these models are presented in Tables I and II, and the optimized geometries are presented in Figs. 1 and 2. As expected, the optimized structures of UO$_2$(OH)(H$_2$O)$_4$$^+$ and PuO$_2$(OH)(H$_2$O)$_4$$^+$ both in the vacuum and in the continuum model were found to exhibit equilibrium structures with one hydroxide and four water molecules in the first coordination sphere. The bonding is a combination of ionic and covalent interactions between actinyl cations and hydroxide anion, which lead to a shorter distance between uranium and hydroxide, for example, a $R(U-OH)$ distance of 2.132 Å, compared to the distance between uranium and water molecules.
TABLE I. Selected bond distance (angstrom) for $\text{UO}_2(\text{OH})^+$, $\text{UO}_2(\text{OH})(\text{H}_2\text{O})^+$, $\text{NpO}_2(\text{OH})(\text{H}_2\text{O})_4$, and $\text{PuO}_2(\text{OH})(\text{H}_2\text{O})_4$ in the gas phase and aqueous solution [the ground state of $\text{UO}_2(\text{OH})(\text{H}_2\text{O})_4$ is a single state, whereas $\text{NpO}_2(\text{OH})(\text{H}_2\text{O})_4$ and $\text{PuO}_2(\text{OH})(\text{H}_2\text{O})_4$ are triplet states].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Method</th>
<th>Gas phase</th>
<th>Aqueous solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{UO}_2(\text{OH})^+$</td>
<td>B3LYP</td>
<td>1.729, 1.727</td>
<td>1.757, 1.760</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>1.766, 1.767</td>
<td>1.782</td>
</tr>
<tr>
<td></td>
<td>B3LYP$^*$</td>
<td>1.741</td>
<td>2.545–2.598</td>
</tr>
<tr>
<td></td>
<td>MP2$^*$</td>
<td>1.764</td>
<td>2.528–2.536</td>
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<tr>
<td>$\text{UO}_2(\text{OH})(\text{H}_2\text{O})_4$</td>
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<td>1.775, 1.760</td>
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<tr>
<td></td>
<td>MP2</td>
<td>1.776</td>
<td>1.782</td>
</tr>
<tr>
<td></td>
<td>CCSD</td>
<td>1.751, 1.750</td>
<td>2.537–2.588</td>
</tr>
<tr>
<td></td>
<td>B3LYP$^*$</td>
<td>1.770</td>
<td>2.545–2.597</td>
</tr>
<tr>
<td></td>
<td>MP2$^*$</td>
<td>1.791</td>
<td>2.512–2.571</td>
</tr>
<tr>
<td>$\text{NpO}_2(\text{OH})(\text{H}_2\text{O})_4$</td>
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<td>1.794, 1.821</td>
<td>1.785, 1.792</td>
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<tr>
<td></td>
<td>MP2</td>
<td>1.771, 1.789</td>
<td>1.798</td>
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<tr>
<td></td>
<td>CCSD</td>
<td>1.751, 1.750</td>
<td>2.537–2.588</td>
</tr>
<tr>
<td></td>
<td>B3LYP$^*$</td>
<td>1.770</td>
<td>2.545–2.597</td>
</tr>
<tr>
<td></td>
<td>MP2$^*$</td>
<td>1.791</td>
<td>2.512–2.571</td>
</tr>
<tr>
<td>$\text{PuO}_2(\text{OH})(\text{H}_2\text{O})_4$</td>
<td>B3LYP</td>
<td>1.761, 1.767</td>
<td>1.741</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>1.752</td>
<td>1.724–2.572</td>
</tr>
</tbody>
</table>

$^*$The Stuttgart basis set and the 60-electron RECP for U.

$R(\text{U–OH}_2)$, 2.567–2.626 Å. Moreover the axial bond distances $R(\text{U=O})$ are 1.748 and 1.750 Å at the DFT/B3LYP level.

In Table I we compared the results obtained for $[\text{UO}_2(\text{OH})\text{H}_2\text{O}]^+$ by the use of two different ECPs, one with the large-core 78e RECPs and the other using 60e small-core Stuttgart ECPs. We fully optimized the geometries using the corresponding large basis sets in conjunction with 60e ECPs that included up to 5g functions. As can be seen from Table I, the computer geometries and the ground states obtained by the two methods agree quite well. The U=O axial distances are within 0.01 Å of each other. The U–O=H equatorial bond distances which tend to be more sensitive are within 0.021 Å of each other. Consequently, our computed geometries of larger complexes are expected to be accurate to 0.01 Å for the equatorial distances and 0.021 Å for the axial distances.

We also carried out computationally intensive MP2 computations of $[\text{UO}_2\text{OH}(\text{H}_2\text{O})_4]^+$ as these computations used the Stuttgart [14s13p10d8f6g/6s6p5d4f3g] basis sets on U together with 60-e RECPs for U. The equilibrium geometries were fully optimized using these basis sets and ECPs for $[\text{UO}_2\text{OH}(\text{H}_2\text{O})_4]^+$ at both B3LYP and MP2 levels. As can be seen from Table I, at the B3LYP level the differences in the U=O axial bond lengths are 0.02 Å in comparing 78e RECP results at the same level of theory. The corresponding differences in U=OH and U–OH2 distances are 0.018 and 0.022–0.03 Å, respectively, at the B3LYP level. The differences in the U=O axial bond lengths at the MP2 level are 0.025 Å in comparing 60e RECPs and 78e RECPs. The corresponding MP2 differences in bond lengths of U–OH and U–OH2 are 0.03 and 0.03–0.04 Å, respectively. Thus the B3LYP method works reasonably well for all bond distances and the MP2 method also compares favorably with the CASSCF/ MRSDCI techniques as the ground states of these complexes are predominantly single configurational in their characters.

The DFT method tends to yield longer equatorial An–OH2 and An–OH bond distances and somewhat shorter O=An=O axial bond distances uniformly compared to MP2 and other methods. The discrepancy of almost 0.04 Å between the DFT/B3LYP and the MP2 levels is definitely due

TABLE II. Selected bond distance (angstrom) for $\text{UO}_2(\text{OH})(\text{H}_2\text{O})_3$ in the gas phase and aqueous solution at the DFT/B3LYP and the MP2 levels.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Method</th>
<th>Gas phase</th>
<th>Aqueous solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$R(\text{An=O})$</td>
<td>$R(\text{An–O}_2)$</td>
</tr>
<tr>
<td>cis-ortho</td>
<td>B3LYP</td>
<td>1.758, 1.761</td>
<td>2.218, 2.236</td>
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<tr>
<td></td>
<td>MP2</td>
<td>1.785, 1.784</td>
<td>2.217, 2.234</td>
</tr>
<tr>
<td>trans-ortho</td>
<td>B3LYP</td>
<td>1.787, 1.782</td>
<td>2.221, 2.230</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>1.787, 1.782</td>
<td>2.221, 2.230</td>
</tr>
<tr>
<td>cis-meta</td>
<td>B3LYP</td>
<td>1.766, 1.757</td>
<td>2.246, 2.217</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>1.788, 1.787</td>
<td>2.240, 2.216</td>
</tr>
<tr>
<td>trans-meta</td>
<td>B3LYP</td>
<td>1.763, 1.762</td>
<td>2.243, 2.211</td>
</tr>
<tr>
<td></td>
<td>MP2</td>
<td>1.785, 1.790</td>
<td>2.241, 2.219</td>
</tr>
</tbody>
</table>
to the inadequate accounting of the dispersion interactions that are integral part of the An–OH₂ and An–OH bonds. In accordance with previous studies,⁴⁶ the DFT method does not include dispersion interactions and does not perform very well for water molecules bonded to actinides in comparison to higher level methods such as the CCSD or MP2 techniques. It can be seen from Table I that an incremental addition of water molecules to the complexes results in a systematic elongation of the O=An=O axial bond, as a result of competition for equatorial bonding by added water molecules.

The influence of solvent is significant on the optimized geometries of these continuum calculations, especially in comparing how the equatorial and axial bonds alter. Such changes between the geometries of the gas phase and solution structures have been documented earlier in the literature.⁶³ As can be seen from Table I, the complexes in the continuum PCM model exhibit elongated An=O axial bonds compared to the gas phase due to long range interactions (solvent effects). The change in structures owing to the solvent effects is modest in magnitude, in agreement with a previous work.⁴⁰ The continuum beyond the first hydration sphere changes R(An=O) axial distance by 0.01 Å in UO₂(OH)(H₂O)₄⁺ and PuO₂(OH)(H₂O)₄⁺. However, the An–OH₂ and An–OH distances are more sensitive to the solvent effects due to the weaker nature of their interactions. We found that the R(U–OH) bonds elongate up to 0.080 Å in contrast with a contraction of up to 0.025 Å for R(U–OH₂) from gas phase to aqueous solution. Moreover, the difference in O=An=O bond angle is significant. The gas phase structure of UO₂(OH)(H₂O)₄⁺ exhibits a nonlinear angle of 170.3°, while the complex in aqueous solution exhibits a bond angle of 175.9°, bringing it closer to linearity. The O=Pu=O bond angle changes from 178.7° to 179.4° after PuO₂(OH)(H₂O)₂⁺ was immersed in a polarizable continuum. The overall changes in the structures of these complexes accentuate the importance of long-range interactions and the need for structural reoptimization in solution.

We also considered explicit quantum chemical treatment of water molecules in the second hydration sphere. As a result of the large size of the resulting complex and basis sets only DFT/B3LYP geometry optimizations are feasible for a large complex as AnO₂(OH)(H₂O)₅⁺ as well as UO₂(H₂O)₂⁺. We also carried out geometry optimizations of UO₂(OH) ×(H₂O)₂⁺ in both gas phase and aqueous solution in order to assess the role of water molecules in the second hydration sphere. Our optimized structures are shown in Fig. 3 while the select important bond distances are compared in Table I. As can be seen from Table I, the inclusion of water molecules in the second hydration sphere elongates the An=O axial bonds compensated by shortening of the An–OH₂ equatorial bonds. These changes are smaller in aqueous solution as one can see from Table I by a critical comparison of UO₂(OH)(H₂O)₄⁺ and UO₂(OH)(H₂O)₂⁺ in aqueous solution. We also note that the primary coordination remains unchanged for the complexes with complete first hydration shells such as UO₂(OH)(H₂O)₄⁺, NpO₂(OH)(H₂O)₄⁺, and PuO₂(OH)(H₂O)₄⁺ in comparison with the corresponding complexes that have second hydration spheres. Furthermore the An–OH distances which are the primary focus of the current work are very little changed. For example, the U–OH distance for the complex with completed first hydration shell is 2.114 Å while the corresponding value for the complex with second hydration shell is 2.172 Å. Likewise similar trends are noted for the neptunyl and plutonyl complexes.

As we are using a combination of quantum chemical and continuum model for estimating the solvation energies, it is important to discuss the effects of atomic radii used in the continuum model. We note that the water molecules that are directly attached to the complex are treated fully quantum chemically using the MP2 or DFT methods and only those water molecules that are not involved in direct bonding are treated in a continuum. However it is important to note that the atomic radii used in the continuum model have a large
energy isomer contains a four-membered ring with the second-

over their calculations predicted for trans-UO$_2$ shown in Fig. 2, in solution and gas phase. Whereas the such a contrasting difference is seen in gas phase versus continuum PCM model. However, this is not the first time four-coordinated complexes are preferred in the gas phase both vibrational predissociation spectroscopy and $ab$ initio geometries for the hydrated complex.

The Mulliken populations displayed in Table III show that the short-range interactions between the actinyls and their closest water molecules and hydroxide ions are very strong and involve an appreciable amount of charge transfer, which cannot be properly determined by pure continuum models. Although Mulliken populations are not physical observables, they provide insight into the nature of charge transfer and individual orbital populations when considered only as qualitative properties. The Mulliken population analysis shows that the electronic charges on the central actinyl ions are only modified up to 0.18e from the gas phase to the cluster in a dielectric cavity. As can be seen in Table III, the charges of actinides in solvated complexes should be more positive in solution due to the solvent polarization effects compared to the gas phase.

The equilibrium structures of NpO$_2$(OH)($H_2O$)$_4$ and UO$_2$(OH)$_2$(H$_2$O)$_4$ complexes are dramatically different as shown in Fig. 2, in solution and gas phase. Whereas the four-coordinated complexes are preferred in the gas phase with a fifth water molecule in the second shell, five-coordinated complexes are the equilibrium structures in the continuum PCM model. However, this is not the first time such a contrasting difference is seen in gas phase versus solution complexes. For example, an analogous structural contrast was noted for the solvated NH$_4^+$ by Chang and co-workers through their spectroscopic studies. A number of structural isomers have been observed by the use of both vibrational predissociation spectroscopy and $ab$ initio calculations. Among the observed isomers, the one with a filled first solvation shell is lowest in energy for $n=4$. Moreover their calculations predicted for $n=5$ that the lowest energy isomer contains a four-membered ring with the second-

shell H$_2$O acting as a double-proton acceptor. Bruge et al. found that NH$_4^+$ is on average coordinated with five water molecules in the solution phase. Four water molecules form a long-lived tetrahedral cage around the ion, each molecule being hydrogen bonded with one proton of NH$_4^+$. The fifth water molecule in the second hydration shell exhibits facile exchanges with one of the four molecules in the tetrahedral cage. Thus, reoptimization in aqueous solution is necessary for providing realistic pictures of NpO$_2$(OH)(H$_2$O)$_4$ and UO$_2$(OH)$_2$(H$_2$O)$_3$ in aqueous environment.

As expected the interactions between actinyl cations and hydroxide anions are ionic, which lead to shorter An–O distances for the An–OH bonds and as a consequence the symmetry of hydration shell breaks. Analogous to the magnesium ion, uranyl ion has a facile inner coordination sphere. On the basis of our computed solvation Gibbs free energies obtained by using the combined explicit-continuum model, we considered that five and six coordinations are equally preferred. Generating a hydroxide ion by deprotonating one of six water molecules around the uranyl ion elicits a spontaneous change from hexa- to pentacoordination. Figure 4 shows one of possible transition structures for the migration of a water molecule from the first solvation shell into the second shell.

We considered four kinds of isomers of UO$_2$(OH)$_2$(H$_2$O)$_3$, i.e., cis-ortho, trans-ortho, cis-meta, and trans-meta in the continuum IEFPCM model. We use the labels ortho to refer to the isomer in which two OH groups are adjacent to each other and the label meta is used when the OH groups are placed in positions 1 and 3 of the equatorial pentagonal arrangement. Moreover cis- and trans- is used to designate the relative geometrical arrangement of the OH groups, that is, if they point in the same direction then it is cis- and if they point in the opposite direction it is designated trans-. Thus in all we have four isomers for the UO$_2$(OH)$_2$(H$_2$O)$_3$ structures. The optimized structural parameters are shown in Table II. The four isomers optimized within the continuum model were found to have all oxygens of hydroxides and water molecules on the equatorial plane, as exemplified in Fig. 2. As seen from Table II, the differ-
ences in the structures are insignificant, especially between the cis- and trans-isomers. For example, even for the weakly interacting uranyl and water molecules, the $R(\text{An-O_w})$ distances change at most by 0.003 Å between the cis- and trans-isomers at the MP2 level. Furthermore, the difference is only 0.078 Å at most between ortho- and meta-isomers. In addition, the DFT/B3LYP An–O_w bond distances are longer by 0.08 Å compared to the MP2 distances since the DFT/B3LYP method does not include the effects of dispersion accurately.

We calculated the Gibbs free energies and total electronic energies of four UO$_2$(OH)$_2$(H$_2$O)$_3$ isomers. Meta-isomers are more favorable in energy than the orthoisomers, and trans-complexes are slightly favored over the cis-complexes. In aqueous solution, trans-meta-complex is the most stable structure, whereas the differences both in absolute energies and Gibbs free energies are less than 2 kcal/mol among these four isomers. This suggests that all four isomers may exist in aqueous solution with a possibility of facile exchange among the isomers, in agreement with the conclusion of Tsushima et al.$^{16}$

The facile exchange of water molecules predicted by our computational study has been observed earlier by Clark et al.$^{14}$ through the $^{17}$O NMR (Nuclear Magnetic Resonance) spectroscopic studies on these complexes in aqueous solution. These authors obtained the luminescence spectra of uranyl hydroxide complexes as a function of hydroxide ion concentration; the spectra showed that both [UO$_2$(OH)$_4$]$^{2-}$ and [UO$_2$(OH)$_5$]$^{3-}$ species exist in equilibrium in aqueous solution. From the vibronic structure of the luminescence bands, these authors measured a vibrational energy of 790 cm$^{-1}$ for [UO$_2$(OH)$_5$]$^{3-}$. They also obtained the $^{17}$O NMR and $^{16}$O/$^{18}$O Raman spectra, both of which confirmed facile ligand exchanges between the axial oxygen atoms and the solvent oxygen atoms. An activation enthalpy barrier of about 9.8 kcal/mol was estimated from the $^{17}$O NMR line broadening data. Although the exact mechanism of this facile exchange between the axial ligand and bulk solvent is not
fully understood at present, it seems fluxional dynamics of the solvated complex may be facilitated by a mechanism analogous to Berry pseudorotation observed in such inorganic molecules.

The spin-orbit effects could be especially important for the PuO$_2$$^{2+}$ and NpO$_2$$^{+}$ complexes as these complexes exhibit open-shell ground states, although for UO$_2$$^{2+}$ complexes the spin-orbit effects are nearly zero, as they are in closed-shell ground states. Hay et al. estimated the spin-orbit effects of the actinyl ions and their hydrated complexes. These authors also noted how the CI computations yield substantially different ground states compared to the DFT method for PuO$_2$$^{2+}$. The overall spin-orbit effects for PuO$_2$$^{2+}$ ($f_0$) states were found to be about $-0.84$ eV. This effect is similar for NpO$_2$$^{+}$ and in overall agreement with the values reported by Matsika and Pitzer for NpO$_2$$^{+}$. Hay et al. also compared the relative contributions of the spin-orbit effects for the reduction potentials of the AnO$_2$$^{2+}$ pentahydrated complexes to yield [AnO$_2$(H$_2$O)$_3$]$^3+$. For the UO$_2$$^{2+}$ and PuO$_2$$^{2+}$ species the spin-orbit contributions to the reduction potentials are 0.31 and 0.21 eV, respectively. The corresponding spin-orbit contributions to NpO$_2$$^{+}$ reduction potentials are at most 1.12 eV. The ground state of [UO$_2$(H$_2$O)$_3$]$^2+$ exhibits a closed-shell $f_0$ configuration and thus the spin-orbit contribution to energy splitting is zero for the ground state. In analogy we expect the same result of zero spin-orbit effect to hold for the hydroxyl complexes of UO$_2$$^{2+}$ that we considered here, as all of these species exhibit closed-shell ground states. The spin-orbit contribution to [NpO$_2$(H$_2$O)$_3$]$^3+$ complexes are $-0.35$ eV, on the basis of $f_0$ configuration for Np in these species. Consequently, the spin-orbit contributions to the energies of all Np hydroxide complexes considered here are expected to be at most $-0.35$ eV. The [PuO$_2$(H$_2$O)$_3$$^{2+}$ complexes are $-0.84$ eV in the $f_0$ Pu states. Thus we expect PuO$_2$$^{2+}$ hydroxyl complexes in $f_0$ states to exhibit the greatest spin-orbit effects, up to $-0.85$ eV. Our multireference relativistic CI computations of PuO$_2$OH(H$_2$O) complex yield a spin-orbit contribution of $-0.8$ eV and the corresponding value for PuO$_2$OH(H$_2$O)$_2$ is very close to PuO$_2$OH(H$_2$O) indicating that the addition of water molecules does not change the spin-orbit contribution. This is because the basic 5$f^2$ shell structure is retained in all of these plutonyl complexes and because the spin-orbit contribution is primarily determined by the 5$f^2$ shell; the SO contribution remains invariant to the addition of water molecules. Thus we conclude that the spin-orbit effects are predictable with reasonable accuracies for the hydroxide complexes from the corresponding computations of the free actinyl ions and hydrated complexes that have been carried out before. Thus final cumulative errors in computations when spin-orbit, correlation, and solvation corrections are all considered should be about 2.5–5 kcal/mol.

**B. Vibrational frequencies**

We obtained the vibrational frequencies of all of the complexes at both DFT/B3LYP and MP2 levels. Among the computed vibrational frequencies the O–An–O axial stretching harmonic vibrational frequencies of all complexes in the gas phase and in aqueous solution are of particular interest.

The effect of bulk solvent was treated using a self-consistent reaction field PCM model. The results of vibrational frequencies are shown in Table IV together with experiment results for comparison. The computed IR spectra in the gas phase and aqueous solution are also presented in Fig. 5.

As can be seen from Table IV, differences of axial stretching frequencies between the DFT/B3LYP and the MP2 levels are modest in the gas phase and even smaller in aqueous solution. The O–U–O stretching frequencies of the UO$_2$(OH)(H$_2$O)$_4$ cluster were obtained as 905 cm$^{-1}$ (symmetric) and 1010 cm$^{-1}$ (asymmetric) in the gas phase at the DFT/B3LYP level, whereas the corresponding values are 893 cm$^{-1}$ (symmetric) and 995 cm$^{-1}$ (asymmetric) at the MP2 level.

Due to the elongation of the O–An bonds upon solvation, the O–An–O stretching frequencies exhibit redshifts in aqueous solution. As can be seen from Fig. 5, which juxtaposes the IR spectra of gas-phase complexes and solvated complexes, the solvated complexes that possess covalently bound water molecules in the first hydration sphere exhibit considerable solvent-induced frequency redshifts that are evident in the IR spectra. In the continuum model, the calculated values for UO$_2$(OH)(H$_2$O)$_4$ are 882 cm$^{-1}$ (symmetric) and 970 cm$^{-1}$ (asymmetric) at the DFT/B3LYP level, which are very close to 881 cm$^{-1}$ (symmetric) and 961 cm$^{-1}$ (asymmetric) at the MP2 level. The symmetric stretching frequency at the MP2 level in aqueous solution is close to the experimental value of 849 cm$^{-1}$.

The $cis$- and $trans$- conformers of uranyl dihydroxide complexes have almost the same O–U–O stretching frequencies, for example, 799 cm$^{-1}$ (symmetric) and 854 cm$^{-1}$ (asymmetric) for $cis$- and $trans$-ortho-UO$_2$(OH)(H$_2$O)$_3$, compared to 793 cm$^{-1}$ (symmetric) and 851 cm$^{-1}$ (asymmetric) for $cis$- and $trans$-meta-UO$_2$(OH)(H$_2$O)$_3$ at the MP2 level. The formation of actinyl complexes with hydroxide ligands leads to weakening of the axial bonds. As can be seen from Table IV, the O–U–O stretching frequencies of UO$_2$(OH)$_2$(H$_2$O)$_3$ are smaller than those of UO$_2$(OH)$(\times$(H$_2$O)$_4$) complexes, consistent with the increasing axial bond length. Moreover, as seen from Table IV, the computed frequency differences between meta- and ortho- conformers of uranyl dihydroxide complexes are also significant, although the values of metacomplexes are slightly lower than those of orthocomplexes.

For the purpose of comparison, we also calculated the axial stretching frequencies of uranyl hydroxide complexes within the pure continuum model. It can be seen from Table IV that the explicit inclusion of aquo ligands in the first solvation shell has noticeable effects on the stretching frequencies, although the frequencies tend to be overestimated for UO$_2$(OH)$^+$ and UO$_2$(OH)$_2$. The stretching frequencies of UO$_2$(OH)$^+$ were calculated to be 896 cm$^{-1}$ (symmetric) and 966 cm$^{-1}$ (asymmetric) in the pure continuum model, comparing to 881 cm$^{-1}$ (symmetric) and 961 cm$^{-1}$ (asymmetric) in the combined explicit-continuum model. As can be seen from Fig. 5, there are appreciable differences in the frequencies and intensities of the IR spectra of these complexes between the gas phase and the solution phase. A general trend is that more lines are seen with higher intensity in the solu-
tion primarily due to the splitting of lines resulting from the breaking of symmetry in solution or owing to redshifts relative to the gas phase.

C. Hydrolysis reactions

The deprotonation reaction of AnO$_2$(H$_2$O)$_5^{2+}$ species in water to form the hydroxide complexes received considerable attention in the literature. The reaction is facile at low pH values and involves deprotonation of one of the water molecules in the first solvation shell. In solution the Gibbs free energy change for the hydrolysis reaction of UO$_2$(H$_2$O)$_5^{2+}$ was predicted to be $+17$ kcal/mol by Hay et al. and $-0.3$ kcal/mol by Tsushima et al., respectively. For both of them, Gibbs free energies in solution were computed by combining thermodynamic Gibbs free energies in the gas phase with a dielectric continuum model to include the solvent effects.

In a recent paper, we reported that the bulk solvent effects are important for modeling actinide complexes in an aqueous environment, and the solvent alters the structures and spectra of the hydrated actinyls, especially with regards to the An–OH$_2$ bonds as well as subtle variations in the An–O equatorial and axial bonds. Consequently, structural reoptimization of the complex in a dielectric cavity seems inevitable if one needs to seek subtle structural variations in the solvent and to correlate with the observed spectra and thermodynamic properties in solution. After the equilibrium geometries were reoptimized in solution, our computed Gibbs free energy of hydrolysis reaction of UO$_2$(H$_2$O)$_5^{2+}$ in solution is 7.27 kcal/mol at the DFT/B3LYP level and 8.11 kcal/mol at the MP2 level; the results are in good agreement with experimental value of 7.1 kcal/mol. These findings demonstrate that even subtle structural rearrangements from the gas phase to aqueous solution produce significant energy changes, even though the axial stretching frequencies do not undergo substantial shifts. In addition, Tsushima et al. computed the Gibbs free energy change of UO$_2^{2+}$ + 2H$_2$O $\rightarrow$ UO$_2$(OH)$_2^{+}$ + 2H$_2$O as $-31.4$ kcal/mol, far from the observed value, demonstrating that water molecules in the first solvation shell can form the most stable complex with uranyl. Thus it is important to include water molecules bound to the complex for a proper treatment of the hydrated complex and the dielectric cavity. As shown in Table V, the reaction Gibbs free energy with the sixth ligand in the second shell was calculated to be 4.9 kcal/mol. The water molecules in the second shell do not have to be included explicitly in the quantum chemical treatment as demonstrated by our careful quantum chemical consideration of these molecules. Instead the second hydration sphere can be treated within the continuum model. Thus the water molecules in the second hydration sphere do not affect the reaction Gibbs free energies significantly. In accordance with a previous study, the use of a discrete model that considers inclusion of more sol-
vent molecules beyond the first solvation shell with a continuum does not lead to improved results for solvation energies.

Our calculations demonstrate that the Gibbs free energy change for the hydrolysis reaction of $\text{UO}_2(\text{H}_2\text{O})_{2+}^{2+}$ is exothermic in the gas phase and endothermic in aqueous solution, in agreement with the conclusion of Hay et al.\textsuperscript{15} As shown in Table V, we also computed the Gibbs free energy changes of hydrolysis reactions to be 29.4 kcal/mol for $\text{NpO}_2(\text{H}_2\text{O})_5^+$ and 3.9 kcal/mol for $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$, respectively. We note that owing to retention of the spin multiplicity in the reactant and product sides of the reactions listed in Table V for Pu and Np containing species, the spin-orbit effects cancel out, as demonstrated by our explicit spin-orbit computations on Pu-containing species. The Gibbs free energy changes of $\text{UO}_2(\text{H}_2\text{O})_5^{2+}+2\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{H}_2\text{O})_3(\text{OH})_2^++2\text{H}_3\text{O}^+$ were computed to be 26.8 kcal/mol at the DFT/B3LYP level and 28.7 kcal/mol at the MP2 level, respectively. Although these results differ with limited experimental data that are available for these reactions, we note that the experimental values are tentative at best. Moreover the MP2 and B3LYP results are in accord with accurate CCSD values.
which are to be considered most accurate for these systems as the species involved are single configurational in nature.

IV. CONCLUSIONS

We investigated the equilibrium structures, vibrational frequency, and the nature of bonds of both gas-phase and solvated $\text{UO}_2(\text{OH})(\text{H}_2\text{O})_2^+$, $\text{UO}_2(\text{OH})(\text{H}_2\text{O})_3$, $\text{NpO}_2(\text{OH})_2(\text{H}_2\text{O})_4^-$ complexes at both DFT/B3LYP and MP2 levels. The solvated species were further reoptimized at the DFT/B3LYP and the MP2 levels by using a combined discrete-contumuum model in which the solute and the solvent molecules in the first shell are treated quantum mechanically while the long-range solvent effects are simulated by the continuum IEFPCM model. The computed results show that the bulk effects are important and have substantial influences on the structures and vibrational frequencies of the hydrated actinyl hydroxide complexes, especially the $\text{UO}_2(\text{OH})(\text{H}_2\text{O})_3$ and $\text{NpO}_2(\text{OH})(\text{H}_2\text{O})_4$ complexes. Our computations reveal substantial differences in the gas-phase and solution structures of $\text{UO}_2(\text{OH})(\text{H}_2\text{O})_2$, and $\text{NpO}_2(\text{OH})(\text{H}_2\text{O})_4$ complexes in that these complexes were found to be four-coordinated species with a water molecule in the second shell in the gas phase, whereas these are five-coordinated species in the continuum PCM model. Moreover, with the equilibrium geometries reoptimized in aqueous solution, the computed Gibbs free energy of hydrolysis reaction of $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ in solution is 7.27 kcal/mol, which is in good agreement with the experimental value. Therefore, structural reoptimization of complexes in a dielectric cavity seems inevitable for the computation of relative energies and subtle variations in the spectra caused by solvent effects. Our computed structures, spectra, and energetics in solution correlate with the observed spectra and thermodynamic properties in the aqueous environment. The computed results are consistent with the previously observed facile exchanges between the complex and the bulk solvent molecules as inferred by their $^{17}\text{O}$ NMR, suggesting fluxional dynamics of the solvated actinyl complex. Our computations demonstrate that it is necessary only to include water molecules explicitly in the first hydration sphere by a quantum chemical treatment and the water molecules in the second hydration sphere and other outer spheres can be treated in a continuum model.

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