Fluxional motions and internal rotational barriers of water molecules bound to $\text{UO}_2^{2+}$, $\text{NpO}_2^+$, and $\text{PuO}_2^{2+}$

K. Balasubramanian a,b,c,*, Zhiji Cao a

a Department of Mathematics and Computer Science, California State University, East Bay, Hayward, CA, United States
b University of California, Chemistry and Material Science Directorate Lawrence Livermore National Laboratory Livermore, P.O. Box 808 L-268, CA 94550, United States
c Glenn T Seaborg Center, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, United States

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Abstract

We have computed the torsional tunneling barriers for water molecules bound to actinyl ions, $\text{UO}_2^{2+}$, $\text{NpO}_2^+$, and $\text{PuO}_2^{2+}$ using high-level relativistic computations in aqueous solution. We show that the barriers drop substantially as a function of number of water molecules, which could assist facile exchange of water molecules from the solvent to the complex. Our findings are consistent with the $^{17}\text{O}$ dynamical NMR studies of Farkas et al.

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1. Introduction

There has been significant interest in hydrated actinyl ions such as $\text{UO}_2^{2+}$, $\text{NpO}_2^+$, and $\text{PuO}_2^{2+}$ and their complexes [1–22], as they occur in the environment as a result of migration of actinides in high-level nuclear wastes. Such hydrated actinyl complexes are formed through sorption of migrating actinides in both geochemical and biological environments. These complexes that occur in the natural ground water close to geological repositories of high level nuclear wastes, which are typically sorbed onto clay, minerals, plants and bacteria and the sorption process is key to the transport of actinide species in high level wastes. Consequently, hydrated actinyl species have been the topics of numerous experimental [1–13] and theoretical studies [14–22]. There have also been general theoretical studies on actinide chemical bonding by Pyykkö and coworkers [23,24].

One of the fascinating experimental observations concerning the aquo actinyl complexes is that there appears to be facile exchange of water molecules from the solvent to the complex. Farkas et al. [11] have studied the hydration of $\text{UO}_2^{2+}$ species using NMR spectroscopy. As seen from Fig. 1 of Farkas et al.’s paper [11], the temperature dependence of rate constant of acidic $\text{UO}_2^{2+}$ (aq) obtained from dynamic $^{17}\text{O}$ NMR spectroscopy reveals that only at $\sim 260$ K the exchange of water molecules between the complex and solvent ceased for $\text{UO}_2^{2+}$ (aq) species. These studies show non-rigid behavior of aquo complexes which exhibit exchange of water molecules between the complex and solvent primarily through dissociative interchange mechanism. This would suggest a small energy barrier to the rotation and or exchange of water molecules in such complexes. Clark et al. [8] have shown that the uranyl ions under alkaline conditions exhibited oxoligand exchange with the solvent using $^{17}\text{O}$ variable temperature width NMR. Clark et al. have established that the $^{17}\text{O}$ NMR spectra behavior is consistent with a facile ligand exchange between $\text{U=O}$ with the solvent. A remarkable finding by Clark et al. is that the $^{17}\text{O}$ NMR spectra of the uranyl species in solution showed either no oxoresonance or only a weak signal due to U and O. The enthalpy of activation
for oxoligand exchange has been estimated for UO$_2^{2+}$ in HClO$_4$. A similar observation was made for UO$_2$(OH)$_{2-n}$$^+$ species where it is believed that the solvent H$_2$O molecule through hydrogen bond formation with the complex oxoligands results in exchange of oxoligands. There have also been other studies concerning $^{17}$O spectroscopy of uranyl complexes [12,13]. A SCF theoretical study of UO$_2$(H$_2$O)$_{2-n}$ reveals a rather small barrier for internal rotation of water molecules for motions of one and two water molecules [10].

The barriers for internal rotations of water molecules could provide significant insight into the mechanisms of the observed facile water molecule exchanges, although we have not explicitly computed the energy barriers for this exchange. Moreover, the rovibronic spectra of these species in the gas-phase would exhibit tunneling splittings due to small internal rotation barriers. The spectra of non-rigid species would exhibit considerable torsional tunneling and thus it is important to understand the extent of non-rigidity of species and the barrier for tunneling. In this investigation we show with high levels of theory including coupled cluster methods and relativistic effects that barriers for internal rotations of water molecules in actinyl complexes strongly vary as a function of number of water molecules bound to the actinyl ions. Fully hydrated species exhibit substantially smaller energy barriers, which could result in tunneling splittings of the rotational levels and thus rovibronic-tunneling splittings in the spectra of these species even in the gas-phase. In solution the same motion thus rovibronic-tunneling splittings in the spectra of these species would exhibit considerable torsional tunneling and rovibronic-tunneling splittings in the spectra of these species even in the gas-phase. In solution the same motion could provide for a channel for water exchange between the species even in the gas-phase. In solution the same motion could provide for a channel for water exchange between the species even in the gas-phase.

We provide for insight into these non-rigid processes using our high level relativistic quantum computations.

We have carried out high level quantum computations on the fluxional motions of water molecules bound to actinyl ions, in particular, UO$_2^{2+}$, NpO$_2^{2+}$ and PuO$_2^{2+}$. We have employed a variety of methods including the coupled cluster method at the highest level. We have computed the barriers to internal rotation of water molecules as a function of the number of water molecules bound equatorially to the actinyl ions. It is shown here that the barriers to internal rotations in fully hydrated complexes are so small that the complex would be fluxional thus explaining the observed facile exchange of water molecules between the solvent and the complex.

2. Methods of computation

The equilibrium geometries of the actinyl complexes with water molecules are generally known to accommodate water molecules on the equatorial plane with the O=U=O being on the axial position. Thus a potential surface scan for internal rotation about the An–O equatorial single bond was obtained by allowing the dihedral angles between water molecule and actinyl to vary by 20° increments from 0° to 180°. All the remaining parameters were optimized using the DFT [25], second order Møller-Plesset perturbation (MP2) [26], and coupled cluster singles + doubles (CCSD) approaches. Full geometry optimizations and frequency calculations have been carried out to determine and characterize the stationary points. The DFT approach utilized Becke’s three-parameter functional [27] with Vosko et al.’s [28] local correlation part and Lee et al.’s [29] non-local part (abbreviated as B3LYP). All the calculations were carried out using relativistic effective core potentials (RECPs) [30] which replace the 78 core electrons of uranium, neptunium, and plutonium. The 6s and 6p core electrons, as well as the valence 5f, 6d, and 7s electrons, were explicitly treated using Gaussian basis sets, i.e. [3s3p3d2f] for U, [5s3p3d2f] for Np, and [4s4p3d3f] for Pu [30]. To maintain consistency oxygen atoms were also treated with RECPs that retain the outer 2s, and 2p shells in the valence space [31]. The corresponding basis set for oxygen, taken from Ref. [31], was augmented with a six component 3d Gaussian function ($\sigma_d=0.85$) adopted from Dunning and Hay [32]. The Van Duijneveldt [33] 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 [22].

All the calculations were carried out using GAUSSIAN 03 package of codes [34]. Geometry optimization and frequency calculations at the CCSD level were performed on Lawrence Livermore’s uv machine which consists of 992 IBM SP4 processors.

3. Results and discussion

In order to consider the internal rotation barriers as a function of the number of water molecules, we have considered full geometry optimizations for UO$_2$(H$_2$O)$_{2-n}$, NpO$_2$(H$_2$O)$_{2-n}$ and PuO$_2$(H$_2$O)$_{2-n}$ ($n=1,4,5$) species. The optimized structures of AnO$_2$(H$_2$O)$_5$ and AnO$_2$(H$_2$O)$_3$ were found to have all oxygens of water molecules on the equatorial plane as exemplified in Fig. 1, and hydrogens symmetrically above and below the equatorial plane. The optimized structure for AnO$_2$(H$_2$O)$_5$ has four water molecules oriented out of the equatorial plane analogous to the complex with four H$_2$O and the fifth water molecule is on the equatorial plane. In order to determine the barriers to internal rotation of the water molecules, one water molecule at a time was rotated about An–O equatorial single bond from 0° to 180°. For AnO$_2$(H$_2$O)$_3$, the rotational barriers for the water molecule on the equatorial plane were calculated, as this appears to be the smallest. We have optimized the geometry at each of the torsional angle and final optimized energies were plotted for each angle.

Figs. 2–4 show our computed energies as a function of the internal rotation angle for torsional tunneling of the water molecules for the complexes that we have considered here. Although the barrier heights change significantly as a
function of the actinide and water molecules, all of the computed barriers to torsion of water molecules are small particularly for the fully hydrated complexes, suggesting non-rigid nature of the water molecules bound to actinyl ions. The results presented in Table 1 show that for $\text{UO}_2(\text{H}_2\text{O})^ {2+} n$, the barrier heights change from 6.88 kcal/mol ($n = 1$) to 3.93 kcal/mol ($n = 4$) to 0.17 kcal/mol ($n = 5$) at the DFT/B3LYP level. That is consistent with their average binding energies per water molecule with uranyl which are $-77.66$ kcal/mol for $n = 1$, $-66.25$ kcal/mol for $n = 4$, and $-60.43$ kcal/mol for $n = 5$, respectively, at the MP2 level. As expected, with the increase of water molecules, interactions between actinyls and water molecules are weakened since more ligands distribute the electrostatic potential of actinide center, and bond lengths between actinyls and water molecules are elongated. Consequently the fluxional character of the water molecules also increases.

Of course the saturation of the coordination is reached with 5 water molecules and thus if any more water molecules are added it may not bind to the first hydration shell. Thus the non-rigidity is not impacted by additional water molecules which would enter the second and surrounding hydration spheres. The $\text{NpO}_2(\text{H}_2\text{O})^ + n$ and $\text{PuO}_2(\text{H}_2\text{O})^ {2+} n$ species have similar trend with the change of hydrated water molecules.

Table 1 contains the barrier heights for internal rotation of water as obtained using the CCSD, MP2, and DFT/B3LYP level of theories. As can be seen from Table 1, the MP2 results are quite close to the CCSD results. The differences between the MP2 and CCSD results are less than 0.32 kcal/mol for $\text{UO}_2(\text{H}_2\text{O})^ {2+} n$ and $\text{NpO}_2(\text{H}_2\text{O})^ + n$.
The DFT calculations show larger differences compared with the CCSD barrier heights. This is understandable since the DFT method does not include the effects of dispersion and hydrogen bonding weak interactions accurately.

The relative trend of how the barriers vary as a function of the actinyl ion is also quite interesting as can be seen from Figs. 2–4. The DFT method predicts a lower energy of the actinyl ion is also quite interesting as can be seen accurately.

The DFT method does not yield the correct trend for this case while the MP2 and CCSD methods provide for a consistent result. That is the stronger is the bonding of water molecules to the actinyl ions, the better is the reliability of the DFT method in predicting the barrier height.

Fig. 5 shows the relative trends of barrier heights for AnO$_2$(H$_2$O)$_n^{2+}$ as a function of n, the number of water molecules. The main finding is that the barrier drops substantially from 4 to 5 water molecules. Once five molecules are in the first hydration sphere, saturation of the coordination is reached and thus the fifth water molecule is loosely bound to the actinyl ions compared to four or fewer molecules. The availability of the actinide 6d and 5f orbitals for electron density acceptance for fewer water molecules is the primary cause. Thus when saturation is not reached, the water molecules are bound strongly thus resulting in larger barriers to internal rotation.

In aqueous solution of course saturation of the first hydration shell is reached quickly and thus the fifth water molecule in the primary hydration sphere will readily undergo torsional tunneling. This feature results in the facile exchange of the bound water molecule from the first hydration sphere to the surrounding water molecules in the second hydration sphere. The rather low barrier of 0.17 kcal/mole suggests that the fifth H$_2$O molecule is non-rigid and this combined with weaker binding of the fifth H$_2$O would suggest that facile exchange of H$_2$O from the first hydration sphere to the bulk solvent and the exchange should occur primarily through dissociative interchange. The observed temperate dependence of kinetic rate constant for water interchange, as inferred from $^{17}$O dynamical NMR spectra acidic UO$_2^{2+}$ (aq) reported by Farkas et al [11], seems to be consistent with this. The temperature dependence of the exchange rate constant is suggestive of facile exchange of the water molecule bound to the actinyl ion and water molecules in the second hydration sphere.

**4. Conclusions**

We have computed the barriers to internal rotations of water molecules of hydrated complexes of actinyl ions as a function of the number of water molecules for UO$_2^{2+}$, NpO$_2^{2+}$, and PuO$_2^{2+}$. We have shown that the CCSD and MP2 methods are more reliable for the prediction of barriers to water internal rotations compared to the DFT method. The DFT method predicts incorrect trend especially for NpO$_2^{2+}$, which exhibits less binding to water molecules compared to UO$_2^{2+}$ or PuO$_2^{2+}$. We have shown that the barrier for internal rotation drops dramatically for five-coordinated water complex compared to a four-coordinated water complex. This facilitated an interpretation of the observed temperature dependence of exchange rate constants inferred from $^{17}$O NMR spectra of acidic UO$_2^{2+}$ (aq) which showed substantial increase at higher temperatures and decrease only at ~260 K. The tempera-

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**Table 1** Calculated H$_2$O rotational barrier energies (in kcal/mol)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Method</th>
<th>Barrier energy</th>
<th>Molecule</th>
<th>Method</th>
<th>Barrier energy</th>
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ture dependence suggested facile exchange of the water molecule bound to the actinyl ion in the first hydration sphere with other water molecules in the solvent such as those in the second hydration sphere. Our computed near-zero internal rotation barrier for the fifth $H_2O$ weakly-bound to $UO_2^{2+}$ is consistent with this observation and supports dissociative exchange of water molecule between the first and second hydration spheres.

Acknowledgements

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