Systematic analysis of structural and topological properties: new insights into PuO$_2$(H$_2$O)$_n^{2+}$ ($n = 1–6$) complexes in the gas phase

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The equilibrium structure, stabilities, electronic structures, chemical bonding and topological properties of PuO$_2$(H$_2$O)$_n^{2+}$ ($n = 1–6$) complexes in the gas phase have been systematically investigated by different levels of theory. The results indicate that all the ground states of these complexes are triplet. The five water molecules of PuO$_2$(H$_2$O)$_m^{2+}$ ($m = 1–5$) are arranged on the equatorial plane of plutonyl. Reactivity analysis of PuO$_2$(H$_2$O)$_5^{2+}$ shows that the oxygen atom of the sixth water molecule is connected by hydrogen-bonds to the two water molecules which are on the equatorial plane of PuO$_2$(H$_2$O)$_5^{2+}$. The optimized geometries are in agreement with available theoretical and experimental results. The weak covalent interactions of Pu–ligand bonds were evaluated by the electron localization function and atoms in molecules analyses. The orbital interactions were investigated by analysis of total, partial, and overlap population density of state diagrams. Besides, a reduced density gradient approach was implemented to analyze the weak interactions and steric repulsions present in PuO$_2$(H$_2$O)$_6^{2+}$ and PuO$_2$(H$_2$O)$_5^{2+}$ complexes.

1 Introduction

The chemistry of dipositive actinyl ions, particularly plutonyl complexes, is of major importance in nuclear waste reprocessing cycles and safe storage.$^{4–6}$ It is worth mentioning that Pu ions have a higher-valence above +4 (e.g., +5, +6, and +7), and can easily form a variety of complexes with other ligands. Another interesting topic of this area is the active 5f elements having a high oxophilicity feature.$^{7}$ Therefore, the interactions of plutonyl with other ligand molecules have attracted considerable attention.$^{8–18}$ In particular, researches have focused on the interaction of plutonyl with H$_2$O molecules, which is a major issue in secure nuclear storage, because H$_2$O plays a catalytic role in plutonium corrosion.$^{19,20}$

Theoretical research in this area is more common than experimental; this may be due to the high activity and radioactivity which causes difficulties for experimental studies. In a recent experimental study,$^{11}$ the hydration and oxidation of gas-phase plutonyl monovalent ions were investigated by electrospray ionization mass spectrometry (ESI-MS), and the ESI mass spectra of PuO$_2$(H$_2$O)$_m^+~(n = 0–5)$ were obtained. In contrast, tremendous theoretical works have been performed to exploring the properties of PuO$_2$(H$_2$O)$_n^{2+}$ complexes.$^{12,13,16,17,21–24}$ Cao et al. have utilized density functional theory (DFT) methods to investigate the structural properties and vibrational frequencies of PuO$_2$(H$_2$O)$_m^{2+}$ complexes ($m = 4–6$).$^{16}$ Most of the previous studies predicted that plutonyl(II) ions will be the favorable structure, therefore, the equilibrium structure of PuO$_2$(H$_2$O)$_5^{2+}$ has been well studied.$^{12,13,16,17,20,21}$ On the other hand, these theoretical studies significantly suggest that DFT is an appropriate and successful method to access the nature of PuO$_2$(H$_2$O)$_m^{2+}$ complexes.

As seen from the above survey of PuO$_2$(H$_2$O)$_m^{2+}$ complexes, there are uncertainties of the bonds characterization, bonding mechanism and the effect of plutonyl orbitals in the interaction. Therefore, detailed interaction mechanisms and the topological properties as well as orbitals information need to be systematically examined.

The main focus of the present work is to perform a new thorough investigation of the PuO$_2$(H$_2$O)$_n^{2+}$ complexes ($n = 1–6$). The optimized geometries and electronic state properties of these complexes are reported. The covalent interactions were evaluated for Pu–ligand bonds in these complexes with electron localization function (ELF) and atoms in molecules (AIM) analyses. The roles of plutonyl orbitals were analyzed by total and partial density of state (TDOS and PDOS), and overlap population density of state (OPDOS) analysis. In addition, the weak interactions and steric repulsions exist in these complexes were studied by reduced density gradient (RDG) approach.

2 Computational details

Geometry optimization and frequency calculation of the stable structures were performed at the B3LYP,$^{25,26}$ B3PW91,$^{27}$ PBE0 (ref.
28) and PW91PW91 (ref. 29) methods, along with Stuttgart–Dresden–Bonn relativistic effective core potential (RECP)\(^a\) for Pu atom. This small core RECP, named as SDD, replaces 60 electrons in inner shells,\(^4\) leaving the 5s, 5p, 5d, 5f, 6s, 6p, 6d and 7s shells as the valence electrons. For O and H atoms, the 6-311++G(d,p) basis sets by Pople and coworkers were employed.\(^31\) Calculations were carried out by using the Gaussian 03 programs.\(^32\) The geometry structures of these complexes were identified to be one minimum in potential energy, and their stability were examined by molecular dynamics. The current computational scheme has been successfully performed in actinide systems.\(^6\)\(^,\)\(^33\)\(^–\)\(^40\) Specifically, previous works show that B3LYP/SDD and PW91/SDD methods have good performance in the structure and frequencies computation for Pu–H\(_2\)O system.\(^6\)

With the aim of deeply investigate the nature of the bonding, a systematic topological description of these complexes was performed. The wavefunction files (.wfn) which obtained from geometry optimization and frequency calculation were used as input files of the Multiwfn\(^5\) package to perform the ELF\(^6\)\(^,\)\(^41\) and AIM\(^4\)\(^a\) analysis. In order to gathering insights about the participation of plutonyl orbitals in the chemical bonds of complexes, TDOS, PDOS, and OPDOS\(^5\)\(^,\)\(^46\) analysis were also performed. In addition, the reduced density gradient proposed by Yang et al.\(^47\) was used to obtain a deep insight into the weak interactions and steric repulsions in titled complexes.

3 Results and discussion

To evaluate the accuracy of current computational schemes for plutonyl systems, first, we calculated the bond distances and vibrational frequencies of PuO, PuO\(_2\) and PuO\(_2^z\) molecule. The results are listed in Table 1 along with the corresponding available experimental values and previous theoretical results. As can be seen, our results are in agreement with available experimental values, and have good consistency with other theoretical results.

3.1 Geometric structures and electronic properties

In order to obtain minimum energy structures, dozens of possible structures of PuO\(_2\)(H\(_2\)O)\(_n^z\) complexes \((n = 1–6)\) were constructed, and taking into account different possible spin states. Geometry optimization was performed without symmetry constrain, and their corresponding ground state geometries in the gas phase were located. Moreover, the stability of these stable structures was confirmed by Born–Oppenheimer molecular dynamics (BOMD)\(^22\) simulations at 300 K. Geometric parameters are reported in Fig. 1 for different levels of theory.

As can been seen from Fig. 1, the optimized geometries show little dependence on the level of theory. Our results indicate that the ground electronic state of these complexes are triplet. In terms of geometry, we can see that water molecules of PuO\(_2\)(H\(_2\)O)\(_m^z\) \((m = 1–5)\) are arranged on the equatorial plane of the plutonyl group. In particular, water molecules wherein PuO\(_2\)(H\(_2\)O)\(_3^z\) and PuO\(_2\)(H\(_2\)O)\(_2^z\) are almost in the equivalent position.

To evaluate the sites of six water molecules in PuO\(_2\)(H\(_2\)O)\(_6^z\), we performed the reactivity analysis by using electrostatic potential (ESP) on molecular vDW surface of PuO\(_2\)(H\(_2\)O)\(_6^z\). ESP on vDW surface has been proved as a critical for studying intermolecular interaction, and widely used for prediction of nucleophilic and electrophilic sites. More negative ESP signifies this region has the stronger ability to attract electrophiles, on the contrary, more positive ESP site has the stronger ability to attract nucleophiles.\(^44\)

The ESP-mapped vDW surface of PuO\(_2\)(H\(_2\)O)\(_5^z\) is shown in Fig. 2. It can be seen that, the surface maximum of ESP present at the H atoms of water molecule. Therefore, from ESP point of view, these H atoms of the PuO\(_2\)(H\(_2\)O)\(_5^z\) are the primary bonding site of O atom. After optimization, as seen from Fig. 1, we found that the oxygen atom of sixth water molecule is connected to the two water molecules which on the equatorial plane of PuO\(_2\)(H\(_2\)O)\(_5^z\) by hydrogen-bonds.

In terms of bond length, with the increase of water molecules, the bond length of Pu–O\(_1\) and Pu–O increased slightly. Taking the calculation result of BLYP/SDD as an example, for bond length of Pu–O\(_1\) 2.293 Å for PuO\(_2\)(H\(_2\)O)\(_5^z\) and 2.469 Å for PuO\(_2\)(H\(_2\)O)\(_6^z\); for bond length of Pu=O, 1.673 Å for PuO\(_2\)(H\(_2\)O)\(_5^z\) and 1.705 Å for PuO\(_2\)(H\(_2\)O)\(_6^z\), respectively.

3.2 Bonding features

The bonding nature of Pu–O for these complexes have been investigated using ELF and AIM analytical method. It is worth mentioned that ELF and AIM are appropriate and successful tools to analyzing bonding mechanism and have been applied in many actinides complexes investigations. In addition, ELF...
obtained from small-core RECP has been proven to correctly analyze the topological properties.\textsuperscript{55,56}

The ELF shaded-surface-projection map of the titled complexes are displayed in Fig. 3. As can be seen, these are disynaptic valence basins between the Pu and Oyl atoms, which indicate that there are covalent bonds formation between plutonyl and H\textsubscript{2}O molecules.

In order to further exploring the chemical-bonding natures of these complexes, we employ a more quantitative method, the atoms in molecules (AIM) analysis. The different topological properties including electron density $\rho(r)$ and its Laplacian $\nabla^2 \rho(r)$, kinetic electron energy density $G(r)$, potential energy density $V(r)$ and the total energy density $H(r)$ of the (3, $-1$) bond critical points (BCP) were calculated. The corresponding results are shown in Table 2.

As the criterion proposed by Cremer and Kraka:\textsuperscript{57} $|V(r)| > G(r)$, $H(r)$ is negative, corresponds to covalent interactions; conversely, for closed-shell interactions, $|V(r)| < G(r)$, $H(r)$ is positive. This criterion was proved to be very sufficient to explore the bonding characteristics for actinide system.\textsuperscript{37–39} As shown in Table 2, the $H(r)$ values of all calculated BCPs in the PuO\textsubscript{2}(H\textsubscript{2}O)\textsubscript{n}\textsuperscript{2+} are negative,

\begin{align*}
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A') \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\end{align*}

Fig. 1 Structures and selected geometric parameters of PuO\textsubscript{2}(H\textsubscript{2}O)\textsubscript{n}\textsuperscript{2+} complexes (n = 1–6), which were optimized at the B3LYP/SDD, B3PW91/SDD, PBE0/SDD and PW91/SDD levels of theory (from top to bottom rows, respectively). \(r(\text{Pu}=\text{O})\) represents the bond length of plutonyl. Bond distances are in Å, and angles are in degrees.

\begin{align*}
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\end{align*}

Fig. 2 ESP-mapped molecular vdW surface of PuO\textsubscript{2}(H\textsubscript{2}O)\textsubscript{n}\textsuperscript{2+}. The unit is in kcal mol\textsuperscript{-1}. Surface local minima and maxima of ESP are represented as green and orange spheres, respectively.

\begin{align*}
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\text{PuO}_2(OH)_{2}^{2+} & \quad (\tilde{X}^3A) \\
\end{align*}

Fig. 3 Two-dimensional filled-color diagrams of ELF ($q = 0.70$) at the B3PW91/SDD level of theory.
The corresponding \( |V(r)|/\rho(r) \) ratio exceeds 1.0. The \( H(r) \) values of Pu-O\(_{\text{H}}\) bonds are relatively small (around \(-0.003\)), and with the increase of water molecules, this value is decreasing. These quantities suggest that the Pu-O\(_{\text{H}}\) bonds belong to weak covalent interactions. This conclusion is consistent with the ELF analysis. In term of the connection of sixth water molecule, there are two (3, \(-1\)) BCPs between the oxygen atom of sixth water molecule and two water molecules in the vertical plane of PuO\(_2\)(H\(_2\)O\(_6\))\(^{2+}\). The corresponding \( \rho(r) = 0.039 \), \( H(r) = -0.002 \), indicating that these two bonds are hydrogen bonds.

### 3.3 Orbital interactions

As can be seen from the above discussion, on the basis of PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\) complex, the additional water molecules will no longer bonding with the main PuO\(_2\)\(^{2+}\) molecule directly. To get more in-depth information about the roles that plutonyl orbitals play in the formation of plutonyl-water complexes, the TDOS, PDOS and OPDOS of PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\) and PuO\(_2\)(H\(_2\)O\(_6\))\(^{2+}\) were calculated and plotted with Gaussian curves, the corresponding full width at half maximum (FWHM) is 0.05 \(\text{a.u.} \). The TDOS, PDOS and OPDOS graphics are depicted in Fig. 4. The vertical dashed line indicates the position of the HOMO level. Fragment 1 is defined as the plutonyl orbitals and fragment 2 is defined as the oxygen and hydrogen atom orbitals.

As seen in Fig. 4, at the position of the HOMO level, the H\(_2\)O orbitals approached the TDOS line, which means that most of the contributions to the HOMO came from the H\(_2\)O orbitals. The OPDOS values of plutonyl and H\(_2\)O orbitals are almost zero, which means that there are weak covalent characters in PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\) and PuO\(_2\)(H\(_2\)O\(_6\))\(^{2+}\) complex. Comparing the two subgraphs, we found that the addition of the sixth water molecule had little effect on the overall DOS.

### 3.4 Weak interactions

With the aim of investigating the weak interactions of the PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\) and PuO\(_2\)(H\(_2\)O\(_6\))\(^{2+}\) complexes, we performed reduced density gradient (RDG) analysis. The RDG was defined as follows:

\[
s(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla \rho(r)|}{\rho(r)^{4/3}}
\]

where \( \rho(r) \) is electron density. The RDG \( s(r) \) isosurfaces are mapped with values of \( s(r)\text{sgn}(\lambda_2) \), where \( sgn \) is the sign function, and \( \lambda_2 \) is the sign of the second eigenvalue of the Hessian of the \( \rho(r) \).

Fig. 5 shows the 3D isosurfaces \((s = 0.5)\) and scatter plots of the RDG vs. \( \rho(r)\text{sgn}(\lambda_2) \) were generated for PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\) and PuO\(_2\)(H\(_2\)O\(_6\))\(^{2+}\) complexes. From the isosurfaces, we can see that the Pu–O\(_{\text{H}}\) interaction in PuO\(_2\)(H\(_2\)O\(_6\))\(^{2+}\) is slightly weaker than that in the PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\). The \( \rho(r)\text{sgn}(\lambda_2) \) value of Pu–O\(_{\text{H}}\) interaction in the PuO\(_2\)(H\(_2\)O\(_6\))\(^{2+}\) is ~0.0335 \(\text{a.u.} \), and the corresponding value in PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\) is ~0.034 \(\text{a.u.} \). In addition, there are two spikes in RDG vs. \( \rho(r)\text{sgn}(\lambda_2) \) of PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\), one is around ~0.01 \(\text{a.u.} \) corresponding the van der Waals interaction between the adjacent water molecules; the other one is around ~0.01 \(\text{a.u.} \), represents the steric repulsion effects between Pu and H\(_2\)O molecules which on both sides of Pu–O\(_{\text{H}}\). Differently, the RDG vs. \( \rho(r)\text{sgn}(\lambda_2) \) of PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\) is one more spike than that of PuO\(_2\)(H\(_2\)O\(_6\))\(^{2+}\) in the region of 0 to ~0.4 \(\text{a.u.} \). This spike around ~0.034 is corresponds to the hydrogen-bond interaction of the sixth H\(_2\)O molecule and two water molecules in the vertical plane of PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\).

In order to quantitatively gauge the bond strengths, in Table 3, we computed bond dissociation energies (BDE) of Pu–O\(_{\text{H}}\) bond for PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\), PuO\(_2\)(H\(_2\)O\(_4\))\(^{2+}\) and PuO\(_2\)(H\(_2\)O\(_3\))\(^{2+}\) as well as hydrogen-bond for PuO\(_2\)(H\(_2\)O\(_5\))\(^{2+}\) complexes. It can be clearly seen that, as the H\(_2\)O number increases, the BDE of Pu–O\(_{\text{H}}\) bond decrease. Taking PW91/SDD results as an example, the
BDE of Pu–Oyl for PuO$_2$(H$_2$O)$_x^{2+}$ as much as 49.788 kcal mol$^{-1}$/C$_0$1, which is larger than that computed for the PuO$_2$(H$_2$O)$_4^{2+}$ (36.675 kcal mol$^{-1}$/C$_0$1) and more larger than that for the PuO$_2$(H$_2$O)$_5^{2+}$ (27.145 kcal mol$^{-1}$/C$_0$1). In the case of O–H hydrogen-bond for PuO$_2$(H$_2$O)$_6^{2+}$, by contrast, the BDE is smaller (12.287 kcal mol$^{-1}$/C$_0$1 in PW91/SDD method).

4 Conclusions

The equilibrium structure, stabilities, electronic structures, chemical bonding and topological properties of PuO$_2$(H$_2$O)$_n^{2+}$ ($n = 1–6$) complexes in gas phase have been systematically investigated by different levels of theory. The following conclusions were refined from the present results.

1) The ground state geometry of these complexes was found, and our results show that all the ground states of these complexes are triplet. The water molecules of PuO$_2$(H$_2$O)$_m^{2+}$ ($m = 1–5$) are arranged on the equatorial plane of plutonyl. Reactivity analysis and optimization results of PuO$_2$(H$_2$O)$_6^{2+}$ show that, the oxygen atom of sixth water molecule connected with two water molecules in the vertical plane of PuO$_2$(H$_2$O)$_5^{2+}$ by hydrogen-bonds. These optimized geometries are in agreement with available theoretical and experimental results.

2) The properties of the chemical-bonding of these complexes were evaluated with ELF, AIM and TDOS, PDOS and OPDOS analyses. The ELF and AIM analyses indicate the Pu–Oyl bonds have weak covalent interaction. This conclusion is consistent with the OPDOS analysis. The TDOS results show that most of the contributions to the HOMO of PuO$_2$(H$_2$O)$_5^{2+}$ and PuO$_2$(H$_2$O)$_6^{2+}$ came from the H$_2$O orbitals.

3) The RDG approach was implemented to analyze the weak interactions and steric repulsions existed in PuO$_2$(H$_2$O)$_5^{2+}$ and PuO$_2$(H$_2$O)$_6^{2+}$ complexes. In addition to explaining weak covalent interactions of Pu–Oyl, the RDG results also suggest that the interactions of the sixth H$_2$O molecule and two water molecules in the vertical plane of PuO$_2$(H$_2$O)$_5^{2+}$ are hydrogen-bonds.

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References