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Plutonium complexes in water: new approach to ab initio modeling

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Abstract: Geometry optimization and the electronic structure calculations of Pu^{Z+} complexes ($Z = 3-6$) in water solution have been performed, within the framework of the DMol³ and Relativistic Discrete-Variational (RDV) methods. For the simulation of Pu^{Z+} molecular environment in aqueous solution we used 22 and 32 water molecules randomly distributed around cation. To model the effect of bulk solvent environment we used COSMO (Conductor-like Screening Model) potential for water ($\epsilon = 78.54$). The obtained results showed that this approach allows the modeling of water dissociation and the formation of hydrolysis products. Our previously suggested scheme for the calculation of interaction energies between selected fragments of multi-molecular systems provides the quantitative estimation of the interaction strengths between plutonium in various oxidation states and each ligand in the first and second coordination shells in water solution.

Keywords: DFT calculations; hydration and hydrolysis; stability of plutonium complexes.

1 Introduction

The structure and stability of the complexes formed by the actinide ions in water and acidic solutions is important because these species are the main forms of occurrence and transport of these metals in natural waters. On the other hand, the formation of actinide complexes with the organic ligands in the processing of spent nuclear fuel requires that they must compete with the ligands formed by the hydration and hydrolysis of the metal ions [1].

It is well known [2, 3] that plutonium in solution may exist in the four oxidation states simultaneously: III, IV, V and VI. In contrast, the uranium is commonly present in solution as UO_2^{2+} (uranyl ion) and the minor actinides normally exist in aqueous media as An^{3+} cations [2]. According to review [2], in the neutral and acidic solutions, Pu^{3+} exists as a simple cation coordinated to the water molecules and to the anions such as NO_3^- or Cl^- . The tetravalent Pu^{4+} in acidic solution also exists as a simple cation coordinated to the water molecules and acid anions, while in the pure water, the formation of $\text{Pu}(\text{OH})_x(\text{H}_2\text{O})_y^{4-x}$ is possible [2, 3]. The pentavalent Pu^{5+} in an aqueous media is commonly present as the linear plutonyl ion PuO_2^+ , which do not hydrolyze further until $\text{pH} = 9$ [3]. Hexavalent Pu^{6+} cations in aqueous solutions also immediately hydrolyze to form the linear plutonyl PuO_2^{2+} ion [4]. Further hydrolysis of PuO_2^{2+} may occur at $\text{pH} > 4$ and the formation of $\text{PuO}_2(\text{OH})_x(\text{H}_2\text{O})_y^{2-x}$ has been proposed [3]. Over the last decades, there has been a large increase in the theoretical simulations on actinide complexes [5] (and references therein) using various approaches for the inclusion of the aqueous solvation effects. However, a significant amount of calculations has been devoted to the uranium species, while there was less work on those of plutonium.

Blaudeau et al. [6] investigated the hydration of Pu^{3+} ions using DFT calculations of bare $\text{Pu}(\text{H}_2\text{O})_n^{3+}$ ($n = 6-12$) clusters and obtained that $n = 8$ corresponded to the most stable complex. In the more recent DFT simulations of Wiebke et al. [7] and Horowitz and Marston [8], the similar $\text{Pu}(\text{H}_2\text{O})_n^{3+}$ ($n = 7-9$) and $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ clusters respectively were embedded in the COSMO potential (Conductor-like Screening Model) to model a bulk dielectric medium. In the former work, the obtained mean $\text{Pu}^{3+}-\text{OH}_2$ distances of 2.56 Å ($n = 8$) and 2.60 Å ($n = 9$) [7] were larger than the experimental values of 2.48–2.51 Å [9–12]. However, the inclusion of water molecule in the second hydration shell induced the noticeable shortening of the bond length from 2.56 to 2.508 Å [7]. According to Refs. [6, 8], the obtained average $\text{Pu}^{3+}-\text{OH}_2$ bond lengths in the most stable $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ complexes (2.50–2.53[6] and 2.50 Å [8]) were in good agreement with experiment, although the experimental coordination numbers (CN) of Pu^{3+} in aqueous solution were larger: CN = 9 [9, 10] and CN = 10 [11, 12]. The explicit modeling of Pu^{3+} complexes in water

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solution was carried out by Odoh et al. [13] using a version of ab initio molecular dynamic approach (AIMD) with 64 water molecules in the periodic supercell. As shown, complex with the eight water molecules ($R_{\text{Pu-OH}_2} = 2.53 \text{ \AA}$) was also by $\sim 20 \text{ kJ/mol}$ (4.9 kcal/mol) more stable than $\text{Pu}(\text{H}_2\text{O})_9^{3+}$ deduced in experiment, and $\text{Pu}^{3+}\text{-OH}_2$ bond length in the latter cluster ($2.56 \text{ \AA}$) was larger than the experimental values.

According to the experimental studies of Pu^{4+} ion hydration [9, 14], the first solvation sphere of metal ion contains eight ligands with the average $\text{Pu}^{4+}\text{-O}$ distance of $2.38\text{--}2.39 \text{ \AA}$. In the works of Horowitz and Marston [8] and Odoh and Schreckenbach [15], the DFT calculations of Pu^{4+} ion in water were carried out for $\text{Pu}(\text{H}_2\text{O})_8^{4+}$ cluster using the COSMO – PCM approach (Polarizable Continuum Model) for the inclusion of solvation effects. The obtained mean $\text{Pu}^{4+}\text{-O}$ bond lengths (2.38 [8] and $2.39 \text{ \AA}$ [15]) were in excellent agreement with experiment. However, the more sophisticated calculations of Banik et al. [16] (spin-orbit CASPT2 multi-reference correlated approach) predicted that the complex with nine water molecules ($R_{\text{Pu-OH}_2} = 2.41 \text{ \AA}$) was more stable than those with $\text{CN} = 8$ and 10 . On the other hand, AIMD simulations of Pu^{4+} in the supercell with 64 water molecules [13] showed that $\text{Pu}(\text{H}_2\text{O})_9^{4+}$ complex was about 6 kJ/mol (1.4 kcal/mol) less stable than $\text{Pu}(\text{H}_2\text{O})_8^{4+}$, and the obtained mean $\text{Pu}^{4+}\text{-O}$ bond length ($2.41 \text{ \AA}$) in the latter cluster was also in good agreement with experiment. The similar good agreement with experimental structural data was obtained in MD + DFT modeling of $\text{Pu}(\text{H}_2\text{O})_8^{4+}$ and $\text{Pu}(\text{H}_2\text{O})_9^{4+}$ complexes reported by Acher et al. [17]. The largest $R_{\text{Pu-OH}_2}$ value of $2.45 \text{ \AA}$ for $\text{Pu}(\text{H}_2\text{O})_9^{4+}$ complex was obtained using Gaussian package in the works of Wang et al. [18], Xiao et al. [19] and Wu et al. [20].

In all DFT studies of Pu^{5+} hydration, the geometry optimization of metal complexes started from a linear PuO_2^+ plutonyl ion with the five or four water molecules in equatorial plane. However, the experimental numbers of these water molecules were highly variable [4]. According to Ref. [9], the four H_2O are the nearest neighbors of plutonyl ($R_{\text{Pu-Oyl}} = 1.84 \text{ \AA}$ and $R_{\text{Pu-OH}_2} = 2.45 \text{ \AA}$), while in Ref. [21], the average number of ligands is 3.3 only ($R_{\text{Pu-OH}_2} = 2.47 \text{ \AA}$); Madic et al. [22] found the five water molecules ($R_{\text{Pu-Oyl}} = 1.81 \text{ \AA}$ and $R_{\text{Pu-OH}_2} = 2.47 \text{ \AA}$), and according to EXAFS measurements of Panak et al. [23], the number of equatorial ligands was 3.8 ($R_{\text{Pu-Oyl}} = 1.82 \text{ \AA}$, $R_{\text{Pu-OH}_2} = 2.48 \text{ \AA}$). In DFT calculations of Hay et al. [24], the obtained $R_{\text{Pu-Oyl}}$ distance ($1.81 \text{ \AA}$) in $\text{PuO}_2(\text{H}_2\text{O})_5^{1+}$ cluster was close to experimental values ($1.81\text{--}1.84 \text{ \AA}$), whereas the mean $R_{\text{Pu-OH}_2}$ bond length of $2.61 \text{ \AA}$ was larger than those measured in the experiment ($2.45\text{--}2.48 \text{ \AA}$). The modeling of solution using COSMO-PCM models in the calculations of

$\text{PuO}_2(\text{H}_2\text{O})_5^{1+}$ cluster [8,15] yielded the similar $R_{\text{Pu-Oyl}}$ distances ($1.8 \text{ \AA}$), while the mean $R_{\text{Pu-OH}_2}$ bond lengths (2.62 [8] and $2.57 \text{ \AA}$ [15]) were also larger than the experimental values. On the other hand, in the work of Austin et al. [25], the 10 water molecules were added to $\text{PuO}_2(\text{H}_2\text{O})_5^+$ cluster to model the second solvation shell, two of which were hydrogen bonded to each of the five equatorial water molecules in the first coordination sphere, and the obtained distances ($R_{\text{Pu-Oyl}} = 1.81 \text{ \AA}$, $R_{\text{Pu-OH}_2} = 2.50\text{--}2.52 \text{ \AA}$) for $\text{PuO}_2(\text{H}_2\text{O})_5^+$ complex were in better agreement with experiment. It is interesting that AIMD simulations of Pu^{5+} ion in the supercell with 64 water molecules [13] showed that the second coordination sphere of $\text{PuO}_2(\text{H}_2\text{O})_4^+$ complex (predicted to be more stable than $\text{PuO}_2(\text{H}_2\text{O})_5^+$) contained approximately 16 water molecules (eight in equatorial and eight in apical region), and the obtained structural parameters ($R_{\text{Pu-Oyl}} = 1.85 \text{ \AA}$ and $R_{\text{Pu-OH}_2} = 2.47 \text{ \AA}$) were close to experimental values.

As mentioned above, Pu^{6+} cations in aqueous solutions immediately hydrolyze to form the linear plutonyl PuO_2^{2+} ion [4]. However, the measured number of the equatorial water molecules in $\text{PuO}_2(\text{H}_2\text{O})_n^{2+}$ complexes varied between 4 and 6 , and the experimental ranges of $R_{\text{Pu-Oyl}}$ ($1.74\text{--}1.79 \text{ \AA}$) and the mean $R_{\text{Pu-OH}_2}$ distances ($2.31\text{--}2.45 \text{ \AA}$) for Pu^{6+} aqua complexes were wider than for other plutonium ions [9, 23, 26]. As in the case of Pu^{5+} , all theoretical simulations started with the configurations containing linear PuO_2^{2+} ion with the few nearest water molecules in equatorial region. Although the obtained $R_{\text{Pu-Oyl}}$ distances (1.74 [8], $1.72\text{--}1.75$ [15], 1.77 [19], $1.79 \text{ \AA}$ [27]) were in agreement with experimental interval ($1.74\text{--}1.79 \text{ \AA}$), the mean $R_{\text{Pu-OH}_2}$ bond lengths for the four and five H_2O molecules (2.44 [15], 2.465 [20], 2.47 [8] and $2.49 \text{ \AA}$ [19, 27]) were slightly larger than the experimental values ($2.31\text{--}2.45 \text{ \AA}$). On the other hand, Spencer et al. [28] investigated the three clusters, where PuO_2^{2+} ion was coordinated to the four, five and six water molecules. They obtained that $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$ was more stable, though the mean value of $R_{\text{Pu-OH}_2}$ ($2.52 \text{ \AA}$) in this complex was noticeably larger than the experimental data. As in the case of Pu^{5+} hydration, Austin et al. [25] added the 10 water molecules to $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$ cluster to model the second solvation shell, and the obtained distances ($R_{\text{Pu-Oyl}} = 1.76 \text{ \AA}$ and $R_{\text{Pu-OH}_2} = 2.40\text{--}2.41 \text{ \AA}$) were in better agreement with experiment. In contrast to all DFT calculations, AIMD simulations of Pu^{6+} hydration [13] predicted that $\text{PuO}_2(\text{H}_2\text{O})_4^{2+}$ complex was more stable than $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$ by 11 kJ/mol (2.55 kcal/mol) and the obtained structural parameters for the former ($R_{\text{Pu-Oyl}} = 1.77 \text{ \AA}$ and $R_{\text{Pu-OH}_2} = 2.38 \text{ \AA}$) were in agreement with the experimental intervals. It is important to note that even in the modeling of large $\text{An}(\text{H}_2\text{O})_{30}^{3+}$, $4+$ and $\text{AnO}_2(\text{H}_2\text{O})_{30}^{+, 2+}$ clusters considered in the works of Clark

et al. [29] and Parmar et al. [30], the numbers of water molecules in the first solvation shell of $\text{An}^{3+, 4+}$ and AnO_2^{2+} were kept constant during geometry optimizations.

Surprisingly, there is no experimental information on the structural parameters of plutonium hydroxides $[\text{Pu}(\text{OH})_m(\text{H}_2\text{O})_{n-m}]^{Z-m}$ neither for Pu^{4+} nor for Pu^{6+} complexes, though the existence of these species in aqueous solutions was experimentally confirmed [1–4, 31–35]. To the best of our knowledge, only one work [25] was devoted to the DFT simulations of $\text{PuO}_2(\text{OH})_5^{-4, -3}$ hydroxide complexes of Pu^{5+} and Pu^{6+} in aqueous solution using $10\text{H}_2\text{O}$ to model the second solvation shell. The obtained mean $R_{\text{Pu}-\text{OH}}$ distances for Pu^{5+} (2.43–2.55 Å) and Pu^{6+} (2.35–2.49 Å) were of the same order as those for the water molecules, whereas $\text{Pu}-\text{O}_{\text{yl}}$ bonds (~1.90 and ~1.83 Å) were longer than those in the complexes with the water ligands. In the recent work of Boguslawski et al. [36], the geometry optimization of the neutral $\text{PuO}_2(\text{OH})_2$ molecule in gas phase was performed predicting the $\text{Pu}^{6+}-\text{OH}$ distance near 2.1 Å.

Thus, in all previous simulations, the two approaches for constructing of Pu^{Z+} aqueous complexes were used: (1) the more or less constrained geometry optimization of the clusters composed of plutonium (or plutonyl) ion with the fixed first solvation shell and some constant number of water molecules modeling the second solvation shell; (2) MD modeling of periodic supercells based on pair-potentials with fitting parameters. Moreover, to the best of our knowledge, there were no examples or even attempts of the “static” quantum-chemical (QC) or “dynamical” MD simulations, which started from Pu^{Z+} ions (released by dissolution of solid species) interacting with the several water molecules and yielded the products of hydrolysis (OH^- or $\text{PuO}_2^{+, 2+}$) at the final stage of geometry optimizations. However, in the cases, where experimental information on the probability of hydrolysis is ambiguous or completely absent, the way to obtain such knowledge during a direct geometry optimizations could be more efficient than the comparison of all more or less probable complexes containing hydrolysis products. From our point of view, the DMol³ method allows one to solve this problem, i.e. to model the dissociation of water molecules and to estimate quantitatively the strength of interaction between actinide ion and its neighbors, namely the water molecules, hydroxide ions, acid anions and organic ligands. Another point of interest concerns the nature of $\text{Pu}5f$ orbitals. Although there is a general consensus that the main plutonium – ligand bonding takes place through the ligand interactions with the $\text{Pu}6d$ states [4], the role of $\text{Pu}5f$ orbitals in bonding could be comparable with that of $\text{Pu}6d$ in the cases of short $\text{Pu}-\text{O}$ distances, as those in plutonyl [37].

In past calculations, the values of total (E_{tot}) or binding energy (E_b) were used to measure the relative stability of various structures. The binding energy of a neutral complex (also called the “total bond energy” or the “atomization energy”) is defined as $E_b = E_{\text{tot}} - \Sigma E_{\text{at}}$, where ΣE_{at} is the sum of total energies of all isolated neutral atoms in the investigated object. In the systems containing several water molecules and other ligands interacting with the actinide ion and with each other, the values of E_{tot} or E_b are not informative, because these energies “include” the interactions between all atoms in a system, some of them are tightly bound with metal, whereas others are in the next coordination spheres and their interaction with the actinide is weak. In the calculations herein, we used the new method [38] for the separate estimation of the energies characterizing the interactions of Pu^{Z+} with each component of the investigated systems: (1) with the water molecules in the first and second layers; (2) with OH^- ions; and (3) with the oxygen atoms in plutonyl cation. Another aim of this work was to study the nature of actinide bonding with the nearest neighbors and the role played by $\text{Pu}5f$ orbitals.

2 Methods of calculations

For the modeling of solutions in QC calculations, the two approaches may be used: (1) continuum (or implicit) solvation model; (2) micro-solvation (or explicit) model. The former approach is based on the so-called COSMO (or PCM) potentials, which replace the solvent by a polarizable continuum [39, 40]. It is evident that these models are not appropriate for the systems, where the direct solute – solvent interactions are important; i.e., in the simulations of hydrogen bonds formation or in the modeling of hydration and hydrolysis reactions. The explicit approach means the inclusion of a finite number of solvent molecules into a system under investigation. The evident problem of the latter model is the ambiguities of a number of solvent molecules, which is enough for the correct description of the investigated processes. Another shortcoming of this approach is the rapid increasing amount of the solvent molecules even in the first layer as the size of solute object increases. On the other hand, it is possible to combine both methods: to use the microsolvation model for the first (and probably for the second) coordination sphere and to simulate the more distant environment by COSMO potential of a corresponding liquid.

Using the typical lengths of the hydrogen bonds and the average volume per one molecule in a water with density $\rho = 10^3 \text{ kg/m}^3$, we constructed manually the first solution coordination sphere of one actinide atom. As a result, we obtained the shell containing at least 22 molecules. In contrast to all previous works, we started with the bare Pu^{Z+} ions (including $Z = 5$ and 6) and the random orientations of water molecules. The shape of this system is shown in Figure 1. As seen, in this initial configuration, we did not divide manually the molecules between the nearest and next nearest solution shells, and the formation of both shells was achieved through geometry optimization. It is

interesting that according to AIMD simulations of the actinide and actinyl ions hydration in the large supercells [13, 41], the obtained approximate total numbers of the water molecules in the first and second coordination shells was between 21 and 23, respectively.

As mentioned above, 22 is the minimum number of water molecules in the first coordination shell; however, one could increase the “thickness” of this shell (of the same cavity size) by the inclusion of additional molecules. The system containing 32 water molecules is also shown in Figure 1. From our point of view, the latter system does not model the two complete solvation layers as supposed in [29, 30], but rather corresponds to the case, which is intermediate between the first and the first plus second coordination shells.

The geometry optimizations of these initial structures were performed using DMol³ method [42] in the all-electron scalar relativistic approximation [43] with double numerical atomic basis set with the polarization functions (“dnp”). The GGA-PBE potential [44] and “fine” grid for numerical integration were used in all calculations. Coulomb potential was computed with the use of model density obtained as the decomposition of charge density into multipolar components including those with $l = 3$ (“octupole”). Optimization of the system geometry was done until change in a value of maximum energy gradients was less than 0.001 Hartree/Bohr, the atomic displacements converged to within 0.001 Å and the global orbital cutoff was 8.0 Å. In DMol³ calculations, the scheme of Hirshfeld [45] was used to compute the atomic charges (Q_{at}).

To investigate the nature of inter-atomic bonding and the role played by 5f electrons in these species we used the original code of the fully relativistic discrete variational method (RDV) [46, 47]. For each geometrical structure obtained by DMol³, the RDV calculation was carried out. The RDV method is based on the solution of Dirac-Slater equation for four-component molecular orbitals (MO) transforming according to the irreducible representations of the double point group. The extended bases of four-component numerical atomic orbitals (AO) obtained as the solution of Dirac-Slater equation for the isolated neutral atoms also included $Pu7p_{1/2}$ and $7p_{3/2}$ functions in addition to the occupied AOs. The effective charges on atoms were computed as the integrals of electron density inside the domains bounded by the points of its minimum [48].

As mentioned above, the total and binding energies of a final optimized system depend on all inter-atomic bonds, while the most interesting are the interactions between metal ion and the components of its complex: nearest water molecules, the hydroxide and oxygen atoms in dioxo cations. To “extract” the energy characterizing the interaction between Pu^{Z+} and any selected component of the investigated system, we suggested the scheme including a set of additional

calculations of the model systems, where the parts of interactions were excluded consecutively [38]. In Figure 2, we illustrate this scheme for $(Pu + 22H_2O)^{4+}$ system, where the formation of $PuOH(H_2O)_8$ complex occurred. After the geometry optimization had been converged, one considers the first model system, where the interactions between Pu and all other atoms are excluded. In this system, the final optimized positions of all O and H atoms are fixed, while the metal ion was shifted away by 200 Å. The difference in energies of the optimized system (E_{opt}) and the model system with distant actinide atom (E_{r1}) allows one to estimate the energy of “net interaction” between Pu and the complete environment (E_i) in the investigated system:

$$E_i = E_{opt} - E_{r1} \quad (1)$$

From our point of view, this value can serve as a measure of actinide complex stability in solution. In the next model system, the interactions of hydroxide group with all other atoms and molecules are excluded (E_{r2}). In the third system, the interactions of actinide and hydroxide ion with all other atoms are excluded (E_{r3}).

After the four energies (E_{opt} , E_{r1} , E_{r2} , E_{r3}) had been computed, it is possible to calculate the energy, which can characterize the “net interaction” between Pu and OH group:

$$E_{Pu-OH} = \frac{1}{2} (E_{opt} - E_{r1} - E_{r2} + E_{r3}) = \frac{1}{2} (E_i - E_{r2} + E_{r3}) \quad (2)$$

To deduce this expression, we supposed that the interactions between metal and each component of a system could be described by the additive energetic parameters (E_i , E_{Pu-OH} , E_{Pu-8H_2O} , etc.). The definition of these *model parameters* is based on the energy changes, when the selected interactions are removed from the investigated system. For example, the obtained values of E_i and E_{Pu-OH} allow one to estimate the energy of plutonium interaction with all other atoms in the system: $E_{Pu-21H_2O+H} = E_i - E_{Pu-OH}$. To calculate the energy of interaction between actinide and the selected group of water molecules, one needs to consider the two new model systems for the calculation of new E_{r2} and E_{r3} : in the first one, the selected water molecules are shifted by 200 Å (new E_{r2}) and in the second model system, these molecules with metal ion are shifted from other atoms in the system (new E_{r3}). Eq. (2) could be easily generalized to any multi-component object. It is important to note that the relative positions of atoms within the separated fragments are the same as in the optimized system, because any additional relaxation will change the interaction between atoms in the subsystems, which one needs to cancel using Eq. (2). It is worth mentioning that the calculations of all model systems have to be carried out using the same method as in the geometry optimization, i.e., the inclusion of COSMO potential in the calculation of E_{opt} requires the use of the same boundary conditions in the calculations of E_{r1} , E_{r2} and E_{r3} .

Since any interaction, which has to be removed from a system, includes a short-range covalent bonding as well as a long-range ionic bonding, the separation of interacting objects by 5–10 Å is quite enough to remove the former, while for the exclusion of long-range ionic bonding, the shifts of hundreds angstroms are needed (especially if the screening COSMO potential is absent). In the present calculations, we used the value of 200 Å, which provides the residual energy of interaction between Pu^{Z+} and the singly charged ions (such as OH^- or H^+) less than 0.1 eV (~10 kJ/mol). It is evident that the alternative way to exclude an interaction between the selected fragments is the complete removal of some of the interacting fragment from the system; however, this can change the charge state of the system accompanied by additional and unpredictable changes in the calculated energies.

Figure 1: (Color online) The structures of starting systems containing one metal atom (large sphere) and 22 water molecules (left) or 32 water molecules (right).

Figure 2: (Color online) The scheme for estimation of the interaction energy between metal and hydroxide ion in $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ system.

3 Results and discussion

The initial $(\text{Pu} + 22\text{H}_2\text{O})^{Z+}$ and $(\text{Pu} + 32\text{H}_2\text{O})^{Z+}$ systems shown in Figure 1 were subjected to geometry optimization, leading firstly to the formation of hydrogen bonds and then to the formation of plutonium complexes with 7–9 water molecules, i.e. the distances between metal and some water molecules decreased, while the rest molecules became more distant. The oxidation states of plutonium in pure water were modeled by the reduction of the number of electrons in $(\text{Pu} + 22\text{H}_2\text{O})^{Z+}$ and $(\text{Pu} + 32\text{H}_2\text{O})^{Z+}$ systems ($Z = 3-6$). Initially we planned to carry out the two sets of calculations, one set with the COSMO boundary conditions and the second set without this potential. However, in the modeling of cationic systems corresponding to $Z = 4-6$, we obtained that some part of the excess charge was distributed among the water molecules, and in the absence of screening potential, the ionic repulsion induced the dissociation of the system during geometry optimization; i.e., the distances between actinide and some water molecules increased up to 20–30 Å. For this reason, the COSMO potential for water ($\epsilon = 78.54$) was used in the geometry optimization of all systems, and only in the case of $(\text{Pu} + 22\text{H}_2\text{O})^{3+}$, we performed the two types of calculations. Unfortunately, we could not estimate the role of this potential for all oxidation states of plutonium, as in the work of Parmar et al. [30], wherein the considerable enlargement of $\text{U}(\text{H}_2\text{O})_n^{Z+}$ clusters up to $n = 41$ and 77 improved the agreement with experiment only without PCM boundary conditions, while their inclusion induced the increase of disagreement between calculated and experimental hydration energies. It is worth mentioning that the calculations of large clusters [30] also showed that the systems with 30 H_2O optimized the cancellation of errors when PCM potentials were used.

Since the results of geometry optimization of polyatomic system depend on the initial structure, we considered the various starting geometries with different initial Pu–OH₂ distances and orientations of water molecules. In the

simulations of smaller systems, we used 9–10 starting configurations, where the positions of H₂O molecules were changed by ~0.5–1.0 Å. As a result, the final positions of water molecules in the optimized systems were also different, and the CN of metal ion varied between 7 and 9. It is worth mentioning that even in the calculations of smaller system, the convergence was achieved after the several hundreds of geometry iterations, and the final positions of water molecules were considerably different from those in the initial structures (Figure 1). Since the geometry optimization of the larger system was considerably more time-consuming, in each case, we used only five starting geometries created by the shifts of water molecules by 0.5–1.0 Å. In contrast to the smaller systems, in these simulations, the similar compositions and geometries of the optimized plutonium complexes were obtained for all starting configurations. It is important to note that in all simulations, the variation of E_{opt} due to different final positions of water molecules was less than 1% in the smaller systems and less than 0.1% in the systems with 32 H_2O . The variation of interaction energies (E_i) due to the different starting geometries in the smaller systems was near 10%, whereas the variation of these energies in the larger systems was less than 5%. Therefore, we can suggest that the properties of the most stable complexes obtained in our modeling were close to those of the unknown global minima. We also can suggest that the calculations of larger systems allow one to estimate some parameters of the true ground structures upon “single” geometry optimization.

There exists an opinion that the best initial configurations (“initial structural sampling”) for the QC geometry optimization of metal-water clusters could be extracted from the results of MD modeling for the large supercells. To verify this idea we performed the MD simulations for Pu^{3+} complex using Universal Force Field (UFF) method [49], as implemented in deMon software [50]. The Pu^{3+} ion was immersed into periodic $24.65 \times 24.65 \times 24.65$ (Å) supercell containing 500 H₂O molecules, hence, corresponding to the water with density $\rho = 10^3 \text{ kg/m}^3$. The MD

simulations were performed during 1 ns with the time step 1.0 fs for canonical (NVT) ensembles at the temperature $T = 350$ K using the global Berendsen thermostat with the time constant of 100 fs. Finally, the spherical $\text{Pu}(\text{H}_2\text{O})_{22}^{3+}$ cluster (where Pu^{3+} appeared to be coordinated to eight nearest H_2O molecules) was removed from a center of supercell and subjected to geometry optimization using DMol³ with COSMO boundary conditions. The results of this calculation showed that the structure obtained using pair potentials was far from equilibrium when the more accurate ab initio QC method was applied, and the stability of the final optimized $(\text{Pu} + 22\text{H}_2\text{O})^{3+}$ system as well as of $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ complex was by 20 kJ/mol lower than that of the most stable complex obtained from initial configuration with randomly distributed water molecules. Note, as reported in the paper of Parmar et al. [30], they performed the MD modeling for the generation of five configurations for the clusters containing the rigid $\text{U}(\text{H}_2\text{O})_8^{Z+}$ (or $\text{UO}_2(\text{H}_2\text{O})_5^{Z+}$) complexes surrounded by 33 (or 36) and 69 (or 72) water molecules, whereas in the cases of uranium and plutonium systems with $30\text{H}_2\text{O}$, the single geometry optimization was performed using NWChem package [29, 30].

In the cases of $Z = +4$, $+5$ and $+6$, we also tested the “completeness” of hydrolysis in the obtained optimized systems. For this purpose, one hydrogen atom of the nearest to Pu^{Z+} water molecule was shifted by 0.5–1.0 Å toward a molecule in the second solvation shell, and then the geometry optimization was performed again. In all calculations, the hydrogen atom either moved back to the “parent” molecule or became a part of H_3O^+ (oxonium) ion in the second coordination sphere. The comparison of E_i obtained before and after this manipulation showed which configuration could be considered as the ground state of the Pu^{Z+} complex. Earlier [51], we used a similar procedure to search for the more stable positions of actinide atoms inside the C_{60} fullerene.

3.1 Pu^{3+} complexation

In the case of various starting configurations of the $(\text{Pu} + 22\text{H}_2\text{O})^{3+}$ system, the formation of complexes containing 7–9 water molecules took place and the most stable one was $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ presented in Tables 1 and 2. In the larger system, only one type of complex containing eight molecules was obtained. As seen, the coordination number of metal was the same in both systems, and the energies of Pu interaction with eight water molecules forming the nearest hydration envelope ($E_{\text{Pu}-8\text{H}_2\text{O}}$) were similar (–954 and –957 kJ/mol). Consequently, the average energies of the metal ion interaction with each

H_2O molecule in the predicted complexes were close to –120 kJ/mol. The difference between E_i and $E_{\text{Pu}-8\text{H}_2\text{O}}$ for both systems showed that the energies of interaction between actinide and the rest part of water molecules was –97 and –72 kJ/mol, respectively; i.e., the interaction of plutonium with the second layer of water molecules is only 8–10% of the bonding with the nearest ligands.

According to our results, the average distances between actinide and the oxygen atoms in the hydration envelope of the most stable complexes were 2.54 Å ($22\text{H}_2\text{O}$) and 2.53 Å ($32\text{H}_2\text{O}$) (Table 1). As mentioned above, the experimental studies reported that CN for An^{3+} aqua ions are highly variable (8–10) and the mean $R_{\text{Pu}-\text{OH}_2}$ distances are between 2.48 and 2.51 Å [9–12]. On the other hand, the results of DFT and AIMD calculations [6–8, 13] also predicted that the complexes with eight coordinating water molecules were the most stable for Pu^{3+} aqua ion and the $R_{\text{Pu}-\text{OH}_2}$ distances (2.50–2.56 Å) were similar to our values.

3.2 Pu^{4+} complexation

In this case, the hydrolysis of one water molecule took place in both kinds of systems (Table 1). We also found that these most stable actinide complexes had 8 and 7 water molecules in addition to the hydroxide ligand. However, in the geometry optimization of $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ system, we also obtained the configuration with “non-hydrolyzed” $\text{Pu}(\text{H}_2\text{O})_8^{4+}$ complex, which was by ~60 kJ/mol less stable than $\text{PuOH}(\text{H}_2\text{O})_8^{4+}$. We used this “non-hydrolyzed” $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ system for the comparison of our free energy of hydration with experiment and other calculations (vide infra). Though the CN value of $\text{PuOH}(\text{H}_2\text{O})_7^{4+}$ complex in the larger system was less than that of $\text{PuOH}(\text{H}_2\text{O})_8^{4+}$ in the smaller system, the corresponding $|E_i|$ for the former (1256 kJ/mol) was larger than that obtained for the latter complex (1220 kJ/mol). The hydrolysis reactions were accompanied by the appearance of released H^+ ions. In all investigated systems, these protons initially moved to the nearest water molecules, and the formation of oxonium ions H_3O^+ occurred. However, in all calculations, this process was continued by the association of oxonium with a more distant (from metal site) water molecule with the formation of di-oxonium ion H_5O_2^+ . These results of our calculations are in agreement with experiment [52] and ab initio simulations [53].

As mentioned above, E_i value of –1220 kJ/mol calculated for the $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ system can be present as a sum of the four energies for the interactions between Pu and the four components of optimized system: (1) with hydroxide

ion ($E_{\text{Pu-OH}}$); (2) with eight water molecules in the nearest hydration envelope ($E_{\text{Pu-8H}_2\text{O}}$); (3) with dioxonium ion H_5O_2^+ ($E_{\text{Pu-H}_5\text{O}_2^+}$); and (4) with 11 water molecules in the second coordination sphere ($E_{\text{Pu-11H}_2\text{O}}$). In this case, the relation

$$E_i = E_{\text{Pu-OH}} + E_{\text{Pu-8H}_2\text{O}} + E_{\text{Pu-H}_5\text{O}_2^+} + E_{\text{Pu-11H}_2\text{O}} \quad (3)$$

could be numerically fulfilled with some approximation, so we used this system to test the accuracy of our calculations. Since the main origin of errors is the non-complete exclusion of the interactions between selected components due to the finite shift from each other, we performed the three sets of calculations with the shifts of 20, 200 and 2000 Å. In the calculations of model systems, we found (in kJ/mol): $E_i = -1224$ (20 Å) and -1220 for both shifts of 200 and 2000 Å; $E_{\text{Pu-OH}} = -304$ (20 Å) and -305 (for 200 and 2000 Å); $E_{\text{Pu-8H}_2\text{O}} = -869$ (20 Å) and -865 (200 and 2000 Å); $E_{\text{Pu-H}_5\text{O}_2^+} = +17$ (20 Å) and $+19$ (200 and 2000 Å); $E_{\text{Pu-11H}_2\text{O}} = -72$ (20 and 200 Å) and -71 (2000 Å). Thus, the sums of the four “partial” energies for the shifts of 20, 200 and 2000 Å are: -1228 ($E_i = -1224$), -1223 ($E_i = -1220$) and -1222 ($E_i = -1220$), respectively. As seen, even the shift of 20 Å provided the reasonable accuracy of calculations.

The obtained value for $E_{\text{Pu-8H}_2\text{O}}$ in $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ system means that the energy of metal atom interaction with each H_2O molecule is close to -108 kJ/mol. For $(\text{Pu} + 32\text{H}_2\text{O})^{4+}$ system, the energy per one molecule is close to -123 kJ/mol. Note, both specific energies are similar to the corresponding values obtained for the Pu^{3+} complexes. As shown for the $(\text{Pu} + 32\text{H}_2\text{O})^{4+}$ system, the energies of Pu interaction with OH^- and with dioxonium H_5O_2^+ (-326 and $+44$ kJ/mol) were slightly different than those obtained for the smaller system. Note, in the larger system, the sum of $E_{\text{Pu-OH}}$, $E_{\text{Pu-7H}_2\text{O}}$ and $E_{\text{Pu-H}_5\text{O}_2^+}$ (-1143 kJ/mol) differs from E_i by -113 kJ/mol,

which can be referred to the interaction with the water molecules in outer layer.

The average distances between Pu^{4+} and the oxygen atoms of coordinating water molecules in the most stable complexes were near 2.53 Å ($22\text{H}_2\text{O}$) and 2.47 Å ($32\text{H}_2\text{O}$) (Table 1). In the experimental study of Pu^{4+} ions hydration [9], the presence of eight water molecules with an equal $\text{Pu}^{4+}\text{-O}$ distance of 2.39 Å was obtained, whereas in the experimental work of Rothe et al. [14], the uncertainty on CN from eight to nine with $\text{Pu}^{4+}\text{-O}$ distance of 2.38 ± 0.02 Å was reported. The noticeable difference between our results and the experiment was evidently due to the presence of hydroxide ions in the most stable complexes. Indeed, in the less stable $\text{Pu}(\text{H}_2\text{O})_8^{4+}$ complex also obtained in the geometry optimization of the $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ system, the mean $R_{\text{Pu-OH}_2}$ value of 2.39 Å was in agreement with experiment. Although, there are the numerous experimental evidences that Pu^{4+} ions form the hydrolysis products even in the acidic solutions [4], we had not found any experimental data for the $\text{Pu}^{4+, 6+}\text{-OH}$ distances in the literature. In our calculations, the $\text{Pu}^{4+}\text{-OH}$ bond lengths (2.08 and 2.11 Å) were considerably less than those for the hydrating water molecules, while in the DFT simulations of Pu^{5+} and Pu^{6+} complexes with the five hydroxide groups [25], the obtained mean $R_{\text{Pu-OH}}$ distances for the Pu^{5+} (2.43–2.55 Å) and Pu^{6+} (2.35–2.49 Å) species were of the same order of magnitude as those for the water molecules. However, the decreasing number of hydroxide ions in an actinide complex has to induce the shortening of the corresponding bond lengths. Indeed, the geometry optimization of the neutral $\text{PuO}_2(\text{OH})_2$ molecule in a gas phase [36] predicted the $\text{Pu}^{6+}\text{-OH}$ distance near 2.1 Å, which is close to our values.

Table 1: Obtained compositions of plutonium complexes, coordination numbers of metal atom (CN) and average distances (Å) between actinide and oxygen atoms of water molecules ($R_{\text{Pu-OH}_2}$), hydroxide ions ($R_{\text{Pu-OH}}$) and plutonyl ions ($R_{\text{Pu-Oyl}}$) obtained in this work and in experiment [9–12, 14, 21–23, 26].

Z	Complex	(CN)	$R_{\text{Pu-OH}_2}$		$R_{\text{Pu-OH}}$	$R_{\text{Pu-Oyl}}$	
			This work	Exper.		This work	Exper.
(Pu + 22H ₂ O) ^{Z+}							
3	Pu(H ₂ O) ₈	(8)	2.54	2.48–2.51	–	–	–
4	PuOH(H ₂ O) ₈	(9)	2.53	2.38–2.39	2.08	–	–
5	PuO ₂ (H ₂ O) ₅	(7)	2.55	2.45–2.48	–	1.86	1.81–1.84
6	PuO ₂ (H ₂ O) ₅	(7)	2.44	2.31–2.45	–	1.81	1.74–1.79
(Pu + 32H ₂ O) ^{Z+}							
3	Pu(H ₂ O) ₈	(8)	2.53	2.48–2.51	–	–	–
4	PuOH(H ₂ O) ₇	(8)	2.47	2.38–2.39	2.11	–	–
5	PuO ₂ (H ₂ O) ₅	(7)	2.53	2.45–2.48	–	1.86	1.81–1.84
6	PuO ₂ (OH) ₂ (H ₂ O) ₃	(7)	2.48	2.31–2.45	2.30	1.83	1.74–1.79

Table 2: Effective charges (e) and spin densities S_{Pu} (μ_B) on actinide atom obtained using DMol³ – Hirshfeld scheme and RDV-Integral procedure, binding energies (kJ/mol) of optimized systems (E_b), energies of Pu interaction with all atoms (E_i), with the nearest water molecules ($E_{\text{Pu}-n\text{H}_2\text{O}}$), with hydroxide ions ($E_{\text{Pu}-\text{OH}}$) and with oxygen atoms of plutonyl ($E_{\text{Pu}-2\text{Oyl}}$).

Z	Complex	$Q_{\text{Pu}}/S_{\text{Pu}}$ DMol ³	Q_{Pu} RDV	E_b	E_i	$E_{\text{Pu}-n\text{H}_2\text{O}}$	$E_{\text{Pu}-\text{OH}}$	$E_{\text{Pu}-2\text{Oyl}}$
(Pu + 22H ₂ O) ²⁺								
3	Pu(H ₂ O) ₈	0.79/4.94	2.31	−22,549	−1051	−954	—	—
4	PuOH(H ₂ O) ₈	0.84/4.08	2.45	−21,966	−1220	−865	−305	—
5	PuO ₂ (H ₂ O) ₅	0.69/3.19	2.87	−21,354	−1573	−575	—	−1074
6	PuO ₂ (H ₂ O) ₅	0.81/2.15	3.10	−20,755	−1382	−518	—	−866
(Pu + 32H ₂ O) ²⁺								
3	Pu(H ₂ O) ₈	0.80/4.93	2.29	−33,141	−1029	−957	—	—
4	PuOH(H ₂ O) ₇	0.84/4.06	2.60	−32,578	−1256	−861	−326	—
5	PuO ₂ (H ₂ O) ₅	0.73/3.20	2.90	−32,126	−1524	−604	—	−1060
6	PuO ₂ (OH) ₂ (H ₂ O) ₃	0.79/2.18	3.09	−31,480	−1627	−355	−499	−999

3.3 Pu⁵⁺ complexation

The geometry optimization of the (Pu + 22H₂O)⁵⁺ system from the various starting configurations revealed the complete dissociation of one and two water molecules leading to the formation of the PuO(H₂O)₈³⁺, PuO(OH)(H₂O)₅²⁺ and PuO₂(H₂O)₅¹⁺ complexes. Although the binding energy of the optimized system with the latter cluster was only slightly lower, the absolute value of E_i was by ~100 kJ/mol larger than those for the two other complexes. As mentioned above, the numerous experimental data [1–5] confirmed the possibility of PuO₂⁺ formation in the latter case. In the calculations of (Pu + 32H₂O)⁵⁺ system, the various starting configurations converged to the formation of PuO₂⁺ unit (with Pu–O bonds of 1.86 Å), which was coordinated to the five water molecules with the average Pu–O bond length of 2.53 Å (Table 1). The shape of the optimized (Pu + 32H₂O)⁵⁺ system is shown in Figure 3.

It is worth mentioning that O–Pu–O angle in the plutonyl ions obtained in both systems was near 179°; i.e., the geometry of these cations was close to linear in agreement with experiment. However, the calculated Pu–O_{yl} bonds (1.86 Å) were at least 0.02 Å longer than the experimental values (1.81–1.84 Å) [9, 22, 23] and the calculated mean Pu–OH₂ distances (2.55 and 2.53 Å) were noticeably longer than those reported in the experimental works (2.45–2.48 Å) [9, 21–23]. Note, the similar overestimation of Pu–OH₂ bonds in PuO₂(H₂O)₅⁺ complexes was also obtained in other DFT and AIMD calculations [8, 13, 15, 24, 25].

In addition to E_i , $E_{\text{Pu}-5\text{H}_2\text{O}}$ and $E_{\text{Pu}-2\text{Oyl}}$ obtained for the (Pu + 32H₂O)⁵⁺ system (−1524, −604 and −1060 kJ/mol) we also calculated the interaction energies of Pu⁵⁺ with the four H₅O₂⁺ ions, which were formed after the dissociation of the two water molecules ($E_{\text{Pu}-4\text{H}_5\text{O}_2^+} = 180$ kJ/mol). As in

the previous case, the sum of the three values (−1484 kJ/mol) differs from E_i by −40 kJ/mol, which can be referred to the interaction with the water molecules in outer layer. The mean energy of Pu⁵⁺ interaction with each nearest H₂O molecule (−121 kJ/mol) was close to the corresponding values of −120 and −123 kJ/mol obtained for (Pu + 32H₂O)³⁺ and (Pu + 32H₂O)⁴⁺ systems.

3.4 Pu⁶⁺ complexation

In this case, the formation of PuO₂ groups was also obtained in both kinds of systems. The shape of optimized (Pu + 32H₂O)⁶⁺ system, where the dissociation of six water molecules occurred, is shown in Figure 3. The formation of Pu⁶⁺ complexes with the pentagonal bipyramidal geometry was also detected in the experiment [5]. The calculated energies for the internal interactions in PuO₂(OH)₂(H₂O)₃ complex ($E_{\text{Pu}-2\text{Oyl}} = -999$ kJ/mol, $E_{\text{Pu}-\text{OH}} = -499$ kJ/mol and $E_{\text{Pu}-3\text{H}_2\text{O}} = -355$ kJ/mol) showed that the former value is of the same order as $E_{\text{Pu}-2\text{Oyl}}$ obtained for the Pu⁵⁺ complex (−1060 kJ/mol) and the energy of Pu⁶⁺ interaction with each water molecule (−118 kJ/mol) was also similar to those in the previous cases. However, the absolute energy per one OH[−] (250 kJ/mol) was noticeably less than those obtained for the interaction with one hydroxide ion in the Pu⁴⁺ complexes (305 and 326 kJ/mol). This result correlated with the noticeable increase of Pu–OH[−] bond length from ~2.1 Å (Pu⁴⁺) to 2.3 Å (Pu⁶⁺). The presence of the two hydroxide ions also induced the increase of Pu–O_{yl} distances (1.81 Å) and Pu–OH₂ (2.44 Å) in the smaller (Pu + 22H₂O)⁶⁺ system up to 1.83 and 2.48 Å in the PuO₂(OH)₂(H₂O)₃ complex (32H₂O). As expected, the former values were closer to the experimental intervals for $R_{\text{Pu}-\text{Oyl}}$ (1.74–1.79 Å) and $R_{\text{Pu}-\text{OH}_2}$ (2.31–2.45 Å)

Figure 3: (Color online) The shapes of optimized $(\text{Pu} + 32\text{H}_2\text{O})^{5+}$ (left) and $(\text{Pu} + 32\text{H}_2\text{O})^{6+}$ (right) systems corresponding to Pu^{5+} and Pu^{6+} in water solution. The dark spheres correspond to the oxygen atoms of plutonyl.

reported for the $\text{PuO}_2(\text{H}_2\text{O})_4$, $\text{PuO}_2(\text{H}_2\text{O})_5$ and $\text{PuO}_2(\text{H}_2\text{O})_6$ complexes of the Pu^{6+} [9, 22, 23, 26].

As mentioned above, the interaction energies could be calculated between any groups of atoms in a system. For example, one can compute these energies for the interactions between plutonyl and other components of actinide complexes. In the three cases of $\text{PuO}_2(\text{H}_2\text{O})_5^{+,2+}$ clusters, we obtained $E_{\text{PuO}_2-5\text{H}_2\text{O}} = -514$ and -533 kJ/mol for the $(\text{Pu} + 22\text{H}_2\text{O})^{5+}$ and $(\text{Pu} + 32\text{H}_2\text{O})^{5+}$ systems and -563 kJ/mol for $(\text{Pu} + 22\text{H}_2\text{O})^{6+}$. Thus, the absolute value of interaction energy of $\text{PuO}_2^{+,2+}$ with each water molecule (~ 103 – 113 kJ/mol) was less than the corresponding values for the interaction with “individual” metal ion (~ 120 kJ/mol). In the case of $\text{PuO}_2(\text{OH})_2(\text{H}_2\text{O})_3$ complex in $(\text{Pu} + 32\text{H}_2\text{O})^{6+}$ system, the values of $|E_{\text{PuO}_2-3\text{H}_2\text{O}}| = 319$ kJ/mol and $|E_{\text{PuO}_2-2\text{OH}}| = 436$ kJ/mol were also less by ~ 36 kJ/mol than those computed for the single plutonium ion (Table 2).

3.5 Estimation of hydration energies and effects of finite temperature

To the best of our knowledge, there were seven works, where the calculations of hydration energies E_H (or G_H) for Pu^{3+} , Pu^{4+} , PuO_2^{+} and PuO_2^{2+} were carried out [6, 7, 17, 28, 29, 54, 55]. These energies were approximated as the difference between the energy of the complex and those of its components:

$$E_H = E[\text{Pu}(\text{H}_2\text{O})_n^{Z+}] - E[\text{Pu}^{Z+}] - nE[\text{H}_2\text{O}] \text{ or } E_H = E[\text{PuO}_2(\text{H}_2\text{O})_n^{Z+}] - E[\text{PuO}_2^{Z+}] - nE[\text{H}_2\text{O}] \quad (4)$$

where $E[\text{Pu}^{Z+}]$, $E[\text{PuO}_2^{Z+}]$ and $E[\text{H}_2\text{O}]$ are the energies of isolated Pu^{Z+} ($Z = 3, 4$), PuO_2^{Z+} ($Z = 1, 2$) and water molecule, respectively. In the DFT calculations of $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ complex in gas phase [6], E_H was estimated neglecting thermodynamical and solvation effects, and the interval of obtained energies from -1959 to -2039 kJ/mol (depending on the various orientations of water molecules) was considerably

different from the experimental Pu^{3+} hydration free energies ($T = 298.15$ K): -3235 kJ/mol [53] and -3313 ± 42 kJ/mol [56]. According to another gas phase simulations [7], the dissociation energy of the most stable $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ complex was close to 1883 kJ/mol (19.52 eV); however, the inclusion of PCM-COSMO and thermodynamical corrections yielded 2998 kJ/mol for the standard Gibbs free energy of Pu^{3+} hydration, which was of the same order of magnitude as the experimental values. In the more recent and sophisticated calculations [55] (where the energy of water cluster $E[(\text{H}_2\text{O})_n]$ instead of $nE[\text{H}_2\text{O}]$ was also used in equation (4)), the computed gas phase dissociation energy for the similar $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ cluster was 1666 kJ/mol and the final free energy of hydration -3239 kJ/mol was close to the experimental value of Marcus [57]. It is worth mentioning that the value of $G_H = -3134$ kJ/mol for Pu^{3+} hydration obtained by David and Vokhmin [54] using simple ionic model was also in reasonable agreement with the experimental free energy of Marcus [57]. On the other hand, the agreement with lower experimental G_H values of -3313 ± 42 kJ/mol [56] was achieved in the calculations of Clark et al. [29], where the free hydration energy of -3290 kJ/mol (-786.3 kcal/mol) was obtained for $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ complex explicitly surrounded by $22\text{H}_2\text{O}$ molecules plus bulk solvent correction.

In our calculations of the free energies of Pu^{Z+} hydration, we used the similar scheme as in the works of Wiebke et al. [7], Heinz et al. [55] and Parmar et al. [30]: for the optimized structure of $\text{Pu}^{Z+} + n\text{H}_2\text{O}$ system, the gas phase hydration energy E_H^g was calculated according to Eq. (4) using gas phase binding energies, then the single point COSMO calculations were performed “on all species except the bare ions” [30]. The obtained gas phase and liquid phase binding energies were used for the calculations of solvent correction ΔE_H^{aq} [7]:

$$\Delta E_H^{aq} = E_b^{\text{COSMO}}[\text{Pu}(\text{H}_2\text{O})_n^{Z+}] - E_b^g[\text{Pu}(\text{H}_2\text{O})_n^{Z+}] + n(E_b^{\text{COSMO}}[\text{H}_2\text{O}] - E_b^g[\text{H}_2\text{O}]) \quad (5)$$

It is interesting to note that our value for $E_b^{\text{COSMO}}[\text{H}_2\text{O}] - E_b^g[\text{H}_2\text{O}] = -29$ kJ/mol was nearly the same as

in Ref. [7]. Finally, after the addition of enthalpy (including ZPVE) and entropy terms ($T = 298.15$ K) calculated for the gas phase structure we obtained the free energy of hydration:

$$G_H = E_H^g + \Delta E_H^{aq} + \Delta H^g - TS^g \quad (6)$$

As in the works of Clark et al. [29] and Parmar et al. [30], the standard state corrections (SSC) were not included in our calculations because these corrections were quite small relative to other terms in Eq. (6). Indeed, in the simulations of Heinz et al. [55], these values amounted to 0.4% of the free energy of Pu^{3+} hydration. The results of our calculations are listed in Table 3.

In the calculations of Pu^{3+} hydration energies, we considered two types of objects: (1) optimized $(\text{Pu} + 22\text{H}_2\text{O})^{3+}$ systems containing plutonium complexes with $8\text{H}_2\text{O}$, (2) small $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ clusters removed from the optimized $(\text{Pu} + 22\text{H}_2\text{O})^{3+}$ systems. As mentioned above, in the case of $(\text{Pu} + 22\text{H}_2\text{O})^{3+}$ system we performed two geometry optimizations: one with COSMO boundary conditions and one without it. Thus, the two different optimized $(\text{Pu} + 22\text{H}_2\text{O})^{3+}$ structures as well as two $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ clusters were used in the calculations of G_H . In the case of gas phase optimization, the single point calculation with COSMO potential was performed to obtain ΔE_H^{aq} , whereas in the case of liquid phase optimization, the single point calculation without COSMO was carried out to obtain E_H^g , ΔE_H^{aq} and thermodynamical terms. In Table 3, these results are labeled “optg” and “optl”, respectively.

As observed in Table 3, the final free energies of Pu^{3+} hydration obtained as the results of geometry optimizations with and without COSMO boundary conditions were close, i.e. the corresponding difference in G_H was near 20 kJ/mol. The comparison of our values for Pu^{3+} with experiments [56, 57] showed that although the absolute values of G_H obtained for small $\text{Pu}(\text{H}_2\text{O})_8^{3+}$ clusters were better than those of Wiebke et al. [7] and David and Vokhmin [54], the difference between our G_H and that of Marcus [57] was near 40 kJ/mol, and the difference between our G_H and the upper edge of experimental interval reported in [56] was near 80 kJ/mol. On the other hand, our results obtained for the $(\text{Pu} + 22\text{H}_2\text{O})^{3+}$ systems were within the experimental interval [56] and were closer to its center than those of Clark et al. [29].

The variation of experimental free energies of Pu^{4+} hydration (-6560 [57] and -6105 ± 42 kJ/mol [56]) is quite noticeable. Therefore, the results of David and Vokhmin [54] (-6444 kJ/mol) computed using ionic model and of Clark et al. [29] (-6173 kJ/mol) obtained in DFT calculations of $\text{Pu}(\text{H}_2\text{O})_8^{4+}$ complex surrounded by 22 water molecules were within the interval of possible experimental values of

G_H between -6063 and -6560 kJ/mol. Although in our modeling of $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ systems, the most stable optimized structure contained $\text{PuOH}(\text{H}_2\text{O})_8$ complex as the result of hydrolysis, we also obtained the “non-hydrolyzed” configuration with $\text{Pu}(\text{H}_2\text{O})_8^{4+}$ complex (vide supra), which was by ~ 60 kJ/mol less stable than $\text{PuOH}(\text{H}_2\text{O})_8^{4+}$. To compare our results with experiment, we used this “non-hydrolyzed” $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ optimized structure and the small $\text{Pu}(\text{H}_2\text{O})_8^{4+}$ cluster removed from this optimized system for the calculation of free energy of Pu^{4+} hydration. Since all geometry optimizations of Pu^{4+} systems were performed with COSMO boundary conditions, the single point calculations without COSMO were carried out for the optimized $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ system and isolated $\text{Pu}(\text{H}_2\text{O})_8^{4+}$ cluster to obtain E_H^g , ΔE_H^{aq} and thermodynamical corrections. As seen in Table 3, the free energy obtained for small $\text{Pu}(\text{H}_2\text{O})_8^{4+}$ cluster -6336 kJ/mol was just between the values calculated in [29, 54]. On the other hand, the absolute free energy computed for $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ system was by 25 kJ/mol larger than that reported by Marcus [57]. Since this discrepancy accounted for 0.4% of the experimental G_H value, we can conclude that our results were in agreement with experiment.

To the best of our knowledge, the experimental measurements of hydration energies for PuO_2^+ (or Pu^{5+}) and PuO_2^{2+} (or Pu^{6+}) are absent, however there were two works [28, 29], where the calculations of PuO_2^+ and PuO_2^{2+} hydration energies were carried out. It is interesting to note that the inclusion of screening potential in the simulations of $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$ complex [28] ($T = 0$ K) induced the opposite transformation of PuO_2^{2+} hydration energy from -1071 kJ/mol (-0.4079 Ha) in gas phase to -571 kJ/mol (-0.2175 Ha) in the dielectric continuum representing the bulk of the liquid. As explained in [28], this opposite effect of COSMO inclusion in their liquid-phase calculations was due to the fact that their hydration energy was “related to the unbinding of the complex while still in solution and is not be mistaken for the enthalpy of bulk hydration”, which “is always larger than the enthalpies of formation of cation – water complexes in gas phase”. It is worth mentioning that our energy of interaction between PuO_2^{2+} and the nearest $5\text{H}_2\text{O}$ in the $(\text{Pu} + 22\text{H}_2\text{O})^{6+}$ system ($E_{\text{PuO}_2-5\text{H}_2\text{O}} = -563$ kJ/mol) obtained using Eq. (2) (vide supra) was close to E_H for the PuO_2^{2+} hydration in $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$ complex (-571 kJ/mol) computed in [28]. Clark et al. [29] used the above mentioned scheme for the calculation of free hydration energies, and the obtained values of -2034 kJ/mol (-486.1 kcal/mol) and -2224 kJ/mol (-531.6 kcal/mol) for PuO_2^+ and PuO_2^{2+} , respectively, were considerably different from those reported in [28].

Table 3: Calculated energies (kJ/mol) of optimized systems and their components in gas and liquid phases, the bulk solvent correction (ΔE_H^{aq}) and free energies of Pu^{3+} , Pu^{4+} , Pu^{5+} and Pu^{6+} hydration (G_H).

Object	E_b^g	E_b^{COSMO}	ΔE_H^{aq}	G_H
Pu^{3+}	4099			
Pu^{4+}	8004			
H_2O	−1002	−1031		
$\text{Pu}(\text{H}_2\text{O})_8^{3+}$ (optg)	−5985	−7614	−1861	−3195
$\text{Pu}(\text{H}_2\text{O})_8^{3+}$ (optl)	−6085	−7596	−1743	−3175
$\text{Pu}(\text{H}_2\text{O})_{22}^{3+}$ (optg)	−21,352	−22,534	−1820	−3329
$\text{Pu}(\text{H}_2\text{O})_{22}^{3+}$ (optl)	−21,209	−22,549	−1978	−3307
$\text{Pu}(\text{H}_2\text{O})_8^{4+}$	−3932	−6839	−3139	−6336
$\text{Pu}(\text{H}_2\text{O})_{22}^{4+}$	−19,737	−21,906	−2807	−6585
PuO_2^+	−411	−766		
$\text{PuO}_2(\text{H}_2\text{O})_5^+$	−6041	−6355	−814	−928
PuO_2^{2+}	1283	155		
$\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$	−4831	−5673	−2115	−2740
H_5O_2^+	−1553	−1880		
$\text{PuO}_2(\text{H}_2\text{O})_{12}(\text{H}_5\text{O}_2)_4^+$	−17825	−21354	−5540	−2852
$\text{PuO}_2(\text{H}_2\text{O})_{12}(\text{H}_5\text{O}_2)_4^{2+}$	−16136	−20755	−7403	−4793

As in the case of Pu^{3+} , $^{4+}$, we considered two types of objects: (1) optimized $(\text{Pu} + 22\text{H}_2\text{O})^{5+, 6+}$ systems containing plutonyl complexes with $5\text{H}_2\text{O}$, (2) small $\text{PuO}_2(\text{H}_2\text{O})_5^{+, 2+}$ clusters removed from these systems. Since the geometry optimizations of $(\text{Pu} + 22\text{H}_2\text{O})^{5+, 6+}$ systems were performed with COSMO boundary conditions, the single point calculations without COSMO were carried out to obtain E_H^g , ΔE_H^{aq} and thermodynamical values. As seen in Table 3, the free energy of −928 kJ/mol obtained for small $\text{PuO}_2(\text{H}_2\text{O})_5^+$ cluster was almost one half of the value calculated in [29] for the $\text{PuO}_2(\text{H}_2\text{O})_4^+$ complex surrounded by 26 water molecules. On the other hand, our absolute free energy of PuO_2^{2+} hydration computed for small $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$ cluster was by ~500 kJ/mol larger than that calculated by Clark et al. [29].

In contrast to the simulations [29], where the investigated systems contained only $\text{PuO}_2^{+, 2+}$ and 30 water molecules, we considered $(\text{Pu} + 22\text{H}_2\text{O})^{5+, 6+}$ systems, where the formation of plutonyl ions occurred during geometry optimization as the result of hydrolysis, which was also accompanied by the formation of four H_5O_2^+ (di-oxonium) ions after the dissociation of water molecules (vide supra). It is important to note that the binding energies of our optimized $(\text{Pu} + 22\text{H}_2\text{O})^{5+, 6+}$ systems also depend on the formation of hydrolysis products. Thus, the G_H values obtained for these systems using Eqs. (4)–(6) (with the contributions from H_5O_2^+ ions) correspond to the hydration of Pu^{5+} and Pu^{6+} instead of PuO_2^+ and PuO_2^{2+} hydration in the calculations of our small clusters and the large systems in

[29]. As seen in Table 3, the absolute values of our free hydration energies for Pu^{5+} and Pu^{6+} ions were more than two times larger than those computed for PuO_2^+ and PuO_2^{2+} groups in small clusters and also noticeably larger than the energies of plutonyls hydration obtained in [29]. Since in the latter work, only the final G_H values were reported, we can not define the origin of this discrepancy. On the other hand, the comparison of our $G_H(\text{Pu}^{Z+})$ values obtained for the hydration of bare ions shows that the relative tendency of various oxidation states to form complexes in water follows the trend: $\text{Pu}^{4+} > \text{Pu}^{6+} > \text{Pu}^{3+} > \text{Pu}^{5+}$, which agrees with the general properties of Pu^{Z+} ions [2, 3].

Unfortunately, the calculations of enthalpy (including ZPVE) and entropy terms even for the $(\text{Pu} + 22\text{H}_2\text{O})^{Z+}$ systems using DMol³ were very time consuming, therefore we did not perform such computations for the larger $(\text{Pu} + 32\text{H}_2\text{O})^{Z+}$ systems. However, the application of statistical thermodynamics to the systems with 22 water molecules allowed us to estimate the influence of finite temperature on some of the obtained results. As mentioned above, the binding energy of the most stable complex of Pu^{4+} with hydroxide ion (Table 2) was by ~60 kJ/mol lower than that of “non-hydrolyzed” $(\text{Pu} + 22\text{H}_2\text{O})^{4+}$ optimized structure (Table 3). The addition of enthalpy and entropy terms ($T = 298.15$ K) obtained in the single point gas phase calculations changed the energy of the latter configuration from −21,906 to −19,987 kJ/mol, while the effect of finite temperature on the most stable structure with hydroxide ion was stronger by 52 kJ/mol, and the corresponding value changed from −21,966 to −19,995 kJ/mol. Thus, the difference in stability of these structures decreased from 60 to 8 kJ/mol on going from $T = 0$ –298.15 K.

As mentioned in Section 2, the interaction energies computed using Eq. (2) are the model parameters, which could be useful for the quantitative comparison of the bonding between plutonium and various ligands. However, in some cases, it is possible to compare these values with experiment. The analysis of the experimental Gibbs formation energies [34] for the four hydroxide complexes of Pu^{4+} : PuOH^{3+} , $\text{Pu}(\text{OH})_2^{2+}$, $\text{Pu}(\text{OH})_3^+$ and $\text{Pu}(\text{OH})_4$ (−719, −956, −1176 and −1378 kJ/mol, respectively) showed that at each step of this row G_f changed by 202–237 kJ/mol, which could be considered as the experimental measure of Pu^{4+} – OH^- interaction. In our calculations, the energy of Pu^{4+} – OH^- interaction in $\text{PuOH}(\text{H}_2\text{O})_8$ complex of −305 kJ/mol (Table 2) corresponded to $T = 0$ K, and for the comparison with experiment we needed to estimate the role of thermodynamical effects. For this reason, we performed the calculations of vibrational frequencies at $T = 298.15$ K and applied the standard statistical thermodynamics also for the corresponding model systems (Figure 2). Using Eq.

(2) we computed the “interaction Gibbs free energy” $G_{\text{Pu-OH}} = -228$ kJ/mol, which was within the experimental interval.

3.6 Effective charges and the structure of chemical bonding

Table 2 also lists the effective charges on actinide atom (Q_{Pu}) obtained for all investigated systems. There are several schemes for the calculation of effective charges on atoms. For the methods using M-T or any other sphere approximation, the partition of electron density between atoms artificially depends on the choice of these spheres. On the other hand, Mulliken population analysis basing on the MO structure depends on the shape of basis functions and on the method of partitioning the overlap populations of each pair of atoms to the individual atoms in a pair. In the scheme of Hirshfeld [45], which was used in our DMol³ calculations, the partition of electron density between atoms was made by the use of “partition function”, which is large for the small distances to nucleus and small for the large distances. On the other hand, it is evident that the “best” boundary for the electron density partition is the points of its minimum [58]. The way for the realization of this idea in the spatial integration of DV and RDV methods was suggested in [48].

Another important issue concerns the influence of relativistic effects on the properties of investigated systems. As shown in Refs. [59, 60], the impact of spin-orbit interaction on the bond lengths and the binding energies of plutonium complexes is quite small. However, as was obtained in our modeling of the large clusters in UO₂ lattice [61], the effective charges on atoms computed using the fully relativistic RDV method ($Q_U = 2.94$ – 2.97) were noticeably larger than those obtained in the non-relativistic version of the same DV method ($Q_U = 2.43$ – 2.45). The inclusion of all relativistic effects also increased the role of U5f and 7s orbitals in bonding [61].

As shown in Table 2, the RDV charges on metal atom *monotonously* increased from 2.31 or 2.29 in the Pu³⁺ complexes to 3.10 or 3.09 for Pu⁶⁺. Note, in the RDV modeling of solid PuO₂ [61], the effective charges on plutonium atoms (~2.50) were similar to the values of 2.45–2.60 obtained for Pu⁴⁺ aqua complexes (Table 2). In the present work, we also estimated the charges on plutonyl ions in the complexes of Pu⁵⁺ and Pu⁶⁺: the values in the intervals from +0.50 to +0.51 (Pu⁵⁺) and from +0.77 to +0.92 (Pu⁶⁺) were noticeably less than the corresponding formal charges (+1 and +2). For the OH[−] ions in the Pu⁴⁺ and Pu⁶⁺ complexes, the similar relation between the calculated (~−0.6) and the formal

charge was obtained. The changes of Q_{Pu} obtained using Hirshfeld scheme were *not monotonous*: after the increase on going from Pu³⁺ to Pu⁴⁺, these charges decreased in the PuO₂(H₂O)₅⁺ complexes and again increased on going from Pu⁵⁺ to Pu⁶⁺. Note, the increase of Hirshfeld charges on Pu⁴⁺ and Pu⁶⁺ correlates with the formation of OH[−] ions in these systems. The similar trends for the Hirshfeld charges on Pu^{Z+} ions were obtained in the CPMD simulations [13], where the correlation between the increase of charges on the metal and the decrease of pK_a for the first hydrolysis reaction was found.

The role of various atomic orbitals in bonding could be compared using the values of overlap populations (n_{ij}) for the various pairs of AOs of metal and each neighboring atom in a complex. The n_{ij} values are useful for the analysis of bond order of the various pairs of atomic states [62]. The overlap populations between Pu5f, 6d, 7s, and O2p AOs obtained in the RDV calculations of the (Pu + 32H₂O)^{Z+} systems are listed in Table 4 (the sums of n_{ij} for the relativistic orbitals corresponding to $j = l \pm 1/2$ are shown for simplicity).

For the bonding between Pu and the coordinating water molecules, we found that the main contributions from Pu6d orbitals decreased in the cases of Pu⁵⁺ and Pu⁶⁺, where the formation of plutonyls took place. On the other hand, the variation of overlap populations of Pu5f AOs correlated with the average Pu–O distances (Table 1): the decrease of bond lengths from 2.53 Å for Pu³⁺ and Pu⁵⁺ to 2.47–2.48 Å for Pu⁴⁺ and Pu⁶⁺ induced the increase of n_{5f-O2p} from 16×10^{-3} to 26×10^{-3} or 28×10^{-3} (Table 4). The most stable bonding behavior across Z variation was obtained for 7s states, which was the second in the bond order after the Pu6d–O2p (H₂O) AOs.

In the case of Pu–OH[−] bonding, the relative contributions from 5f states increased, though the main role was still provided by the 6d shells. The decrease of n_{ij} for the two main Pu6d–O2p and Pu5f–O2p interactions with the hydroxide groups on going from Pu⁴⁺ to Pu⁶⁺ correlated with the variation of corresponding bond lengths (Table 1). The comparison of Pu–O bonding in the complexes of Pu⁴⁺ and in the solid PuO₂ [61] showed that the relative contribution from 5f states (n_{5f}/n_{6d}) in Pu–OH interaction near 40% was close to 43% in plutonium dioxide, whereas, the corresponding value for 7s orbitals in Pu–OH interaction ~11% was considerably less than 36% in solid compound. On the other hand, the latter value was similar to 39% obtained for n_{7s}/n_{6d} ratio in Pu–H₂O interaction. It is worth mentioning that the increase of n_{5f}/n_{6d} and n_{7s}/n_{6d} up to 40 and 39% in water complexes was certainly due to the relativistic effects, because the results of DV and RDV calculations of solid UO₂ [61] showed that the relativistic effects induced

Table 4: The average overlap populations (10^{-3} e) of Pu5*f*, 6*d*, 7*s* orbitals with the nearest oxygen 2*p* AOs of water molecules, hydroxide ions and plutonyls (per one pair of interacting atoms).

Z		Pu ³⁺	Pu ⁴⁺		Pu ⁵⁺		Pu ⁶⁺		
Complex		Pu(H ₂ O) ₈	PuOH(H ₂ O) ₇		PuO ₂ (H ₂ O) ₅		PuO ₂ (OH) ₂ (H ₂ O) ₃		
Orbitals		O2 <i>p</i> : H ₂ O	O2 <i>p</i> : H ₂ O	OH [−]	O2 <i>p</i> : H ₂ O	O _{yl}	O2 <i>p</i> : H ₂ O	OH [−]	O _{yl}
Pu	5 <i>f</i>	16	26	132	16	304	28	60	334
	6 <i>d</i>	110	112	324	82	490	82	152	486
	7 <i>s</i>	46	44	36	52	0	48	54	0

the increase of n_{5f}/n_{6d} from 0.29 to 0.39 and of n_{7s}/n_{6d} from 0.18 to 0.33.

The considerable transformation of the overlap populations for the PuO₂ groups was expected, since in our earlier RDV calculations of the small clusters with plutonyl, neptunyl and uranyl [37, 63], the comparable contributions to bonding from the 5*f* and 6*d* shells were obtained. The comparison of n_{ij} for the Pu5*f* and 6*d* states (Table 4) showed that the maximum n_{5f}/n_{6d} ratio was achieved in the PuO₂²⁺ group (0.69). It is interesting to note that the similar comparable participation of the Pu5*f* and 6*d* AOs in bonding was also predicted for the encapsulation of plutonium atom in the C₂₈ fullerene [64], where the cage

radius (2.4 Å) is noticeably larger than Pu–O_{yl} distances, but the large coordination number of Pu in Pu@C₂₈ cluster led to the “unusual” structure of chemical bonding.

The obtained overlap populations were the result of covalent mixing between Pu 5*f*, 6*d*, 7*s* and 2*p* AOs of oxygen atoms in water molecules, hydroxide and plutonyl ions in the occupied molecular orbitals (MOs) of optimized complexes. To illustrate the hybridization effects, we used the partial densities of states (DOS), which are available in our RDV software. The partial DOS obtained for the PuO₂(OH)₂(H₂O)₃ complex in (Pu + 32H₂O)⁶⁺ system are shown in Figure 4.

Since the partial DOS for relativistic 6*d*_{3/2} and 6*d*_{5/2}, as well as for 2*p*_{1/2} and 2*p*_{3/2} orbitals are close to each other, the sums of DOS for these states are presented in Figure 4. The zero of energy scale and the vertical line correspond to the position of HOMO (highest occupied MO). The energies of HOMO and LUMO (lowest unoccupied MO) differed by 0.11 eV, and the compositions of both orbitals were similar: Pu5*f*_{5/2} 74, Pu5*f*_{7/2} 15, O_{yl}2*p* 3, O_H2*p* 5 and O_W2*p* 3%. The admixtures of O2*p* AOs belonging to water molecules in the second coordination sphere were less than 1%. As seen in Figure 4, the contributions from O_W2*p* orbitals were distributed over all valence “2*p* band” in the interval from −10 to −1 eV, as a result the covalent mixing with Pu6*d* and 7*s* states in the MOs located in the center of this interval and with Pu5*f* AOs in the upper part of this band took place. On the other hand, the contributions from O_{yl}2*p* orbitals were obtained in MOs with the energies between −4.5 and −2 eV, and the with of O_{yl}2*p* and Pu7*s* states was absent (Table 4).

Figure 4: Partial DOS for Pu 5*f*, 6*d*, 7*s* and 2*p* AOs of oxygen atoms in water molecules (O_W), OH[−] (O_H) and plutonyl ion (O_{yl}) in the occupied valence and vacant MOs of the optimized (Pu + 32H₂O)⁶⁺ system.

4 Conclusions

As described in Introduction, there were several investigations on the plutonium aqua complexes in the literature; however, in all previous QC and MD simulations with the implicit or explicit inclusion of solvation effects, there were no examples of modeling the formation of

hydrolysis products such as OH^- or $\text{PuO}_2^{+,2+}$ during the geometry optimizations. Our DMol³ calculations showed that it is possible to model the hydrolysis reaction; moreover, in the systems with 32 or more water molecules, the formation of similar complexes with the hydroxide and plutonyl ions could be obtained from various starting configurations, although all of them were certainly far from the final optimized geometry. Thus, our approach could be useful in the cases, where experimental information on the probability of hydrolysis is ambiguous or completely absent. It is important to note that the structure of our optimized complexes containing the products of hydrolysis is in agreement with available experimental data.

Another important feature of our approach is the possibility for the quantitative estimation of the strength of interaction between actinide ion and its neighbors, namely the water molecules, hydroxide ions, acid anions and other species (e.g. organic ligands). In the recent work of Acher et al. [17], the “fragment interaction energies” defined as the interaction energy of a single water molecule of $\text{An}(\text{H}_2\text{O})_n$ cluster with the remaining $\text{An}(\text{H}_2\text{O})_{n-1}$ fragment were calculated. However, these energies were reported only for the complexes of Th^{4+} , and the variation of obtained values was very large: from ~ -20 to ~ -50 kcal/mol (from -85 to -210 kJ/mol). In our calculations, the obtained intervals of interaction energies for Pu and the various components of optimized complexes in the water solutions are considerably narrower: $|E_{\text{Pu-H}_2\text{O}}|$ varies from 108 to 123 kJ/mol, $|E_{\text{Pu-OH}}|$ varies from 250 to 326 kJ/mol and $|E_{\text{Pu-O}_2}|$ from 999 to 1063 kJ/mol. However, it is evident that these values are sensitive to the composition of complex and to the inter-atomic distances. We also obtained that the energies of plutonium interaction with the water molecules in the second coordination sphere are near 7–13% of those with the nearest water molecules.

Contrary to the ionic interactions, the covalent bonds between atoms are not additive, and as mentioned above, the interaction energies computed using Eq. (2) are the *model parameters* defined using the energy changes, when the selected interactions are removed from the investigated system. From our point of view, these values could be useful for the quantitative comparison of the bonding between plutonium and various ligands in the large multi-molecular systems. In our preliminary calculations [38] and in the present study on plutonium aqua complexes, we verified the applicability of this approach to the various complexes. The results of the present work show that the obtained interaction energies correlate with the corresponding bond lengths and are in agreement with the known chemical activity of the different ligands. Although the direct comparison of these energies with the results of

other calculations and with the experimental data is difficult, we had found that our energy of interaction between PuO_2^{2+} and $5\text{H}_2\text{O}$ in the $\text{PuO}_2(\text{H}_2\text{O})_5^{2+}$ complex (-563 kJ/mol) was very close to the energy of PuO_2^{2+} hydration (-571 kJ/mol) obtained in Ref. [28]. The good agreement was also obtained between our Gibbs free energy of $\text{Pu}^{4+} - \text{OH}^-$ interaction (-228 kJ/mol) and the variation of experimental Gibbs formation energies (202 – 237 kJ/mol) of the hydroxide complexes of Pu^{4+} [34]. To the best of our knowledge, there is no other way to estimate the strength of interactions inside the first coordination shell when the second coordination shell is explicitly included in the investigated system.

The analysis of inter-atomic bonds showed that although the main plutonium – ligand bonding takes place through the ligand interactions with the $\text{Pu}6d$ states, the $\text{Pu}5f$ orbitals are not localized and their role in bonding is certainly comparable with that of $\text{Pu}6d$ shells. In the cases of “typical” Pu–O distances of ~ 2.5 Å, the relative $5f$ contributions (n_{5f}/n_{6d}) are nearly 40%, and in the plutonyl ions with short Pu–O bond lengths, this ratio achieves $\sim 69\%$.

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