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Quantum molecular dynamics investigations of protactinium (V) fluoro and oxofluoro complexes in solution

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Abstract: Quantum Molecular Dynamics simulations of protactinium (V) fluoro and oxofluoro complexes in solution were undertaken using density functional theory with generalised gradient approximation (and the ABINIT software package). The complexes were studied in the gas phase (at 0 K) and in solution (at 298 K) with water molecules as the solvent. We characterised all of the systems, taking into account their structures, dissociation energies, bond lengths and formation enthalpies in solution, and explained their relative stabilities. At ambient temperature, the hydrated species PaF_5 , PaF_4^+ , $PaOF_5^{2-}$, $PaOF_4^-$ and $PaOF_3$ were found to be the most stable (and to exhibit similar stabilities). The calculated formation enthalpies of the complexes are in close agreement with measurements made elsewhere.

Keywords: fluorides; protactinium chemistry; quantum molecular dynamics; thermodynamics.

PACS: numbers: 64.30.-t; 52.38.-r 62.50.-p.

1 Introduction

Protactinium is currently experiencing a renewal of interest, because the isotopes ^{233}Pa and ^{231}Pa are involved in nuclear reactions that occur in the thorium nuclear fuel cycle in reactors that use molten salts (lithium and beryllium fluorides) [1]. The peculiar coordination chemistry of protactinium must be carefully investigated in order to predict its behaviour, not only throughout the entire spent fuel reprocessing procedure, but also in the

environment in the event of an accidental release. In particular, the interaction of Pa with fluoride ions, which are ubiquitous in soil and groundwater, requires a thorough understanding due to the fact that the formation of soluble complexes could favour the migration of Pa within the geosphere [2].

Protactinium is located between thorium and uranium in the actinide series [3, 4], and its most stable oxidation state in solution and at solid state is V with the formal $5f^0$ electronic configuration. That said, Pa(V) exhibits significantly different chemical behaviour compared to the other light actinides, even though some analogies have been observed with its pentavalent transition-metal homologues niobium and tantalum.

In aqueous solution, protactinium (V) exhibits a strong tendency towards hydrolysis and polymerisation. Fluoride anions have often been used to bypass the instability of Pa(V) solutions, regardless of metal concentration. Fluoro complexes are indeed thermodynamically stable with respect to hydrolysis at moderate pH values [5].

The chemistry of pentavalent protactinium with fluoride anions is rich: several species have been identified or proposed in the literature. Moreover, the speciation of Pa(V) depends strongly on free protons and free fluoride concentrations. The PaF_7^{2-} complex has been proved to predominate over a wide range of hydrofluoric acid concentration (from 10^{-3} M to 4–8 M) [4]. This complex was unambiguously characterised for the first time in solids and in aqueous solutions [4, 6, 7]. The existence of a fluoro complex with maximum stoichiometry PaF_8^{3-} has been demonstrated through the conductimetric titration of hydrated protactinium pentoxide with 0.55 N hydrofluoric acid [7]. At low HF concentration, i.e., $<10^{-3}$ M, less fluorinated complexes are present, but their domain of existence is very narrow.

The successive stepwise constants K_1 to K_8 were determined by potentiometry [7]. However, it was postulated that hydroxo complexes could be present for F/Pa ratios lower than three in the determination of K_1 to K_3 [7]. According to Bonnet et al., oxofluoro complexes are formed from $PaOOH^{2+}$ in acidic media of $1 < [H^+] < 3$ M up to

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$[F^-] \approx 10^{-4}$ M; above this concentration, the main species is $HPaF_7^-$ [8]. The formation of complexes of low stoichiometry has been investigated using a solvent extraction method with thenoyltrifluoroacetone (TTA) as the extractant [9, 10]. The stability constants K_1 to K_3 relative to the formation of cationic fluoro complexes were determined [9, 10], but the formulation of the species differs from one author to another. At low fluoride concentration ($<10^{-6}$ M) and high acidity ($1 < [H^+] < 3$ M), Guillaumont identified three oxofluoro complexes of composition $PaF_x^{(3-x)+}$ ($x = 1, 2$ or 3), whereas Kolarich et al. identified three pure fluoro complexes, i.e., $PaF_x^{(5-x)+}$. To summarise the knowledge acquired in the 1960s, two species (PaF_7^{2-} and PaF_8^{3-}) predominate in well-defined domains, whereas several other fluoro complexes (PaF_4^+ , PaF_5 and PaF_6^-) coexist due to their narrow domain of existence [11]. There is still no information about the relative stabilities of PaF_4^+ , PaF_5 and PaF_6^- compared to the oxofluoro complexes $PaOF_2^+$, $PaOF_3$ and $PaOF_4^-$, but it is acknowledged that homoleptic fluoro complexes ($PaF_{i=1-3}^{5-i}$) are replaced by oxofluoro complexes ($PaOF_{i=1-3}^{3-i}$) at low fluoride concentration. There is also no available information regarding the higher oxofluoro complexes such as $PaOF_4^-$, $PaOF_5^{2-}$ and $PaOF_6^{3-}$. It is worth noting that the presence of the $PaOF_5^{2-}$ species has been postulated as an explanation for the distribution curves of Pa(V) in 0.35–0.5 N HF by trilaurylamine [12], whereas Ferreira de Miranda and Muxart assigned to this complex an absorption band at 223 nm from a solution of $0.68 \cdot 10^{-3}$ M $PaF_5 \cdot 2H_2O$ dissolved in water at pH 3.4 [13].

More recently, X-ray absorption spectroscopy measurements have confirmed the existence of homoleptic fluoro complexes [14–17]. Nonetheless, only a few theoretical studies of protactinium complexes have been performed [18–21]. Although structural simulations have already been conducted at 0 K on some of these fluoro complexes [7, 16, 22], no quantum molecular dynamics (QMD) results have been published. The relative stabilities of the species under ambient conditions have also not been determined. In QMD simulations, the complexes are free to evolve in water at finite temperature, making it possible to assess other properties such as the structure, the degree of hydration and the relative stability of the different species. Today, QMD-based density functional theory (DFT) codes coupled with actual high-performance computers enable the treatment of ions or molecules in a real water environment

and may, to some extent, mimic the behaviour of species in solution.

We present herein a full theoretical investigation of the structural and thermodynamic properties of the protactinium fluoro and oxofluoro series in ambient conditions using DFT and the ABINIT software package [23].

2 DFT calculations

DFT calculations of protactinium fluoro and oxofluoro systems were performed with quantum molecular dynamics (QMD) using the ABINIT software package and the projector augmented-wave (PAW) formalism [24]. The pseudopotentials of protactinium, oxygen and fluorine were generated for the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [25] using the ATOMPAW code [26]. Inclusion of scalar relativistic effects in the computations is mandatory. For a heavy metal such as Pa, relativistic effects cause the valence orbitals to be shielded from the nuclear charge. Spin-orbit coupling is also taken into account [27], but it has been shown that this phenomenon creates only minor changes in energies, as would be expected for a closed-shell system such as Pa^{5+} [28]. An adequately kinetic energy cutoff of 762 eV was chosen to ensure fully converged total energies for all systems. Calculations on periodic systems of charged ions involve electrostatic interactions between images. The total energies were corrected and only the first order corrections were taken into account. First of all, atomic relaxations at 0 K without water molecules were performed in the gas phase. Next, QMD simulations were performed using 96 water molecules in a cubic simulation box with periodic boundary conditions. All simulations were carried out in the isokinetic ensemble at 298 K at the density of water, i.e., 1 g cm^{-3} . The ionic temperature was controlled during the QMD simulations using a velocity scaling procedure. All simulations were carried out at the Γ point of the Brillouin zone. In the first step, all of the systems were allowed to relax and to pre-equilibrate for a duration of 1 ps (2000 steps, $\Delta t = 0.5$ fs) until the energy reached a steady state on average. In the second step, the dynamics were extended over a longer time period of 3 ps (6000 steps) [29, 30]. Longer simulation times would not have changed the results, but would have been very costly in terms of CPU time. From the results obtained at equilibrium, thermodynamic functions were extracted and the formation enthalpies calculated according to the following equations:

$$\begin{aligned}\Delta_f H_{298}(PaO_n F_m, xH_2O) &= \Delta_f H_{298}(PaO_n F_m, xH_2O) \\ &\quad - \Delta_f H_{298}(Pa_{(s)}) - \frac{1}{2} n \Delta_f H_{298}(O_{2(g)}) \\ &\quad - \frac{1}{2} m \Delta_f H_{298}(F_{2(g)}) \\ &\quad - x \Delta_f H_{298}(H_2O_{(aq)})\end{aligned}\quad (1)$$

with $\Delta_f H_{298}(X)$ representing the enthalpy of each component calculated in the same conditions at 298 K.

$$\begin{aligned}\Delta_f H_{298}(PaO_n F_m, xH_2O) &= \Delta_f H_{298}(PaO_n F_m, xH_2O) \\ &\quad + \Delta_f H_{298}^0(Pa_{(s)}) + \frac{1}{2} n \Delta_f H_{298}^0(O_{2(g)}) \\ &\quad + \frac{1}{2} m \Delta_f H_{298}^0(F_{2(g)}) \\ &\quad + x \Delta_f H_{298}^0(H_2O_{(aq)})\end{aligned}\quad (2)$$

$$\begin{aligned}\Delta_f H_{298}(PaO_n F_m, xH_2O) &= \Delta_f H_{298}(PaO_n F_m, xH_2O) \\ &\quad + x \Delta_f H_{298}^0(H_2O_{(aq)})\end{aligned}\quad (3)$$

with $\Delta_f H_{298}^0(O_{2(g)}) = \Delta_f H_{298}^0(F_{2(g)}) = \Delta_f H_{298}^0(Pa_{(s)}) = 0$
and $\Delta_f H_{298}^0(H_2O_{(aq)}) = -68.38 \text{ kcal mol}^{-1}$ [31]

The tetragonal solid phase of protactinium, molecular diatomic oxygen gas, molecular diatomic fluorine gas and liquid water at 298 K were considered for the elemental enthalpies and calculated in the same conditions as for the fluorides. In the case of crystalline protactinium (SG: I4/mmm), we used $10 \times 10 \times 10$ points in the Brillouin zone and found cell parameters of $a = b = 3.922 \text{ \AA}$ and $c = 3.210 \text{ \AA}$, which are values close to those obtained from a similar GGA + SOC calculation (3.930 \AA , 3.196 \AA) [32].

3 Results of the relaxations at 0 K

Gas-phase structures were first relaxed and determined at 0 K. The dissociation energies or enthalpies ($P = 0$) are obtained by subtracting energies of elements in their atomic form (gaseous) from the total energy of a complex calculated under the same conditions.

$$\begin{aligned}\Delta_d H_0(PaO_n F_m) &= E_0(PaO_n F_m) - E_0(Pa_{(g)}) \\ &\quad - n E_0(O_{(g)}) - m E_0(F_{(g)})\end{aligned}\quad (4)$$

By taking into account the formation of $Pa_{(g)}$, $O_{(g)}$ and $F_{(g)}$ from their stable state, the formation enthalpy $\Delta_f H_0(PaO_n F_m)$ can be written:

$$\begin{aligned}\Delta_f H_0(PaO_n F_m) &= \Delta_d H_0(PaO_n F_m) + \Delta_f H_0^0(Pa_{(g)}) \\ &\quad + n \Delta_f H_0^0(O_{(g)}) + m \Delta_f H_0^0(F_{(g)})\end{aligned}\quad (5)$$

The comparison with experimental measurements requires formation enthalpies at 298 K. With no available data dealing with the variation of standard formation enthalpies with temperature for protactinium compounds, we examined the behaviour of other actinide complexes and found no significant variations (less than $0.5 \text{ kcal mol}^{-1}$) between 0 and 298 K; this was also the case for O and F. Assuming, therefore, that there is also no such variation for protactinium complexes:

$$\Delta_d H_{298}(PaO_n F_m) = \Delta_d H_0(PaO_n F_m) \quad (6)$$

$$\begin{aligned}\Delta_f H_{298}(PaO_n F_m) &= \Delta_d H_0(PaO_n F_m) \\ &\quad + \Delta_f H_{298}^0(Pa_{(g)}) + n \Delta_f H_{298}^0(O_{(g)}) \\ &\quad + m \Delta_f H_{298}^0(F_{(g)})\end{aligned}\quad (7)$$

with $\Delta_f H_{298}^0(O_{(g)}) = 59.6239 \text{ kcal mol}^{-1}$ [31],

$$\Delta_f H_{298}^0(F_{(g)}) = 18.994 \text{ kcal mol}^{-1}$$

$$\Delta_f H_{298}^0(Pa_{(g)}) = 145 \text{ kcal mol}^{-1}$$

These data are presented in Figure 1, along with the corresponding Pa-F and Pa-O bond lengths (0 K). The systems are classified according to the decreasing number of fluorine atoms and increasing number of oxygen atoms in the coordination sphere of Pa. This ordering allows for the easy comparison of the properties of these fluoro and oxofluoro complexes.

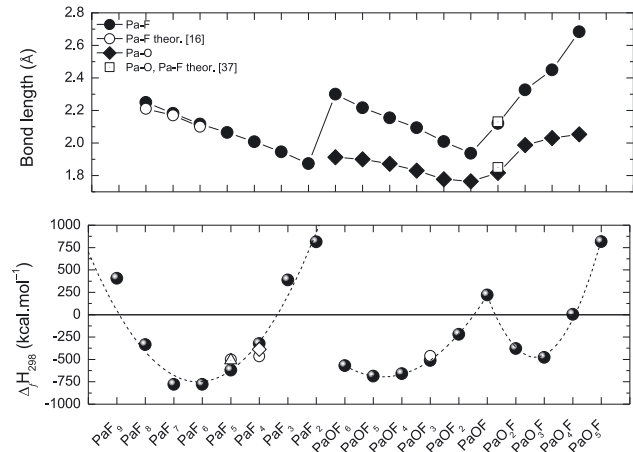


Figure 1: Bond lengths and formation enthalpies of fluoro and oxofluoro complexes of Pa(V). Hollow circles and triangles represent experimental values [16,34–37].

For PaF_5 , we found that a trigonal bipyramidal (D_{3h}) structure was more stable (≈ 1 kcal mol $^{-1}$) than a tetragonal pyramidal (C_{4v}) structure, in agreement with [34]. The calculated geometries and bond lengths for PaF_8^{3-} , PaF_7^{2-} and PaF_6^- are consistent with literature data [16, 22]. These results validate the simulations performed in this work.

Over the course of the simulation, the PaF_9^{4-} complex loses one fluorine anion, transforming into PaF_8^{3-} . The fluorides PaF_3^{2+} and PaF_2^+ , as well as the oxofluoro complex PaO_5F^{6-} located at the end of the third series, present high positive formation enthalpies and are unstable in the gas phase.

In each series, there is one complex (namely, PaF_7^{2-} , $PaOF_5^{2-}$ and PaO_3F^{2-}) whose formation enthalpy exhibits a minimum value; these three values are fairly comparable. These are the most stable complexes, even though a slight loss of stability can be observed as one move from the first series to the third. The last complex of the second series, $PaOF^{2+}$, forms an unstable system. The formation enthalpies are summarised in Table 1.

To the best of our knowledge, the formation enthalpies were previously measured in the 1960s for only PaF_5 , PaF_4^+ and $PaOF_3$ [34]. The reported values of -500 kcal mol $^{-1}$, -465.3 kcal mol $^{-1}$ and -462 kcal mol $^{-1}$, respectively, are very close to our calculations (Table 1). For PaF_4^+ a more recent measurement [35] gave -387.6 kcal mol $^{-1}$, which is also in good agreement with our result. Finally, a DFT study led to a result of -509 kcal mol $^{-1}$ for PaF_5 [36].

Table 1: Bond lengths and formation enthalpies of protactinium fluorides.

Complex	Bond lengths (Å) Pa-F/Pa-O	Formation enthalpy (kcal.mol $^{-1}$)
PaF_9^{4-}	/	+406.9
PaF_8^{3-}	2.249	-334.2
PaF_7^{2-}	2.182	-779.1
PaF_6^-	2.117	-779.0
PaF_5	2.064	-620.1, -509 [36]
PaF_4^+	2.008	-323.1
		-465.3 [34], -387.6 [35]
PaF_3^{2+}	1.946	+386.9
PaF_2^+	1.874	+813.9
$PaOF_6^{3-}$	2.300/1.913	-569.5
$PaOF_5^{2-}$	2.216/1.900	-686.5
$PaOF_4^-$	2.154/1.872	-659.5
$PaOF_3$	2.094/1.830	-511.4, -462 [34]
$PaOF_2^+$	2.009/1.777	-219.4
$PaOF^{2+}$	1.937/1.764	+219.6
PaO_2F	2.120/1.816	-378.8
PaO_3F^{2-}	2.327/1.987	-477.1
PaO_4F^{4-}	2.449/2.030	+3.5
PaO_5F^{6-}	2.684/2.053	+815.1

In the first series (from PaF_8^{3-} to PaF_2^+) the Pa-F bond length decreases in a nearly linear fashion as the protactinium coordination number decreases, in agreement with [16]. This phenomenon could be related to the variation of the ionic radii of Pa^{5+} published by Shannon [38], which increase with coordination number (CN) from 0.92 Å (CN 6) to 1.09 Å (CN 9). This fact also implies a redistribution of charges between Pa and F inside the ion. In order to assess this observation, the Hirschfeld [39] charges carried by the fluorine ions were calculated. Although there is not only one valid way to define charges on the atoms in molecules (AIM), the Hirschfeld partitioning of electron density distributions can be particularly convenient. Because these charges are known to be underestimated, we compared our results to the charge borne by fluorine in PaF_5 . Figure 2 shows the linear relationship between the Pa-F bond lengths and the Hirschfeld charges. Starting from the highest possible coordination number, the subtraction of one fluoride anion from the molecule leads to a redistribution of charges inside the fluoride and to a strengthening of the Pa-F bond. This can be related to a decrease in bond lengths (Figure 1).

The average Pa-F and Pa-O bond lengths follow the same trend in the second series (oxofluoro complexes with one oxygen atom) after a jump in the Pa-F distance values between the two series. The octahedral $PaOF_5^{2-}$ anion reflects a weakening of Pa-F bonds with F as a *cis* ligand (2.224 Å) compared to the *trans* F ligand (2.186 Å). The resulting mean value of the $\langle O-Pa-F_{cis} \rangle$ angle is 93.54°, which is close to the value of 93.0° calculated by O'Grady et al. for $PaOF_5^{2-}$ [37]. This $\langle O-Pa-F_{cis} \rangle$ angle is different from those observed in the analogous transition-metal systems $NbOF_5^{2-}$ and $TaOF_5^{2-}$, in which this angle is between 96° and 102° [28], and a regular *trans* influence is observed. This effect is explained by the difference between *d*- and *f*-block systems [37].

To characterise this effect, the same authors defined a simple parameter named ITI (Inverse Trans Influence):

$$ITI = 100 \cdot \frac{r(Pa - X_{trans})}{r(Pa - X_{cis})} \quad (8)$$

In this study, the ITI value is equal to 98.3%, which is practically identical to the value of 98.5% calculated by Wilson et al. [28].

The third series (oxofluoro complexes with one fluorine atom) also showed a decrease in bond lengths with an increasing number of oxygen atoms in the coordination sphere of Pa. The same effect of charge distribution between the Pa cation and F (O) anions is assumed to some extent.

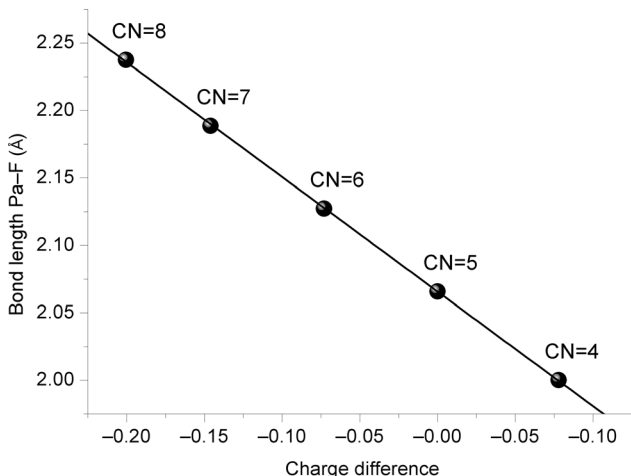


Figure 2: Hirschfeld charges on fluorine in fluoro complexes of Pa(V) for coordination numbers from 4 to 8.

The PaO_2F complex is a *cis*-Type bending structure of non-planar C_{2v} symmetry. The O-Pa-O angle is 162° . With the intention of finding new species, Straka et al. [40] carried out a theoretical investigation of some possible actinyl oxofluoro complexes including PaO_2F . They found a C_{2v} symmetry that was identical to that of UO_2F^+ but higher than the C_s symmetry of isoelectronic ThO_2F^- . Their $\langle O-Pa-O \rangle$ bending angle of about 160° was close to our value. They also determined bond lengths for Pa-O (1.85 Å) and Pa-F (2.13 Å) that were very close to our results, i.e., 1.83 Å and 2.12 Å (Figure 1).

4 Results from quantum molecular dynamics at 298 K

Static DFT studies performed by Siboulet et al. [22, 41] have shown that it is mandatory to explicitly include at least the first and second hydration spheres in the simulations in order to obtain representative properties of protactinium and uranium aqua complexes. They used as many as 21 water molecules in their calculations. Unlike these authors, we are not formulating any hypothesis regarding the structure of water molecules around the complexes. We placed all fluorides and oxofluoride complexes in 96 water molecules in order to mimic the solvent, with each ion being free to move during the QMD investigations. After equilibration, the enthalpies of formation were calculated and each structure was examined (Figure 3). Table 2 presents the number of water molecules in the first and second coordination spheres obtained from the QMD simulations along with formation enthalpies.

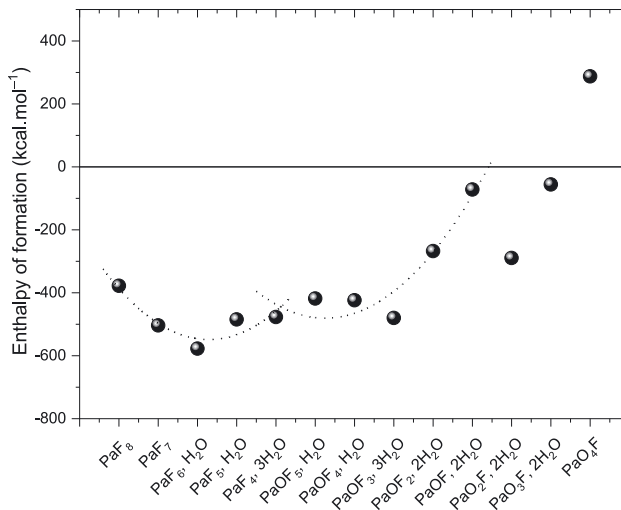


Figure 3: Enthalpies of formation of fluoro and oxofluoro complexes of Pa(V).

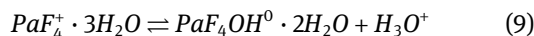
For PaF_5 , PaF_4^+ and $PaOF_3$, the number of water molecules in the first coordination sphere is in agreement with the literature data: $PaF_5 \cdot H_2O$, $PaF_4^+ \cdot 3H_2O$, $PaOF_3 \cdot 3H_2O$ [16].

Fluoro complexes of protactinium are highly charged in aqueous solution. Some of them cannot be stable as simple ions in water and may exist in hydrolysed forms. The general effect of solvation is to reduce the difference in formation enthalpies in solution as compared to the gas phase. Similar formation enthalpies for oxofluoro complexes $PaOF_x$ explain their simultaneous presence in aqueous solution as observed in the $\log[F]-pH$ diagram [42].

Pentavalent protactinium exhibits a maximal coordination number of eight in water. Depending on the systems, lower values may be obtained. As expected, anions are less surrounded by water molecules than by cations in the first coordination sphere.

Our calculations preclude the presence of water molecules in the first coordination sphere of Pa for the complexes PaF_8^{3-} and PaF_7^{2-} , which confirms the conclusion made by [14, 22] regarding PaF_7^{2-} .

At the beginning of the calculation, PaF_4^+ possesses three water molecules, but as the simulation progresses, one hydrogen atom from water leaves the complex, thereby forming an H_3O^+ ion through the reaction:



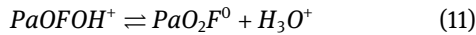
The hydroxide thus formed consists of a plane containing three fluorine atoms and two H_2O around the protactinium atom. The other fluorine atom and the hydroxyl ion are positioned perpendicularly to this plane. One can notice that two additional water molecules

Table 2: Protactinium fluorides and oxofluorides - number of water molecules in the first coordination sphere of Pa, Pa coordination number, number of water molecules in the second coordination sphere of Pa, formation enthalpies.

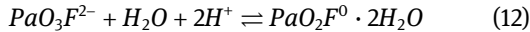
Complex	H ₂ O First sphere	Pa coordination number	H ₂ O Second sphere	Formation enthalpy (kcal.mol ⁻¹)
PaF_8^{3-}	0	8	12	-377.80
PaF_7^{2-}	0	7	12	-503.76
PaF_6^-	1	7	10	-577.47
PaF_5	1	6	12	-484.55
PaF_4^+	3	7	7	-477.13
$PaOF_5^{2-}$	1	7	10	-418.15
$PaOF_4^-$	1	6	9	-423.78
$PaOF_3$	3	7	7	-480.07
$PaOF_2^+$	2	5	11	-267.52
$PaOF^{2+}$	2	5	11	-71.76
PaO_2F	2	5	11	-289.26
PaO_3F^{2-}	2	6	8	-55.76
PaO_4F^{4-}	2	7	11	+287.62

complete the coordination. Their hydrogen atoms point toward protactinium, as observed in anions.

In the third series, $PaOF^{2+}$ is first surrounded by two water molecules, but then evolves towards $PaO(OH)F^+$ and later to the stable oxofluoro complex PaO_2F .



PaO_3F^{2-} and PaO_4F^{4-} present negative dissociation energies and are unstable in water. As previously, PaO_3F^{2-} is unstable in solution and leads to the formation of PaO_2F .



In this series, the oxofluoro $PaO_2F \cdot 2H_2O$ is found to have a negative formation enthalpy. This complex is stable over a lengthy simulation time. To our knowledge, this particular ion featuring an PaO_2^+ entity has never been observed in solution. However, in the solid state, the compound **PaO_2F** has been synthesised and characterised [43].

The initial postulate suggesting the existence of dioxo protactinium cations has never been demonstrated. It is known today that pentavalent protactinium, when associated with oxygen, exists only as a monooxo species, which is stable in aqueous media. Unlike other actinides, which are found as dioxo *actinyl* cations (UO_2^{2+} , NpO_2^+ , etc.), PaO_2^+ has never been observed in aqueous solution [14].

Toraishi et al. [44] have shown that $6d_{xz}$ and $6d_{yz}$ orbitals contribute to some PaO^{3+} bonds, in contrast to the

UO^{4+} bond involving only the $5f$ orbitals. The $6d_{xz}$ and $6d_{yz}$ orbitals formed antibonding orbitals with the $2p$ orbitals of oxygen and destabilised the *trans*-O bond. In such a case, the Pa-O triple bond in PaO^{3+} should be formed from the $6d$ orbitals instead of the $5f$ orbitals, leading to a weakened Pa-O bond. In $PaO_2F \cdot 2H_2O$ one can suppose that the fluoride ion in the *cis* position modifies the chemical bond in such a way that the dioxo ion may then become similar to UO_2^{2+} .

Moreover, Siboulet et al. [22] have shown that the negative charge on the oxygen atoms in PaO_2^+ is higher than the charge found in the corresponding ion UO_2^+ . Two important consequences could result: the formation of very short hydrogen bonds to the *yl* oxygens in aqueous solution, and a very energetically favourable deprotonation. The two O_{yl} atoms can interact with water molecules, forming what are referred to as apical interactions. The distance between O_{yl} and the apical H_{H_2O} is close to 1.55 Å, which is an unusually short hydrogen bond length distance indicating a strong apical link, whereas in hydrated UO_2^+ these authors found a distance of 1.92 Å separating O_{yl} and the apical H_{H_2O} . Aqueous Pa(V) monocations can be found as PaO^{3+} or $PaOOH^{2+}$. In the case of $PaO_2F \cdot 2H_2O$, we calculated a distance of 1.81 Å, which is the typical value for a water-water hydrogen bond. This finding supports the existence and stability of this oxofluoro in aqueous solution. $PaO_2F \cdot 2H_2O$ seems to be comparable to $UO_2F_2 \cdot 2H_2O$.

To summarise, in our thermodynamic conditions and on the basis of enthalpy calculations, some oxo and oxofluoro complexes can exist. The most stable of these are the hydrated PaF_6^- species; there also exist PaF_5 , PaF_4^+ , $PaOF_5^{2-}$, $PaOF_4^-$ and $PaOF_3$ with lower (and similar) stabilities.

5 Conclusions

We performed Quantum Molecular Dynamics simulations on protactinium (V) fluoro and oxofluoro complexes in the gas phase and in solution using density functional theory with generalised gradient approximation (and the ABINIT software package). We showed that the most stable structure in solution is not necessarily the most stable one in the gas phase. Although stable at 0 K, the PaO_nF^{4-2n} family undergoes dissociation to form hydroxides. Solvent effects change the relative thermodynamic stability of some of the ions. The solvation process reduces the differences in formation enthalpies as compared to the gas phase. Finally, according to our QMD simulations, the protactinyl hydrated complex $PaO_2F \cdot 2H_2O$ appears to be stable.

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References

1. Serp J., Allibert M., Bene O., Delpech S., Feynberg O., Ghetta V., Heuer D., Holcomb D., Ignatiev V., Kloosterman J. L., Luzzi L., Merle-Lucotte E., Uhli J., Yoshioka R., Zhimin D. The molten salt reactor (MSR) in generation IV: overview and perspectives. *Prog. Nucl. Energy* 2014, 77, 308.
2. Sivasankar V., Darchen A., Omine K., Sakthivel R. Fluoride: a world ubiquitous compound, its chemistry and ways of contamination. In *Surface modified carbons as scavengers for fluoride from water*; Sivasankar V., Ed. Springer: Netherlands, 2016; pp 5–32; https://doi.org/10.1007/978-3-319-40686-2_2.
3. Kirby H. W., *Protactinium in The chemistry of the actinide elements*; Katz J. J., Seaborg G. T., Mors L. R., Eds. Springer: Netherlands, 1986; pp 102–168; https://doi.org/10.1007/978-94-009-4077-2_4.
4. Muxart R., Guillaumont R. Protactinium. In *Compléments a un nouveau traité de chimie minérale*; Masson: Paris, France, Vol. 2, 1974.
5. Brown D., Maddock A. G. Protactinium. *Q. Rev.* 1963, 289; <https://doi.org/10.1039/qr9631700289>.
6. Grosse A. V. The atomic weight of protactinium. *Proc. Roy. Soc. A* 1935, 150, 363.
7. Bukhsh M. N., Flegenhimer J., Hall F. M., Maddock A. G., Ferreira de Miranda C. The chemistry of protactinium—VII the fluoro-complexes. *J. Inorg. Nucl. Chem.* 1966, 28, 421.
8. Bonnet M., Guillaumont R. Extraction du protactinium, du tantale et du niobium pentavalents par le phosphate tributylrique à partir de milieux fluoro-perchloriques. *Radiochim. Acta* 1969, 12, 98.
9. Kolarich R. T., Ryan V. A., Schuman R. P. Association constants of anionic-protactinium (V) complexes. *J. Inorg. Nucl. Chem.* 1967, 29, 783.
10. Guillaumont R. Contribution à l'étude des espèces ioniques de protactinium en solution aqueuse. *Rev. Chim. Miner.* 1966, 3, 339.
11. Pal'shin E. S., Myasoedov B. F., Davydov A. V. *Analytical Chemistry of Protactinium*; Ann Arbor-Humphrey Science Publishers, Inc.: Ann Arbor, 1970.
12. Guillot P. Physico-chimie du protactinium. In ; Bouissières M., Muxart R., Eds. *Éditions du Centre National de la Recherche Scientifique*: Orsay, Vol. 154, 1965; pp 239.
13. Ferreira de Miranda C., Muxart R. Spectres d'absorption de solutions fluorhydriques de protactinium pentavalent. *Bull. Soc. Chim. Fr.* 1964, 31, 387.
14. Le Naour C., Trubert D., Di Giandomenico M. V., Fillaux C., Den Auwer C., Moisy P., Hennig C. First structural characterization of a protactinium(V) single oxo bond in aqueous media. *Inorg. Chem.* 2005, 44, 9542.
15. Hennig C., Le Naour C., Den Auwer C. Double photoexcitation involving electrons in L3-edge X-ray absorption spectra of protactinium. *Phys. Rev. B* 2008, 77, 235102.
16. Di Giandomenico M. V., Le Naour C., Simoni E., Guillaumont D., Moisy P., Hennig C., Conradson S. D., Den Auwer C. Structure of early actinides(V) in acidic solutions. *Radiochim. Acta* 2009, 97, 347.
17. De Sio S., Wilson R. E. EXAFS study of the speciation of protactinium(V) in aqueous hydrofluoric solutions. *Inorg. Chem.* 2014, 53, 12643.
18. Kaltsoyannis N., Bursden B. E. Electronic structure of f1 actinide complexes. 1. Nonrelativistic and relativistic calculations of the optical transition energies of AnX6q- complexes. *Inorg. Chem.* 1995, 34, 2735.
19. Kaltsoyannis N. Electronic structure of f1 actinide complexes. Part 3 of [1]. Quasi-relativistic density functional calculations of the optical transition energies of PaX₆²⁻ (X=F, Cl, Br, I). *J. Alloys Compd.* 1998, 271, 859.
20. Pershina V. Solution chemistry of element 105. Part I: hydrolysis of group 5 cations: Nb, Ta, Ha and Pa. *Radiochim. Acta* 1998, 80, 65.
21. Pershina V., Bastug T. Solution chemistry of element 105. Part III: hydrolysis and complex formation of Nb, Ta, Db and Pa in HF and HBr solutions. *Radiochim. Acta* 1999, 84, 79.
22. Siboulet B., Mardsen C. J., Vitorge P. What can quantum chemistry tell us about Pa(V) hydration and hydrolysis? *New J. Chem.* 2008, 32, 2080.
23. Gonze X., Jollet F., Abreu Araujo F., Adams D., Amadon B., Applencourt T., Audouze C., Beuken J. M., Bieder J., Bokhanchuk A., Bousquet E., Bruneval F., Caliste D., Côté M., Dahm F., Da Pieve F., Delaveau M., Di Gennaro M., Dorado B., Espejo C. Recent developments in the ABINIT software package. *Comput. Phys. Commun.* 2016, 205, 106.
24. Gonze X., Beuken J. M., Caracas R., Detraux F., Fuchs M., Rignanese G. M., Sindic L., Verstraete M., Zerah G., Jollet F., Torrent M., Roy A., Mikami M., Ghosez P., Raty J. Y., Allan D. C. First-principles computation of material properties: the ABINIT software project. *Comput. Mater. Sci.* 2002, 25, 478.
25. Perdew J. P., Burke K., Ernzerhof M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865.
26. Holzwarth N. A., Tackett A. R., Matthews G. E. A Projector Augmented Wave (PAW) code for electronic structure calculations, Part I: atom-paw for generating atom-centered functions. *Comput. Phys. Commun.* 2001, 135, 329.
27. Dal Corso A. Projector augmented-wave method: application to relativistic spin-density functional theory. *Phys. Rev. B* 2010, 82, 075116.
28. Wilson R. E., De Sio S., Vallet V. Structural and electronic properties of fluoride complexes of Nb^V, Ta^V, and Pa^V: the influence of relativistic effects on group V elements. *Eur. J. Inorg. Chem.* 2016, 5467.
29. Bonin L., Aupiais J., Kerbaa M., Moisy P., Topin S., Siberchicot B. Revisiting actinide–DTPA complexes in aqueous solution by CE-ICPMS and ab initio molecular dynamics. *RCS Adv.* 2016, 6, 62729.
30. Lahrouch F., Siberchicot B., Fèvre J., Leost L., Aupiais J., Solari P. L., Den Auwer C., Di Giorgio C. Carboxylate- and phosphonate-modified polyethylenimine: toward the design of actinide decorporation agents. *Inorg. Chem.* 2020, 59, 128.
31. NIST database (<https://webbook.nist.gov>).
32. Obodo K., Chetty N. First principles LDA + U and GGA + U study of protactinium and protactinium oxides: dependence on the effective U parameter. *J. Phys. Condens. Matter* 2013, 25, 145603.

33. Wagman D. D., Evans W. H., Parker V. B., Schumm R. H., Nuttall R. L. Selected values of chemical thermodynamic properties compounds of uranium, protactinium, thorium, actinium, and the alkali metals. *NBS Tech. Note* 1981, 270-8.
34. Laser M., Merz E. Über die Fluorierung von Protaktinium. *J. Inorg. Nucl. Chem.* 1969, 31, 349.
35. Kleinschmidt P. D. Thermochemistry of the actinides. *J. Alloys Compd.* 1994, 213, 169.
36. Kovács A., Konings R. J. M., Nemecsok D. S. Thermodynamic properties of PaCl_5 and PaF_5 based on quantum chemical calculations. *J. Alloys Compd.* 2003, 353, 128.
37. O'Grady E., Kaltsoyannis N. On the inverse *trans* influence. Density functional studies of $[\text{MOX}_5]^{n-}$ ($\text{M} = \text{Pa}$, $n = 2$; $\text{M} = \text{U}$, $n = 1$; $\text{M} = \text{Np}$, $n = 0$; $\text{X} = \text{F}$, Cl or Br). *J. Chem. Soc. Dalton Trans.* 2002, 1233.
38. Shannon R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. A* 1976, 32, 751.
39. Hirschfeld F. L. Bonded-atom fragments for describing molecular charge densities. *Theor. Chim. Acta* 1977, 44, 129.
40. Straka M., Dyall K. G., Pyykkö P. Ab initio study of bonding trends for f0 actinide oxyfluoride species. *Theor. Chem. Acc.* 2001, 106, 393.
41. Siboulet B., Marsden C. J., Vitorge P. A theoretical study of uranyl solvation: explicit modelling of the second hydration sphere by quantum mechanical methods. *Chem. Phys.* 2006, 326, 289.
42. Morss L. R., Edelstein N. M., Fuger J. *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Springer: Dordrecht, Vol. 1, 2006; p. 216.
43. Brown D., Easey J. F. Protactinium(V) fluorides. *J. Chem. Soc. A* 1970, 3378; <https://doi.org/10.1039/j19700003378>.
44. Toraiishi T., Tsuneda T., Tanaka S. Theoretical study on molecular property of protactinium(V) and uranium(VI) Oxocations: why does protactinium(V) form monooxo cations in aqueous solution? *J. Phys. Chem.* 2006, 110, 13303.