

On the Existence of Oxide Molecules of Plutonium in Highest Oxidation States

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Earlier [1], it has been demonstrated that the ozonation of Pu(VI) hydroxo complexes on heating to 60–85°C is accompanied by volatilization of plutonium compounds. On the basis of several indirect evidences, it has been suggested that the volatile compound is plutonium tetroxide PuO₄. This brings the question of the structure of this molecule.

According to early X α scattered wave calculations (1990, cited in [2]), PuO₄ was assumed to have a tetrahedral equilibrium geometry. This is consistent with the classical postulate [3]: mutual repulsion of the four identical monatomic ligands, other effects being absent, always leads to a tetrahedral structure of similar systems. The condition for the stability of a square configuration is the relatively low electron density in both axial positions as compared with the density in the square plane. At the same time, later density functional theory (DFT) calculations (after 2000) predicted a square-planar structure of the PuO₄ molecule ([4] and references therein).

These results have stimulated our efforts to predict properties of PuO₄ and some other hypothetical oxygen-containing plutonium compounds (Pu₂O₇, PuO₃F) interesting because of their possible volatility by modeling from first principles.

The relativistic model of electronic structure used in this work is based on the high-precision ab initio

shape-consistent two-component pseudopotential of the 60-electron core of the Pu atom [5]. Specific features of this pseudopotential ensuring the reliability of the description of chemical properties of compounds are that the finite nucleus size effects and Breit interactions are taken into account and that its parameters are determined to provide the maximally accurate reproduction of the properties of precisely the valence (7s, 6d, 5f) shells of plutonium. All electronic shells of the second period atoms were explicitly considered. The many-electron problem was solved using the non-collinear variant of the relativistic density functional theory (RDFT) [6] with unrestricted optimization of two-component one-electron spinors, which has recommended itself well in studying the chemistry of the heaviest elements (see [7] are references therein).

Calculations were performed with a [8s8p6d5f2g] basis set of contracted Gaussian functions for plutonium constructed with inclusion of spin-dependent relativistic interactions, which makes it possible to rule out the effects of basis set incompleteness (in particular, basis set superposition errors) when using effective one-particle methods, including DFT. The basis sets for O and F were obtained by augmenting the basis set recommended in [8] with diffuse functions to

Table 1. Calculated decomposition energies of Pu compound molecules (kJ/mol)

Reaction	RDFT/PBE0	RDFT/B3LYP
PuO ₃ → PuO ₂ + 1/2O ₂	126	135
PuO ₄ → PuO ₃ + 1/2O ₂	13	12
PuO ₄ → 1/2Pu ₂ O ₇ + 1/4O ₂	–100	–99
Pu ₂ O ₇ → PuO ₃ + PuO ₄	216	209
Pu ₂ O ₇ → 2PuO ₃ + 1/2O ₂	226	221
PuO ₃ F → PuO ₃ + 1/2F ₂	271	270

Note: Zero-point energy corrections constituting a few kilojoules per mole were neglected.

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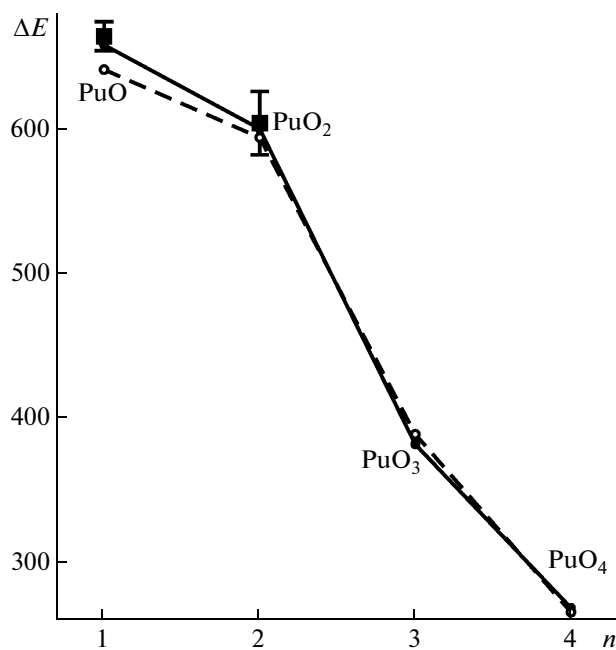


Fig. 1. Bond dissociation energies in PuO_n ($\Delta E \text{ PuO}_n \rightarrow \text{PuO}_{n-1} + \text{O}$, kJ/mol, without ZPE corrections) as a function of n . The RDFT/PBE0 and RDFT/B3LYP calculation results are shown by solid and dashed lines, respectively. Squares correspond to values obtained from experimental data [12] by reducing to zero temperature [13] and excluding ZPE contributions.

[6s4p2d]. For the exchange correlation functional, standard hybrid PBE0 [9] and B3LYP [10] approximations were used in most calculations. It is worth noting that the use of nonrelativistic approximate functional in our model is justified [5], which is not true for the computation schemes with the explicit description of

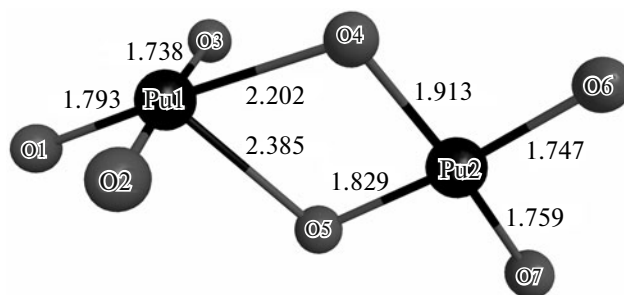


Fig. 2. Equilibrium structure of the Pu_2O_7 molecule. The bond lengths (Å) were obtained by the RDFT/PBE0 method. The use of the approximate B3LYP functional leads to the increase in calculated bond lengths by 0.02–0.03 Å.

core electrons [11]. The accuracy of the approach, as applied to the compounds under consideration, can be judged by the resulting Pu–O bond dissociation energies in PuO and PuO_2 (Fig. 1).

According to previous calculations in the framework of other relativistic models [4], the equilibrium configuration of the free PuO_4 molecule is square (D_{4h}). The energetic characteristics (Table 1) are evidence of the weak thermodynamic stability of PuO_4 with respect to the conversion into PuO_3 , which is expected because of the rapid decrease in the energy of oxygen atom elimination from PuO_n with an increase in n (Fig. 1). We failed to locate isomers with a structure resembling a distorted tetrahedron to an extent (including a peroxide structure). The regular tetrahedral (T_d) configuration corresponds to a saddle point of the potential energy hypersurface of the ground state and is characterized by a very high energy (~240 kJ/mol) with

Table 2. Selected calculated characteristics of the equilibrium structures of plutonium oxide and PuO_3F molecules

Molecule	Parameter	RDFT/PBE0	RDFT/B3LYP
PuO	$r(\text{Pu}-\text{O})$	1.820	1.837
PuO_2 ($D_{\infty h}$)	$r(\text{Pu}-\text{O})$	1.800	1.822
PuO_3 (C_{2v})	$r(\text{Pu}-\text{O}1) = r(\text{Pu}-\text{O}2)$	1.749	1.749
	$r(\text{Pu}-\text{O}3)$	1.853	1.858
	$\angle(\text{O}1-\text{Pu}-\text{O}2)$	170	169
PuO_4 (D_{4h})	$r(\text{Pu}-\text{O})$	1.753	1.774
PuO_3F (C_{2v})	$\angle(\text{F}-\text{Pu}-\text{O}2, \text{O}3)$	87	87
	$r(\text{Pu}-\text{F})$	2.002	2.025
	$r(\text{Pu}-\text{O}1)$	1.778	1.802
	$r(\text{Pu}-\text{O}2) = r(\text{Pu}-\text{O}3)$	1.734	1.756
Pu_2O_7 (C_s) *	$\angle(\text{O}1-\text{Pu}-\text{O}2, \text{O}3)$	93	94
	$\angle(\text{Pu}1-\text{O}4-\text{Pu}2)$	108	108
	$\angle_d(\text{O}1-\text{Pu}1-\text{O}3-\text{O}4)$	177	177
	$\angle(\text{O}4-\text{Pu}2-\text{O}6)$	91	91
	$\angle(\text{O}6-\text{Pu}2-\text{O}7)$	93	93
	$\angle(\text{O}5-\text{Pu}1-\text{O}7)$	93	93

Note: Bond lengths (r) are in angstroms and planar (\angle) and dihedral (\angle_d) angles are in degrees.

* See Fig. 2 for internuclear distances; the symmetry plane passes through the Pu1–Pu2, O1, and O4–O7 atoms.

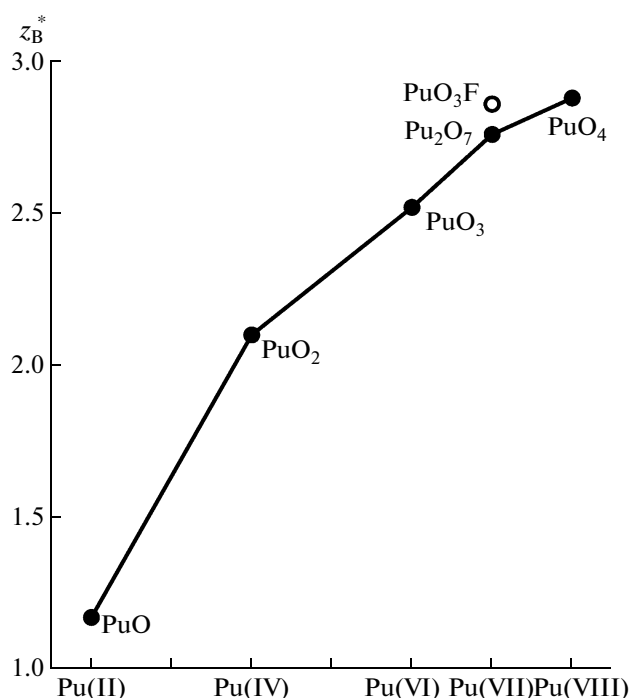


Fig. 3. Bader charges z_B^* on Pu atoms vs. formal oxidation state (RDFT/PBE0 calculations).

respect to the equilibrium configuration. This result is reproduced with different exchange correlation functional approximations.

The Pu₂O₇ and PuO₃F molecules are considerably more stable (Table 1). A quasi-square environment of the Pu atom can be discerned in their geometries (Table 2, Fig. 2). In particular, the Pu₂O₇ structure can be treated as a combination of two perpendicular distorted squares with oxygen bridges. It is evident that the Pu atoms in this molecule are structurally nonequivalent.

It is worth noting that the optimized internuclear distances in PuO₄ are 1.75–1.77 Å (depending on the functional used), and the shortest distances in Pu₂O₇ are 1.74–1.76 Å (Fig. 2).

The net charges on the plutonium atoms in the molecules determined by the Bader analysis [14] generally correlate with the formal oxidation state, although the differences between the charges for Pu(VII) and Pu(VIII) are rather small (Fig. 3). It is important that the Bader charges of the nonequivalent Pu atoms in Pu₂O₇ are nearly the same (+2.76 Pu1/+2.76 Pu2 and +2.74 Pu1/+2.73 Pu2 according to the calculations with the PBE0 and B3LYP functionals, respectively).

Comparison of the Pu–O internuclear distances in isolated PuO₄ and Pu₂O₇ molecules with those in crystalline K₃[PuO₄(OH)₂].2H₂O (the structure was determined by single crystal X-ray diffraction [15]) reveals some shortening of the Pu–O bond in Pu₂O₇ ($r(\text{Pu}–$

O) = 1.866 and 1.912 Å in the crystal against the shortest distances 1.75–1.76 Å in the molecule).

Thus, according to our computation data, Pu₂O₇ should be the most stable molecule in the gas phase in the series of the oxides under consideration. The trioxide PuO₃ in the presence of oxygen is thermodynamically unstable to oxidation to Pu₂O₇. Plutonium trioxofluoride PuO₃F is presumably rather stable. Rather, plutonium tetroxide PuO₄, even if it is formed, can presumably decompose into unstable PuO₃, which can “adhere” to PuO₄ to give Pu₂O₇.

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