Inorganic Chemistry
Article
pubs.acs.org/IC

Oxidation States, Geometries, and Electronic Structures of Plutonium Tetroxide PuO_4 Isomers: Is Octavalent Pu Viable?

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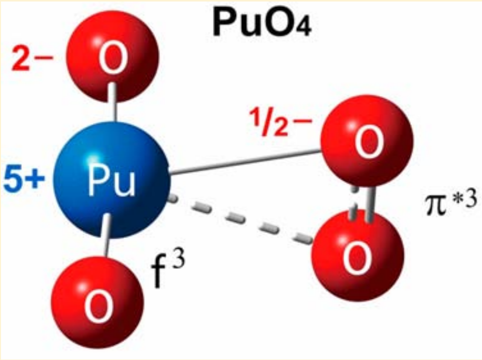
Supporting Information



ABSTRACT: In neutral chemical compounds, the highest known oxidation state of all elements in the Periodic Table is +VIII. While PuO_4 is viewed as an exotic Pu(+VIII) complex, we have shown here that no stable electronic homologue of octavalent RuO_4 and OsO_4 exists for PuO_4, even though Pu has the same number of eight valence electrons as Ru and Os. Using quantum chemical approaches at the levels of quasi-relativistic DFT, MP2, CCSD(T), and CASPT2, we find the ground state of PuO_4 as a quintet $^5C_{2v}$-$(PuO_2)^+(O_2)^-$ complex with the leading valence configuration of an (f^3)plutonyl(V) unit, loosely coupled to a superoxido $(\pi^{*3})O_2^-$ ligand. This stable isomer is likely detectable as a transient species, while the previously suggested planar $^1D_{4h}$-Pu(VIII)O_4 isomer is only metastable. Through electronic structure analyses, the bonding and the oxidation states are explained and rationalized. We have predicted the characteristics of the electronic and vibrational spectra to assist future experimental identification of $(PuO_2)^+(O_2)^-$ by IR, UV−vis, and ionization spectroscopy.

1. INTRODUCTION

Actinide chemistry is essential for nuclear energy and environmental science.[1,2] Because of its important applications, significant environmental risks, and complicated chemical behavior, plutonium chemistry remains a hot topic.[3,4] The early actinide elements exhibit a particularly rich chemistry, since they excel in an abundance of oxidation states (*OS*), in particular the elements from Pa through Am.[1,2] For more than a century, the most common actinide elements Th and U were counted, from chemical points of view, among the ordinary transition metals. This situation changed after 1950, when the concept of 5f-elements, as suggested by Bohr in 1922[5,6] and again by Seaborg in 1945,[7] was gradually introduced into the chemical textbooks.[8,9] In general, the highest *OS* of an element is limited by the number of valence electrons outside the closed, chemically inert core shells. Among neutral compounds the highest overall *OS* known so far is VIII, namely, for p-block element Xe (group 18), for d-block elements Ru and Os (group 8), and for some others.[10−16]

The 5f elements are known to behave as d-like elements with an inner open f shell,[17,18] the later actinides acting like the lanthanides. Among the early actinides, plutonium has a soft [... $(6sp)^8$] Rn core and eight valence electrons in a rich 5f-6d-7s valence shell. The 5f shell is quite contracted in radial distribution with average radius $\langle r \rangle \approx 0.7$ Å and penetrates inside the $(6sp)^8$ semicore shell ($\langle r \rangle \approx 0.9$ Å), although it is not yet too small for some valence-domain orbital overlap interactions. In contrast, the better overlapping 6d shell has $\langle r \rangle \approx 1.7$ Å, and 7s with $\langle r \rangle \approx 2.3$ Å is already somewhat diffuse for significant valence interaction. Because of this intricate situation with regard to multiple orbital radii and energies, Pu compounds exhibit a variety of complicated electronic structures and oxidation states.[3,4,19,20] In general, the highest *OS* occurs in metal complexes with highly electronegative ligands such as fluorine or oxygen. Inasmuch as octavalent PuF_8 is unknown, attention has been paid to plutonium oxides that are spatially less crowded than the former. PuO_x compounds are important not only for general f-block chemistry, but also for nuclear science and technology.[19,21−24]

Plutonium can exist in a number of different oxidation states, depending upon the ligands attached. There are more than three decades of experimental and theoretical searches for unprecedented Pu(VIII) oxides with an empty, strongly electron-attracting $5f^06d^0$ valence shell. Among these efforts, plutonyl(VI) compounds such as hydroxides or $PuO_3 \bullet H_2O$ were oxidized in aqueous alkaline solution with O_3, or in carbohalogen solution with XeF_2; plutonyl was also oxidized by adding fluorine ligands. In addition, Pu was treated with O_2 at high temperature in the gas phase and cooled down to adsorb on a quartz surface. Mixed Li−Pu hexoxide or plutonyl−dioxide layered peroxo solids were also investigated. The experiments were interpreted by assuming the presence of PuO_4 molecules (e.g., as OsO_4 with tetrahedral symmetry) or of anionic $[PuO_6]^{4-}$ or $[PuO_6H_2]^{2-}$ or related species in alkaline solution.[19−22,25−36] On the other hand, no concrete exper-

Received: August 26, 2013
Published: November 25, 2013

imental stoichiometric or structural evidence exist. Efforts to synthesize Pu(VIII)O_nF_{8-2n} have so far not been conclusive; at most, PuO_3F_2 might be stable at liquid nitrogen temperatures. As Pu(VIII) has an extremely high oxidation potential (even toward water), it will subtract electrons from the ligands (as substantiated below) and is assumed to have a low kinetic stability, and half-lives below seconds.[4,21−23,27,28,37−39]

It is thus clear that even with some ambiguous evidence for Pu(VIII) species, the mystery still remains whether they are sufficiently thermodynamic or kinetic stable and whether they are akin at all to the covalently spin-coupled tetrahedral Ru(VIII)O_4 and Os(VIII)O_4 molecules with an octavalent central atom.[40−45] Pyykkö et al. found in 2001 that the electronic structure of PuO_4 is of multiconfigurational spin-singlet character and appears with a quasi-flat D_{4h} geometry.[20] This D_{4h} structure has been reproduced in subsequent literature.[27,30] Recently, through relativistic DFT studies Zaitsevskii et al. found a significantly lower-energy plutonyl(VI) peroxide with C_{2v} symmetry and abnormally short O−O distance, although the spin coupling was not specified.[31] Given the importance of high-OS Pu chemistry, it is therefore necessary to investigate the PuO_4 species in depth.

Oxidation state is a central concept in chemistry, not only for bookkeeping electrons, but in particular for understanding and classifying chemical bonding, electronic structures, and redox reactions. The so-called *common OS* of an element occasionally causes misinterpretations in 'noncommon' cases. For example, oxygen appears in many compounds as a closed shell O^{2-} anion with *common OS*(O) = II. Consequently, in such "ordinary" MO_n oxides, *OS*(M) = +2*n*. Most discussions on PuO_4 and related species consider just this single option of divalent oxygen and then surmise *OS*(Pu) = VIII. However, many poly oxygen compounds of s-block and d-block elements are well-known to violate this simplistic supposition, such as the industrially important solid peroxide Ba(II)O_2 or superoxide K(I)O_2 or the analytically relevant blue Cr(VI)O_5.[9−a,46,47] Another example is the related UO_6 system,[45] in which various geometric and electronic isomers unexpectedly embrace the common *OS*(U) = V or VI, while the ligated oxygen atoms adopt different *OS* varying from −II to 0. In addition to O(II) in the atomic spin-singlet closed-shell oxo-dianion ${}^1O^{2-}$, oxygen may also appear as a monovalent ligand O(I) in two forms (as radicalic atomic oxido ${}^2O^{\bullet 1-}$ ligand or as closed shell diatomic peroxido ${}^1O_2{}^{2-}$ ligand with O−O distances around 1-1/2 Å); as O(−1/2) in radicalic diatomic superoxido ${}^2O_2{}^{\bullet 1-}$ ligands with shorter R_{O-O} values around 1-1/3 Å;[43] in ozonido complexes with ${}^2O_3{}^{\bullet 1-}$ units, with oxygen in formal oxidation state O(−1/2); and finally as O(0) in monomeric, dimeric (${}^3O_2{}^{\bullet\bullet}$, $R_{O-O} \sim$ 1-1/5 Å) or trimeric form (${}^1O_3$).

The Pu-5f orbitals have rather low energies and contracted radial distribution. Pu(VIII) seems difficult to achieve because even the Pu-6p outer core−shell is easier to open up than to remove the last few 5f electrons.[48] In this paper we will address five questions on PuO_4: (a) Which electronic and geometric equilibrium structures are possible for PuO_4 molecular species? (b) Are higher local energy minima kinetically stable above the ground state? (c) How can these structures be described in terms of traditional chemical bonding concepts? Which *OS* should be assigned to the Pu and O atoms in the different isomers? (d) What is the bonding role of the plutonium 6d and 5f valence orbitals? (e) Which spectroscopic footprints can be theoretically predicted for the experimental verification of the PuO_4 ground-state?

The applied theoretical methods are described in section 2, the results are discussed in section 3, and our answers and conclusions are presented in section 4. In contrast to the literature, we find that the PuO_4 ground-state species is a superoxido-plutonyl complex of pentavalent Pu that can be formulated as ${}^5C_{2v}$-$[Pu(V)O_2]^+O_2{}^-$. The previously postulated ${}^1D_{4h}$-Pu(VIII)O_4 structure is shown to be an excited metastable species at significantly higher energy, while the postulated ${}^1T_d$-Pu(VIII)O_4 structure is not even metastable.

2. METHODOLOGY

The calculations were performed by using density functional theory (DFT) and wave function theory (WFT) with various computational chemistry software, including Gaussian 09,[49] ADF 2010,[50] and MOLPRO 08.[51] Weinhold's natural population analyses were performed with the NBO 5.0 code.[52] More detailed citations of the software are given in the Supporting Information (SI) file.

In the DFT calculations, the geometry and electronic structure optimizations were performed using the B3LYP hybrid density functional[53,54] with Gaussian 09. The ECP60MWB relativistic effective core potential (RECP) developed by the Stuttgart-Cologne groups was chosen for Pu.[55−57] Gaussian type one-electron basis sets ECP60MWB_-GUESS[56,57] for Pu and aug-cc-PVDZ[58] for O were used. The local energy minimum character of the structures was checked by vibrational analyses. For comparison with experimental vibrational features, the calculated harmonic frequencies were reduced by a scaling factor of ∼0.97.[59] Further DFT calculations were performed with ADF. The relativistic effects were taken into account using the zero-order regular approximation (ZORA).[60,61] Slater-type TZ2P basis sets were used for both Pu and O.[62] The frozen core approximation was applied to the $[1s^2\text{-}5d^{10}]$ core of Pu and the $[1s^2]$ core of O.[63]

For more accurate single-point energy determinations of the stationary states, we applied the *ab initio* single-reference WFT methods of SCF-MP2 (self-consistent field MO with second order Møller−Plesset perturbation theory)[64−66] and CCSD(T) (coupled-cluster expansion with single, double, and perturbative triple substitutions) as implemented in MOLPRO.[67−71] Electronically excited states were calculated by using multi-reference CASSCF/CASPT2 approaches.[72−75] In order to simulate the relativistic effects in the valence shells, RECPs were applied in the two-component spin−orbit (SO) coupling form. SO coupling effects were accounted for by the state-interacting SI/SO technique.[76] The RECPs and basis sets used here are the same as in the aforementioned Gaussian calculations.

3. RESULTS AND DISCUSSION

3.1. Geometric Structures and Energies of PuO_4 Species. Because of the complexity of the Pu complexes, we have undertaken a comprehensive search on various isomeric structures of PuO_4 with different spin multiplicities. Figure 1 depicts the optimized low-energy stationary structures. (A) ${}^5C_{2v}$ (GS) is the plutonyl(V)-superoxide ground state, $[Pu^{5+}(O^{2-})_2](O_2{}^-)$; the corresponding electronic triplet and singlet species are higher in energy. (B) ${}^1D_{4h}$ (ES planar) is the lowest excited metastable isomer, tetra-oxido-plutonium, Pu-$(O)_4$; its electronic triplet and quintet species are also higher in energy. The other stationary structures are transition-state saddle-points on the triplet, singlet, and quintet potential

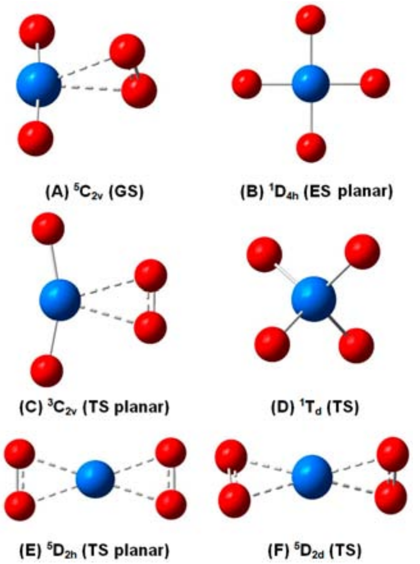


Figure 1. Stationary Born−Oppenheimer states (local PES minima) of Pu●4O species: (A) $^5C_{2v}$ (GS) quintet ground state, plutonyl(V)-superoxide $[Pu^{5+}(O^{2-})_2](O_2^-)$; (B) $^1D_{4h}$ (ES planar) low-lying excited singlet state of PuO_4 type. Four stationary transition states (PES saddle points): (C) $^3C_{2v}$ (TS planar) $[Pu^{5+}(O^{2-})_2](O_2^-)$; (D) ^1T_d (TS) PuO_4; (E) $^5D_{2h}$ (TS planar) $Pu^{4+}(O_2^{2-})_2$; (F) $^5D_{2d}$ (TS) $Pu^{4+}(O_2^{2-})_2$.

energy surfaces (PES), respectively: (C) $^3C_{2v}$ (TS planar) is $[Pu^{5+}O_2](O_2^-)$, (D) ^1T_d (TS) is $Pu(O)_4$, and (E) $^5D_{4h}$ (TS planar) and (F) $^5D_{2h}$ (TS) are plutonium(IV)-diperoxides, $Pu^{4+}(O_2^{2-})_2$. Table 1 lists the energies and geometric parameters of selected low-lying states. The geometries were optimized at the DFT level (B3LYP), and then the single-point energies were determined at the CCSD(T) level.

The plutonyl(V) substructure of the $^5C_{2v}$ species has two short, nearly linear Pu−O bonds (R_{Pu-O} = 176 pm, ∠OPuO = 176°). The dioxygen unit has the typical bond length of a superoxido anion (O_2^-: O−O = 131 pm) and is loosely coordinated in the equatorial plane at the large bidentate distance of R_{Pu-O} = 233 pm. SO coupling of the Pu-5f shell stabilizes the quintet state by 26 kJ/mol.

Our calculations on the spin-singlet PES confirm that PuO_4 can be locally stable as planar $^1D_{4h}$.[20] Depending on the method and basis set, one either finds a flat minimum at D_{4h} symmetry with small harmonic bending frequency or two flat symmetry-equivalent minima of D_{2d} structure with small 'imaginary' frequency at the D_{4h} saddle point. The latter geometry is the average of large-amplitude inversion vibrations toward the ^1T_d saddle points. The four Pu−O distances are short, around 177 pm, the strong Pu−O interactions leading to spin-singlet coupling. However, the planar $^1D_{4h}$ singlet isomer is about 70 kJ/mol above the plutonyl(V) quintet ground-state at the SO-averaged level, and about 90 kJ/mol at the SO coupled level. The $^1D_{4h}$ energy is insignificantly changed by SO coupling due to the vanishing first-order effect.

In order to qualitatively understand the energetic differences of various states, we have determined the linear transit (LT) energy curves between the $^5C_{2v}$ and $^1D_{4h}$ geometries on the singlet, triplet, and quintet PES at the SR and SO coupled DFT levels (Figure 2). For the $^1D_{4h}$ geometry, the three SR or SO states differ in energy each by around 0.8 eV, corresponding to 1- and 2-electron transfers from the oxygen lone-pair shell to the Pu-5f shell. The three PES cross in a joint region around 2 eV above the lowest $^1D_{4h}$ energy, which is further SO-stabilized by about 0.2 eV (see circle in Figure 2).

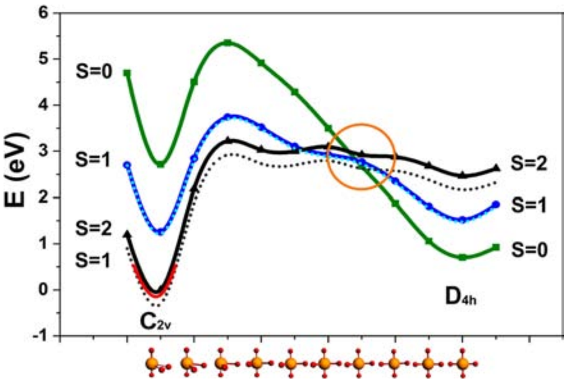


Figure 2. Linear transit energy curves E (in eV) between the $^5C_{2v}$ and $^1D_{4h}$ minimum energy structures for spin singlets, triplets, and quintets at the B3LYP level. Here, S denotes the total spin, full curves represent the SR approximation, dotted curves display the SO coupled energies. The circle indicates the projected crossing region. For the C_{2v} geometry, DFT gives a triplet state (S = 1, short piece of a parabola) below the quintet (S = 2), but CASSCF theory gives lower quintet states.

The situation is more complicated at the C_{2v}-end of the reaction path. In the low-energy region with unpaired electrons in the Pu-5f and the distant O-2p orbitals, different spin-couplings with rather similar energies are possible. At the DFT

Table 1. Calculated Geometries and Energies of Various Pu·4O Structures

				CCSD(T)	B3LYP			
Species[a]	Symmetry	2S+1	Type[b]	$\Delta E^{c,h}$	ΔE^{c}	R_{Pu-O}[d]	R_{O-O}[d]	∠OPuO[d]
(**A**)	C_{2v}	5	GS	−0−	−0−	176.4, 233.1	131.4	176.3, 32.7
(**B**)	D_{4h}	1	ES	+68	+60	177.2		90.0
(**C**)	C_{2v}[e]	3	TS	+165	+179	182.6, 237.4	130.8	159.7, 32.0
(**E**)	D_{2h}[f]	5	TS	+285	+275	214.1	143.4	39.1
(**F**)	D_{2d}	5	TS	+309	+398	215.7	142.3	38.5
(**D**)	T_d	1	TS	+362[g]	+400	181.2		109.5

[a] The geometric structures of species (**A**) to (**F**) are shown in Figure 1. [b] Type: GS = ground state, ES = excited-state isomer, TS = transition states at saddle points on singlet, triplet and quintet Born−Oppenheimer PES. [c] ΔE = BO energy in kJ/mol above GS, from DFT-B3LYP or CCSD(T) with SO-averaged RECP; SO coupling reduces the −0− reference value by −26 kJ/mol. [d] R = interatomic distances in pm, bond angles in degree. [e] Planar, in contrast to (**A**). [f] Planar, in contrast to (**F**). [g] CCD energy is used, as CCSD(T) did not converge. [h] Diagnostic values are given in table S1 of the ESI, e.g. T1 = 0.04 for the GS.

Table 2. Calculated Effective Charges, Weinhold Valences, and Bond-Orders for C_{2v}-$(PuO_2)(O_2)$, D_{4h}-PuO_4, D_{4h}-PuF_4, T_d-RuO_4, and T_d-OsO_4[a]

Molecule	$[PuO_2](O_2)$			PuO_4		PuF_4		PuF_4		OsO_4		RuO_4	
symmetry	${}^5C_{2v}$			${}^1D_{4h}$		${}^5D_{4h}$		${}^5T_d$		${}^1T_d$		${}^1T_d$	
$R_{M\text{-}(O,F)}$/pm	R_{Pu-O}: 176, 233			R_{Pu-O}: 177		R_{Pu-F}: 231		R_{Pu-F}: 204		R_{Os-O}: 172		R_{Ru-O}: 171	
Atom	Pu	O_{Plu}	O_{O2}	Pu	O	Pu	F	Pu	F	Os	O	Ru	O
Aver. effective charge[b]	+1.8	−0.65	−0.25	+1.9	−0.48	+2.1	−0.52	+2.3	−0.58	+1.8	−0.44	+2.1	−0.52
Aver. spin charge[b]	3.43 (3.75)	−0.19 (−0.36)	0.47 (0.49)	–	–	4.2	−0.06	+4.0[c]	−0.01	–	–	–	–
Metal AO populations[d]	6d=1.7 (1.6) 5f=5.1 (4.8)			6d=2.5 (2.6) 5f=4.9 (4.3)		6d=1.0 (1.5) 5f=4.9 (4.2)		6d=1.5 (1.2) 5f=4.6 (5.3)		5d=4.8 (4.2) 6s=0.2 (0.2)		4d=5.4 (4.9) 5s=0.3 (0.3)	
Weinhold covalence	2.87	1.11	1.56	4.59	1.15	1.17	0.29						
Electro-valence	4.35	1.76	0.48	6.50	1.63	6.47	1.62						
M-L Bond order		2.85	0.51		2.77		1.91						

[a] From NBO 5.0 calculations with B3LYP functional (Gaussian & ADF). [b] Weighted average of Voronoi, Hirshfeld, Mulliken, Weinhold, and quadrupole derived charges; average of Weinhold, Mulliken, and quadrupole derived spin charges.[59] [c] +4.22 reported by Dolg et al.[78] [d] B3LYP results (MP2 results in parentheses); d- and f-AOs are polarized by some admixture of s-, p-, d-, or f-AOs, respectively. Values in parentheses are from ab initio post-HF (MP2).

B3LYP level, we find a ${}^3C_{2v}$ state lying just 0.12 eV below the ${}^5C_{2v}$ state (see the short piece of an $S = 1$ curve at the bottom left of Figure 2). At a well-correlated and SO-coupled level of theory (CASSCF/CASPT2/SI-SO, see section 3.3) we find a whole range of states, all strongly configuration-mixed, and the lower ones are all derived from spin-quintet states. Since the current approximate DFT functionals are not reliable enough to investigate the 'finer' details of these complicated states, while the desired CASSCF-based electron correlation approaches are too time-consuming, no further investigation of the intermediate region between the C_{2v} and D_{4h} geometries was performed. We expect the crossing region in the 1.5 eV rage; the ${}^1D_{4h}$ species is expected to have a finite half-life at room temperature, and may be observable in a noble gas matrix at low temperatures, if it could be synthesized at all.

3.2. Electronic Structure and Bonding of the Two PuO_4 Isomers.

Superoxido-Plutonyl(V). The geometric structure of the ${}^5C_{2v}$ GS species (**A**) suggests a superoxido-plutonyl(V) complex, with four spins coupled to form a quintet. This bonding description is supported by the wave function analyses listed in Table 2 and Figures 3 and 4, which indicate one unpaired spin on the superoxido ligand and three unpaired spins in the Pu-5f shell (a ${}^4Pu(f\text{-}\delta^2\phi^1)^{5+}$ configuration at the SO-averaged level).

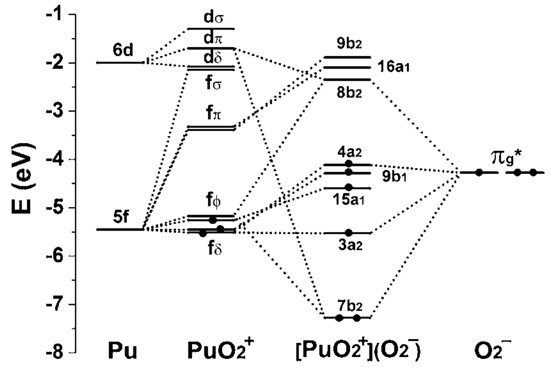


Figure 3. Energy levels (in eV) of the frontier Kohn−Sham valence MOs of ${}^5C_{2v}$-$[PuO_2^+](O_2^-)$ illustrating the plutonyl−superoxido interaction.

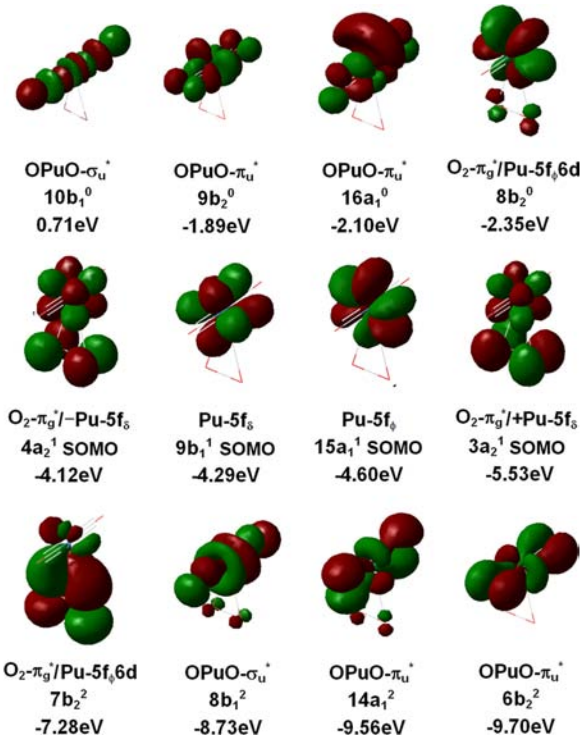


Figure 4. Frontier canonical Kohn−Sham valence MO envelopes of ${}^5C_{2v}$-$[PuO_2](O_2)$ with dominant AO contributions. Value of contour envelopes is 0.05 a.u.

It is not unexpected that there is only one f-electron in the plane of the $O_2^\bullet$ ligand, $15a_1$-$f\phi^1$, and two electrons are somewhat off that plane, $4a_2$,$9b_1$-$f\delta^2$. The $f\sigma$ and $f\pi$ orbitals on and near the plutonyl(V) axis with adjacent O^{2-} ligands remain empty, they are destabilized while stabilizing the plutonyl-oxygen $8b_1$-$2p\sigma$ and $6b_2$,$14a_1$-$2p\pi$ orbitals. The empty $8b_2$-$f\phi$ component and also the higher $d\pi$ stabilize the doubly occupied in-plane $7b_2$-π^* component of O_2^-, forming a dative η^2 bond. The singly occupied $3a_1$-π^* component is triplet-coupled to the $4a_2$-$f\delta$ orbital, which is equivalent (for parallel spin coupling) to the sum and difference of the two O_2-π^* and Pu-$f\delta$ orbitals displayed in Figure 4. Altogether this bonding scenario leads to plutonyl(V) Pu−O bond orders close to 3,

Table 3. Normal Mode Vibration Frequencies (cm^{-1}) and IR Intensities (km/mol) of the Two PuO_4 Isomers Calculated Using the B3LYP Method[a]

	$OPuO_{stretch}$		$Pu<O_{2,stretch}$		$OPuO_{bend}$		$O-O_{stretch}$	
Species	freq.	Int.	freq.	Int.	freq.	Int.	freq.	Int.
$^5C_{2v}$	A_1: 841 (815)	17	A_1: 389 (377)	59	A_1: 269 (261)	9	A_1: 1210 (1172)	29
	B_1: 931 (902)	395	B_2: 392 (380)	4	B_2: 243 (236)	22		
$^1D_{4h}$[b]	$E_{u,ip}$: 915 (887), [920]	293			$B_{2g,ip}$: 378 (367)			
	$A_{1g,ip}$: 867 (840), [873]				$E_u$ip: 356 (345)	6		
	$B_{1g,ip}$: 728 (705), [735]				$A_{2u,oop}$: 272 (264)	29		

[a] Frequencies in parentheses are revised by a scaling factor of 0.9698. [b] Frequencies (of $^1D_{4h}$) in square brackets are from ref 20; subscripts ip and oop mean in-plane and out-of-plane, respectively.

while the Pu-superoxido bond orders are only ~0.5, supporting the description as $[Pu^VO^{II}{}_2](O^{1/2}{}_2)$.

To understand the OS of PuO_4, one can view that when Pu^0-(fds)[8] atoms react with oxygen molecules in the hot gas phase, $O_2{}^0$ will attract 4 electrons from electropositive Pu^0 and form ${}^{-2}O{=}Pu^{4+}{=}O^{2-}$ featuring two strongly bonded O^{2-} atoms in a linear plutonyl unit with electronic configuration Pu-$5f^4$. A second $O_2{}^0$ (R_{OO} = 1.2 Å) can then snatch, however, only one further electron from Pu, yielding $[Pu(V,f^3)O_2]^+(O_2{}^-)$ with a superoxido ligand (R_{OO} = 1.3 Å) with an unpaired electron in the $\pi_g{}^*$ MO. Because of the open-shell feature, SO coupling will stabilize the Pu-f^n (n = 3, 4) species by a few 10 kJ/mol. Our bonding analysis shows that the bonding of $O_2{}^-$ to plutonyl is mainly due to σ-dotation into the Pu-5f6d shell by its in-plane $\pi_u{}^2$ and $\pi_g{}^{*2}$ pairs. The two equatorial Pu(V)−O(−1/2) distances (2.3 Å) are too large to induce a spin-pairing chemical bond between the Pu-5fδ and O-2pπ orbitals, yielding a magnetic *multiradical* molecular spin-quintet state. The situation is similar to photoreduced uranyl $[O{=}U^{\bullet}{-}O^{\bullet}]^{2+}$ with $U(V,f^1)$ coupled to a monovalent $O(I,p^5)$. As in some transition metal poly oxides,[24,85−88] the oxygen atoms in $(PuO_2)(O_2)$ coexist in different OS (i.e., O(II) and O(1/2)).

Usually the energetic order of the d- and f-levels in the actinyls is 5f < 6d and $f\phi < f\delta < f\pi < f\sigma$. In the present case, the fδ orbitals are slightly below fϕ corresponding to the double occupation of fδ vs single occupation of fϕ. The four singly occupied MOs Pu-$f\delta_{4a2}$, $f\delta_{9b1}$, $f\phi_{15a1}$, and O_2-$\pi_{2a2}{}^*$ with 4 electrons in 8 spinors give rise to 70 states, 1 quintet, 15 triplets, and 20 singlets. Under SO coupling, all states are nondegenerate. The lowest state of triplet character appears at 0.4 eV above the ground state of quintet character, corresponding to parallel and antiparallel coupling of weakly overlapping Pu-5f and O_2-π^* electrons (see also section 3.3). At higher energies, the $8b_2$, $16a_1$, and $9b_2$ orbitals contribute as well.

Tetroxido−Plutonium. The chemical interpretation of the oxidation state and electronic structure of the planar high-energy $^1D_{4h}$ isomer of PuO_4 is less obvious. On one hand, the OS is defined by simple rules for integers attributing all electrons of a polar bonding interaction to the more electronegative atom; on the other hand, this coarse assignment of electrons should in some chemically meaningful manner reflect the real charge distribution and atomic characteristics. The Pu−O distances in $^1D_{4h}$-PuO_4 (**B**) are similarly short as in the plutonyl(V) unit, $[Pu({\equiv}O)_2]^+$, which seems to suggest O(II) and Pu(VIII) for (**B**). The Pu−O bond order indices of (**B**) and of the plutonyl(V) unit are comparable, again supporting the O(II) assignment. And in the familiar $Os(VIII)O(II)_4$, the oxo-ligands donate also about 1-1/2 electrons to the metal cation as in the case of PuO_4.

However, the averaged effective charges on the central metal atom in Table 2 do not show a clear correlation with the accepted OS numbers of the various atoms. The averaged effective charges on the oxygen atoms and the metal AO populations would better fit in the PuO_4 case to intermediate OS for Pu around IV to VI and for O around −1 to −1-1/2. The significant $Pu^{8+}{\leftarrow}O^{2-}$ charge transfer in hypothetical $Pu(VIII)O_4$ with donation of about 6 electrons into the open Pu-5f6d shells might suggest the more realistic formula $Pu^{4+}(O^-)_4$ containing O(I) and Pu(IV). The latter scenario is reminiscent of that in UO_6 or in the photoreduced uranyl $(O{\equiv}U{\bullet}{=}{\bullet}O)^{2+}$ species with monovalent oxygen.[45,79] An important aspect in this context is that the ground states of the free atomic octavalent-cations Ru^{8+} and Os^{8+} are known to be closed core−shell singlets $^1S(p^6)$ with empty d^0 valence shells. But in the Pu atoms, it is easier to ionize the 6p outer-core electrons than the last few 4f electrons. In other words, the free Pu^{8+} ion would be derived from a high-spin 'open-core'[7][Rn-$6p^{-3}$]$5f^3$ configuration.

In summary, it seems a matter of taste whether the metastable $^1D_{4h}$-PuO_4 species is described as ionic $Pu^{8+}(O^{2-})_4$ with unusually excited $Pu^{8+}(p^6f^0d^0)^*$ and with unusually strong donation of oxygen lone pairs to Pu^{8+}, or as spin-coupled $^1Pu(5f^4)^{4+}(O^-)_4$ better describing the bonding situation. It is not self-evident whether one should really count the significant electronic Pu-5f shell population as belonging to the O ligands in order to follow the rules toward an oxidation state of Pu(VIII).

3.3. Vibrational, Electronic, and Ionization Spectra of the Two Isomers. As mentioned in the Introduction, experimentalists have simply interpreted some findings as indications of the existence of $Pu(VIII)O_4$. Further, there is claimed experimental evidence for very short lifetimes of Pu(VIII) oxide-hydroxide species.[21,27,28] Our study shows that even in vacuum or gas-phase, Pu•4O in the Pu(VIII) state is only metastable, which casts serious doubt on the existence of any Pu(VIII) oxidation state in solution. Further experimental spectroscopic search for fingerprints of the C_{2v}-$[PuO_2](O_2)$ species is needed to clarify the ambiguity. If synthesized in aqueous solution, there would be water molecules coordinated in the equatorial plane, such as $(O_2){\cdot}[PuO_2]{\cdot}aq_{2,3}$. However, that should not seriously affect the specific vibrations of the $[PuO_2]$ or O_2 or $[PuO_2]$-O_2 groups, nor the dominant electronic excitations inside the $PuO_2{\bullet}O_2$ cluster, by more than the accuracy limits of the present calculations.

Vibrational Features. In C_{2v} symmetry, A_1, B_1, and B_2 vibrations are IR active, while all modes including A_2 are

Table 4. C_{2v}-$(PuO_2)(O_2)$: All Vertically Excited Electronic States (in eV) from CASSCF/CASPT2/SO Calculations up to $\Delta E \sim \lambda = 100$ nm[a]

No.	Dom.Spin	ΔE (in eV)	Leading Term	No.	Dom.Spin	ΔE (in eV)	Leading Term
1	2	−0−	$^5B_1$	29	2	1.582	$^5A_1$
2	2	0.122	$^5B_1$	30	2	1.582	$^5A_1$
3	2	0.124	$^5B_1$	31	2	1.594	$^5A_1$
4	2	0.248	$^5B_1$	32	2	1.596	$^5A_1$
5	2	0.358	$^5A_2$	33	2	1.598	$^5A_1$
6	1	0.414	$^3B_1$	34	2	1.923	$^5B_2$
7	1	0.419	$^3B_1$	35	2	1.923	$^5B_1$
8	2	0.537	$^5A_2$	36	2	2.063	$^5B_1$
9	2	0.537	$^5A_2$	37	2	2.063	$^5B_1$
10	2	0.672	$^5A_1$	38	2	2.168	$^5B_1$
11	2	0.672	$^5A_1$	39	2	2.200	$^5A_2$
12	1	0.678	$^3B_1$	40	2	2.278	$^5A_2$
13	2	0.751	$^5A_1$	41	0	2.294	$^1B_1$
14	2	0.751	$^5B_1$	42	0	2.294	$^1A_2$
15	2	0.807	$^5B_1$	43	2	2.322	$^5A_2$
16	2	0.813	$^5A_1$	44	1	2.374	$^3A_1$
17	1	0.826	$^3A_2$	45	2	2.410	$^5B_2$
18	2	0.929	$^5B_2$	46	2	2.410	$^5B_1$
19	2	0.961	$^5A_1$	47	1	2.536	$^3A_1$
20	1	1.050	$^3A_2$	48	1	2.536	$^3A_1$
21	1	1.051	$^3A_2$	49	0	2.613	$^1A_1$
22	2	1.078	$^5B_2$	50	0	2.798	$^1B_2$
23	2	1.082	$^5B_2$				
24	2	1.216	$^5A_1$	51	2	12.252	$^5B_2$
25	2	1.216	$^5A_1$	52	2	12.254	$^5B_2$
26	1	1.379	$^3B_2$	53	2	12.254	$^5B_2$
27	1	1.389	$^3B_2$	54	2	12.261	$^5B_2$
28	1	1.389	$^3B_2$	55	2	12.261	$^5B_2$

[a] The two bold bars indicate the sole two 'bigger' energy gaps of 0.2 and 0.3 eV, respectively. Dom.Spin = dominant spin-coupling, $S = 2, 1, 0$ means quintet, triplet, singlet, respectively.

Raman active. In the electronic spectra, the A_1 stretching modes of the PuO_2^+ and O_2^- units will show up as progressions in ligand-to-metal charge-transfer (LMCT) transitions. The predicted vibrational normal modes of C_{2v}-$(PuO_2)(O_2)$ and also of D_{4h}-PuO_4 are listed in Table 3. For the C_{2v} species, the expected characteristic IR features are as follows: (i) the intense asymmetric B_1 plutonyl(V) stretching mode around 900 cm^{-1}, and the weaker symmetric A_1 mode around 820 cm^{-1}, (ii) the $O_2Pu(\eta^2$-$O_2)$ A_1 stretching mode around 380 cm^{-1}, (iii) the O−Pu−O A_1 and B_2 bending modes around 250 cm^{-1}, and (iv) the weak O−O A_1 stretching mode near 1200 cm^{-1}, most specific for $(PuO_2^+)(O_2^-)$. This spectrum is quite different from that expected for the D_{4h} species, already predicted in ref 20 and reconfirmed here.

Electronic Excitations. Electronically excited states were determined by using the CASSCF/CASPT2/SO approach, where 24 electrons in the upper 10 doubly occupied, 4 singly occupied, and 3 lower virtual MOs of Pu-5f and O_2-π^* character were included in the active space. The first 55 states are listed in Table 4 and Table S2 of the SI file. The lowest energy electronic excitations are in the region of the plutonyl and superoxido vibrations, meaning the breakdown of the BO approximation and of the electronic-vibrational separability. There is a quasi-continuum of rovibronic states deriving from 33 electronic states in the IR region up to the visibility limit, i.e., λ around 776 nm. The electronic states are rather evenly distributed, due to Coulomb, exchange, and spin−orbit coupling among the three Pu-5f electrons and Coulomb and exchange coupling with the superoxido π^*-hole, indicating the breakdown of the conventional DFT approximation.

A selection of dipole-allowed optical transitions from the ground state with oscillator strengths $f > 10^{-7}$ a.u. are displayed in Table 5. They all have dominating f-f character without pronounced vibrational progressions. One may expect two transitions with $f > 10^{-5}$ in the short-wave IR region near 0.675 and 0.75 eV ($\lambda \sim 1.85$ and 1.65 μm). The strongest visible transition is expected at the red end near 1.60 eV ($\lambda \sim 780$ nm) with $f \approx 10^{-6}$. A strong VUV absorption exists at ~12 eV ($\lambda \sim 100$ nm). Kiselev et al.[16] found a strong absorption band in the $\lambda \sim 270$ nm range (~4-2/3 eV) in the reaction product of PuO_3·aq with oxidant XeF_2. However, no strong absorption in this range is to be expected for the ground state of Pu•4O, which calls for further experimental investigation on this species.

Ionization Features. The photo- and e-2e[80] ionization spectra should also be characteristically different for $^1PuO_4$ and $^5[PuO_2](O_2)$. Concerning the O-1s core ionizations in the 540 eV range, $^1PuO_4$ would show a single line, whereas $^5[PuO_2]$-(O_2) would show 2*2 lines: a chemical shift of about 1.3 eV according to Koopmans' approximation of the more negative

Table 5. C_{2v}-$(PuO_2)(O_2)$: The Optically Strongest Vertical Electronic Excitations (in cm^{-1}) from CASSCF/CASPT2/SO Calculations

Range	No.	ΔE (cm^{-1})	λ (nm)	Leading Term		$10^6 \cdot f$/au
IR	1	−0−		x $^5B_1$	$(\delta^2\phi^1\pi^1)$	-
	10	**5421**	1845	a $^5A_1$	$(\delta^{1.4}\phi^{1.8}\pi^{0.8})$	**11.6**
	13	6055	1652	b $^5A_1$	$(\delta^{1.6}\phi^{1.2}\pi^{1.2})$	1.6
	14	**6056**	1651	b $^5B_1$	$(\delta^{1.4}\phi^{1.2}\pi^{1.4})$	**17.0**
	16	6554	1526	c $^5A_1$	$(\delta^1\phi^2\pi^1)$	1.0
	21	8475	1180	a $^3A_2$	$(\delta^1\phi^{0.8}\pi^{0.2})$	0.5
	24	9808	1020	d $^5A_1$	$(\delta^{1.6}\phi^{1.8}\pi^{0.6})$	0.5
Vis	31	12859	778	e $^5A_1$	$(\delta^{1.4}\phi^{1.2}\pi^{1.4})$	0.7
	34	15507	645	a $^5B_2$	$(\delta^1\phi^{1.8}\pi^{1.2})$	0.2
	37	16640	601	c $^5B_1$	$(\delta^1\phi^2\pi^1)$	0.2
	45	19436	515	b $^5B_2$	$(\delta^{1.6}\phi^1\pi^{1.4})$	0.2
	47	20454	489	a $^3A_1$	$(\delta^1\phi^1\pi^0)$	0.1
VUV	53	**98833**	101	c $^5B_2$	$(\delta^{1.4}\phi^1\pi^{1.6})$	**7.7**
	54	98889	101	d $^5B_2$	$(\delta^{1.6}\phi^1\pi^{1.4})$	0.4

plutonyl(V) oxygens at lower energies vs the O_2^- ligand, and a quintet^0 → sextet$^+$/quartet$^+$ spin splitting with 50% more intensity for the lower energy component. Since remarkable spin density is only on the dioxygen ligand (Table 2), only the higher energy O_2^- doublet will show a remarkable splitting of about 1/2 eV. Also, the valence ionizations will be characteristically different. While the closed-shell oxygens will give rise to features above 8 eV for both isomers, the unpaired Pu(5f) and $O_2(\pi^*)$ electrons of the $^5[PuO_2](O_2)$ ground state will give a rich spectrum in the low-energy region around 4−6 eV.

3.4. Isolelectronic Series of AnO_4^q Species.

Based on our understanding of the electronic structure and oxidation state of PuO_4, it is interesting to examine the possible geometric-electronic structures of the UO_4^{2-}, NpO_4^-, and PuO_4 species as an isoelectronic series. Pyykkö et al.[20] had found that the previous speculations of a tetrahedral spin-singlet species were unfeasible. This conclusion was confirmed again recently by Zaitsevskii et al.[30,31] Our present investigations reveal an intriguing trend across the series: from UO_4^{2-} to PuO_4 the C_{2v} quintet states become stabilized and the T_d singlet states become destabilized when compared with the D_{4h} singlet states. As displayed in Figure 5, $U(VI)O_4^{2-}$ has the ground state as ^1T_d, and the slightly higher $^1D_{4h}$ state appears upon transition to the inverted tetrahedron.[80] We find the near-degenerate $^{3,5}C_{2v}$ species $[U(III,f^3)O_2]^+(O_2)^-$ at much higher energies, exhibiting the preference of U(VI) over U(III) oxides. For $Np(VII)O_4^-$ the $^1D_{4h}$ state is now nearly 2 eV below the ^1T_d transition state,[85] while the $^{3,5}C_{2v}$ states of $[Np(IV,f^3)O_2]^+(O_2)^-$ are only a bit higher, showing the reduced preference of Np(VII) over Np(IV) oxides. Finally for $Pu(VIII)O_4$, the ^1T_d transition state lies much higher than the metastable $^1D_{4h}$ species, while the near-degenerate $^{3,5}C_{2v}$ superoxido ground states of $[Pu(V)O_2](O_2)$ are about 1 eV lower. This shows the preference of Pu(V) over Pu(VIII) oxides. Recently, Zaitsevskii et al.[30,31] also found a C_{2v}-$[PuO_2](O_2)$ species as the lowest state of Pu•4O. While these authors originally described it as a low-spin $Pu(VI)O_2$-peroxide, further inspection of their calculated DFT results verified the characterization of PuO_4 as a high-spin triplet $Pu(V)O_2$-superoxide $^3C_{2v}$-$[Pu(V)O_2]^+(O_2)^-$, which is close to our conclusion that the PuO_4 species should be described as a quintet $Pu(V)O_2$-superoxide. Our DFT results show that the $^3C_{2v}$ state indeed lies ~0.1 eV below $^5C_{2v}$ for all 3 actinides U to Pu at the SR-B3LYP level, these states belonging to the same electron configuration. However, more accurate WFT-based electron correlation calculations with SO-coupling reveal that the SO-split quintet state yields the true ground state.

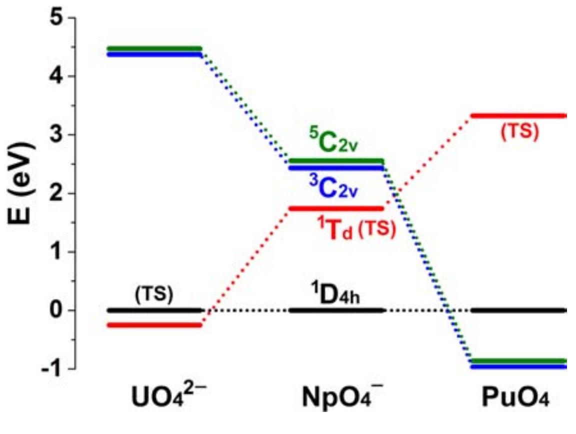


Figure 5. Low-lying energy states of $(An{\cdot}4O)^q$ species calculated using the DFT B3LYP mehod. ^1T_d and $^1D_{4h}$ are $An(f^0)$ tetroxides of U(VI), Np(VII), and Pu(VIII). $^3C_{2v}$ and $^5C_{2v}$ are $An(f^3)$ superoxides $[AnO_2]^+(O_2)^-$ of U(III), Np(IV), and Pu(V). Energy scale is in eV, with the $^1D_{4h}$ energy chosen as the zero reference.

4. SUMMARY AND CONCLUSIONS

Whether Pu(VIII) species can exist has aroused significant attention in actinide chemistry. Previous experiments were interpreted as giving indirect evidence for the existence of Pu(VIII). Based on such assumption, Pu(VIII) was considered to appear as stable or short-living PuO_4, as solvated PuO_6^{2-}, or related species at different temperature ranges. However, the early quantum chemical calculations by Pershina et al.[81−84] and various experiments later had already suggested extreme oxidation potentials of PuO_3F_2, PuO_6^{4-}, $PuO_6H_2^{2-}$, and related Pu(VIII) species. They should be active even toward water and have very short half-live times. The separated fragments of $Pu(VIII)O_4$ are the open-core shell $Pu^{8+}(5f^36p^3)$ and 'soft' $O(2p^6)^{2-}$. If one would from $Pu(VIII)O_4$ from its ionic fragments, the O^{2-} ions would at first fill up the Rn noble-gas shell of Pu^{8+} with 3 electrons, leading to the most probable product of $[Pu^{5+}(5f^3)\ O_2^{2-}]\ (O_2^{1/2-})$, which is the proposed ground state of Pu·4O in the present work. On the other hand, for the metastable $Pu^{8+}(5f^06p^6)O_4$ species, the strong electron-withdrawal power of the empty Pu-5f shell would convert two closed-shell O^{2-} ligands into radicals, which then form the O_2^- ligand over a reaction barrier (Figure 3).

Based on previous experimental and theoretical literature and the present calculations, we conclude that the electrophilicity increases tremendously from U(VI) to Np(VII) to Pu(VIII) so that the highest possible OS becomes more and more unstable and inaccessible. While many stable uranyl(VI) peroxidic compounds are known,[85,86] the electronegativity of the actinide in the highest OS has increased so much from U(VI) to Pu(VIII) that even 3 electrons become detached from the four O^{2-} ions of PuO_4, yielding a plutonyl(V)-superoxide as the ground state. We have shown that in the hypothetical Pu tetroxide, the oxidic electron pairs are attracted so much by Pu^{8+} that the octavalent representation of $Pu(VIII)(O^{2-})_4$ becomes far from reality. Accordingly, compounds with OS ≥ 8 seem very unlikely from Pu onward.

For highly charged actinide cations, the 5f shell soon starts to collapse energetically and contract spatially under the 6p-semicore shell. While those Pu cations have a d-valence shell like Ru and Os, they have in addition deep 5f-shell holes. Therefore, the Pu homologue of ^1T_d-RuO_4 and ^1T_d-OsO_4 becomes an unstable transition state on the potential energy surface and the $^1D_{4h}$ square-planar structure remains a metastable high-energy isomer. Because the large oxidation potentials of the actinides in superhigh OS tend to cause spontaneous oxidation of its ligands, some of the O(II) ligands become reduced to O(1/2) in Pu•4O to form (PuO_2)-(O_2).The previous argument that Pu(VII) could be oxidized further by subtracting an electron from its ligands does not seem to be convincing.[27]

Although our investigations show that Pu(VIII) is not stable in PuO_4, the formation of Pu(VII) seems feasible when an alkalic Pu(VI) solution is ozonized. The possible reaction

$$[\mathrm{Pu(VI,\ 5f^2)O_2}]^{2+} + 1/6\ \mathrm{O_3} + 1/2\ \mathrm{H_2O} \rightarrow [\mathrm{Pu(VII,\ 5f^1)O_2}]^{3+} + \mathrm{OH^-}$$

needs further theoretical and experimental investigation. While Pu^{7+}-$5f^1$ is already rather exotic, Pu^{8+}-$5f^0$ is deemed to be difficult, if not impossible. The often discussed ozonization of Pu(VII) in an alkaline medium might proceed as following to form Pu(V) rather than Pu(VIII), again equatorial OH_2 and OH^- ligands being omitted:

$$[\mathrm{Pu(VII,\ 5f^1)O_2}]^{3+} + 4/9\ \mathrm{O_3} + 2/3\ \mathrm{H_2O} \rightarrow [\mathrm{Pu(V,\ 5f^3)\cdot O_2^-} + 3\mathrm{H^+}]$$

To facilitate future experimental search of the gas-phase $(PuO_2)(O_2)$ species we have predicted its fundamental vibrations in the IR region, the vertical electronic excitations in the NIR−vis−UV regions, and the photoionization energies. Particularly characteristic signatures are the O_2^- vibrational band in the IR- and Raman spectra, and the f → f spectrum in the IR−vis region. The four high-lying spin-'parallel' electrons will give rise to a rich spectrum due to strong electron correlations. The $^5C_{2v}$ structure will give rise to a specific low-energy Pu-5f photoelectron spectrum, and to a structured O-1s core ionization spectrum. While Pu(VII) may exist in solution, a recent thorough thermochromatographic study of volatile plutonium oxides has only shown evidence of OS = 6.[89]

While four oxygen atoms are insufficient to form Pu(VIII) in PuO_4, further theoretical study is needed on the effect of additional ligands of the coordinatively unsaturated plutonly(V) monosuperoxido complex. Pyykkö[20] suggested that plutonyl-tertafluoride PuO_2F_4 might exist as a possible example of Pu(VIII), being energetically below $Pu(VI)O_2F_2$ + F_2. Experimental identification of $(PuO_2)^+(O_2)^-$ and PuO_2F_4 will be interesting to clarify the debate on the existence of octavalent Pu(VIII).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Software references. Table S1: Various isomeric states of PuO_4. Table S2: Vertical electronic excitations from CASSCF/CASPT2/SO calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank V.G. Pershina, P. Pyykkö, S. Riedel, A.V. Zaitsevskii, and a Referee for illuminating comments. This work was financially supported by the Chinese NSFC (grants Nos. 20933003, 91026003, 21201106). The calculations were performed using supercomputers at Tsinghua National Laboratory for Information Science and Technology.

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