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# Structures and stability of $AnO_4$ isomers, An = Pu, Am, Cm: A relativistic density functional study

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Equilibrium structures and energetics of various isomers of molecules with stoichiometry An·4O (An = Pu, Am, Cm) are studied through electronic structure calculations at the relativistic density functional theory level in the frame of an accurate small-core pseudopotential model. In all cases, the global minima of the An·4O potential energy surfaces correspond to dioxo-superoxido-like species, $[AnO_2](O_2)$. The stability of the "true" oxides $AnO_4$ decreases from Pu to Cm, whereas the isomers with two $O_2$ groups become relatively more stable. Correlation between the formal oxidation states and the Bader net charges of actinide atoms is discussed. Structural parameters, vibrational frequencies and charge and spin magnetization density distributions are analyzed in order to characterize the different isomers in chemical terms. Decrease of the An oxidation states along the An series is evident.

## 1 Introduction

The existence of volatile oxides of early transuranium elements in abnormally high oxidation states, in particular in tetroxides, has been supposed several decades ago (see e. g.[1]) and numerous experiments have been performed to identify these species[2–8]. Nevertheless, up to now the experimental information on actinide tetroxides remains scarce and ambiguous. Experimental thermochromatographic observations on ultramicro-amounts of Pu compounds[2,3] have given indications of three kinds of volatile species interpreted as binary oxides; based on arguments of analogy, it was suggested that one of them could be $PuO_4$. However, the formation of volatile $PuO_4$ was not reconfirmed in a similar independent experiment[4]. In 2011 a volatile plutonium compound, assumed to be identified as plutonium tetroxide, was detected by $\alpha$-spectrometry in the products of ozonation of alkaline solutions of macroamounts of Pu(VI) hydroxo complexes at moderate temperatures (60-90 C)[5]. It should be noticed, however, that no Pu(VIII) compounds were detected in Pu(VI) ozonation products by X-ray photoelectron spectroscopy[6]. Very recently, volatilization of an americium compound (probably some higher oxide) from alkaline solutions under ozonation has been reported[7]. In Ref.[8], the results of a gas thermochromatographic study of the products of thermal oxidation of microamounts of $CmH_2$/$CmH_3$ were interpreted as confirming the formation of a highly volatile tetroxide $CmO_4$ under the assumption of the existence of a similar $PuO_4$ species.

According to fully relativistic *ab initio* and density functional theory (DFT) calculations, hypothetical plutonium (VIII) and americium (VIII) tetroxide molecules[9–12] in their ground electronic states have planar (square) equilibrium configuration and the analogy with tetrahedral $OsO_4$ and $IrO_4$ molecules which was supposed earlier (see e. g.[13] and references therein) is rather vague. Furthermore, for a wide range of conditions, $Pu(VIII)O_4$ and especially $Am(VIII)O_4$ are thermodynamically unstable with respect to the decay into lower oxides and molecular oxygen or to the transformation into dioxo-(su)peroxido-like structures $[AnO_2](O_2)$[11,12], An = Pu, Am. It is reasonable to suppose that systems with O–O bond(s) play an important role in interactions of these actinides with oxygen. No theoretical data on the $CmO_4$ system tentatively identified experimentally in[8] can be found in the literature.

The present work reports the results of relativistic DFT (RDFT) calculations on the structures and energetics of low-energy isomers of An·4O molecules, An = Pu, Am, Cm. We also analyze the charge and spin magnetization density distributions and characterize the different isomers in chemical terms.

## 2 Computational details

The computational scheme employed in the present study is essentially the one used in Ref.[11]. The relativity is introduced through accurate shape-consistent two-component pseudopo-

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tentials[14,15] replacing the An inner core shells with main quantum numbers $n \leq 4$. The molecular semicore+valence many-electron problem was solved by the two-component non-collinear relativistic DFT technique[16] with the fully unrestricted optimization of Kohn–Sham one-electron spinors. We used [8s8p6d5f2g] Gaussian basis sets for the actinide atoms[17] and a [$6s4p2d$] one for the oxygen atoms (cf. Ref.[11]). The smallness of the basis set superposition errors, evaluated for the AnO diatomics (less than 1 kJ/mol at their equilibrium internuclear separations, 1.80-1.83 Å), eliminated the need to use any counterpoise corrections. In all calculations, the PBE0 hybrid approximation[18] for the exchange-correlation functional was chosen both because of its (partially) non-empirical nature and the positive experience of its use in electronic structure calculations for other actinide compounds[10,11,19]. The ground-state character of the obtained solutions of the Kohn–Sham equations was carefully checked by swapping higher occupied and lower virtual orbitals and repeating the iterative procedure. Stationary points of the potential hypersurfaces were located by a gradient minimization procedure using a large variety of non-symmetrical starting geometries, including those compatible with relatively short O–O separations implying the existence of O–O bonds. The nature of the located stationary points was determined through computing the Hessian matrices by numerical differentiation of analytical energy gradients. These matrices were also used to compute harmonic vibrational frequencies using the Firefly quantum chemistry code[20]. Bader analysis of charge and magnetization densities was performed with the code described in Refs.[21,22].

## 3 Results and discussion

The main features of the calculated equilibrium geometries of various An·4O isomers are displayed in Table 1 (see also Fig. 1); Fig. 2 summarizes the energetics of these species at 0 K. It is worth noting that the isomerization enthalpies and Gibbs free energies evaluated within the single electronic state / harmonic oscillator / rigid rotator approximation at moderate finite temperatures (∼ 298 K) differ from the corresponding $\Delta H_0^0$ values by just a few kJ/mol. These differences are obviously small compared with typical errors arising from the approximation of the exchange-correlation functional.

The global minima of the ground-state potential hypersurfaces for all three An·4O systems under study correspond to similar dioxido-like actinyl structures $[AnO_2](O_2)$ (Fig. 1a) with the geometries of the actinyl fragments $[O^1AnO^2]$ closely resembling those of the free $AnO_2$ molecules or cations. Spin magnetization density distributions of the three molecules roughly correspond to the localization of one of the unpaired electrons on the $(O^3O^4)$ fragment; the shape of the corresponding isodensity surfaces (an example for An=Pu is given in Fig. 1a) enables one to associate this feature with the singly occupied oxygen antibonding "vertical" $\pi^*$ orbital with nodal planes coinciding with the reflection planes of the symmetry group. It is thus logical to classify these systems as dioxo-actonide (actinyl) superoxides. This is fully confirmed by the structural and vibrational data (short O–O bond lengths of ca. 1.3 Å, and O–O stretching vibrational frequencies above 1100 $cm^{-1}$ typical for superoxides) and the total charge distribution analysis (very small Bader net charges of $O^3$ and $O^4$ of $-0.32$ to $-0.33$, or 36–41 % of those for $O^1$ and $O^2$), see Table 2.

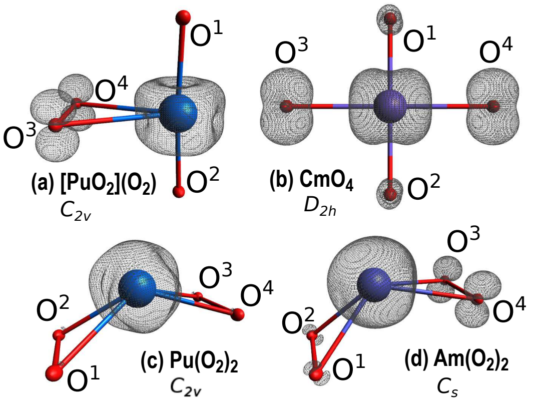

**Fig. 1** Equilibrium structures and plots of absolute values of spin magnetization densities for some An·4O systems

$PuO_4$ and $AmO_4$ are "true tetroxides" with short An–O bonds (ca. 1.75 Å) and without O–O bonds (O-O separation nearly 2.5 Å). The equilibrium structure of $CmO_4$ is slightly different; it is planar too but, in contrast to the former systems with four equivalent short ("double") bonds, $CmO_4$ is predicted to have two bonds ($Cm–O^3$ and $Cm–O^4$ in Fig. 1b) which are markedly longer ($>$ 2.0 Å) than typical An–O double bonds. Furthermore, the bond stretching force constant $\partial^2 E/\partial r(\mathrm{Cm}-\mathrm{O})^2$ for the longer bonds (0.117 a.u.) is much smaller than for the shorter ones (0.420 a.u.), which is in turn comparable to its counterparts in $PuO_4$ (0.461 a.u.) and $AmO_4$ (0.443 a.u.). These facts, along with significant spin magnetization density localized on $O^3$ and $O^4$ and relatively small net charges of these two atoms (Table 1), suggest that two bonds in $CmO_4$ should be considered as single and thus the formal Cm oxidation state in this system would be only +6. The thermodynamical instability of "true" curium tetroxide with respect to isomerization to the dioxo superoxide (Fig. 2) or decay into molecular oxygen and lower oxides is even more pronounced than in the cases of $PuO_4$ and $AmO_4$ (for example, the present estimate $\Delta H_0^0(CmO_4 \longrightarrow CmO_3 + 1/2\ O_2) = -116$ kJ/mol should be compared with $-52$ and $+7$ kJ/mol for the analogous reactions of Am and Pu tetroxides, respectively[11]).

We have also determined the lowest local minima on the po-

**Table 1** An·4O isomers (RDFT/PBE0 level of theory): Equilibrium geometries (internuclear distances $r$ in Å, angles ∠ in degrees), harmonic vibrational frequencies of predominant stretching character $\omega_e$ (in $cm^{-1}$; degeneracy number in parentheses), dipole moments $\mu$ (in atomic units), Bader net charges $z^*$ and magnetisations $m^*$ (in $\mu_B$) of the oxygen atoms

| Actinide tetroxides with O(II) or O(I) | $PuO_4$ $^{a}$) | $AmO_4$ $^{a}$) | $CmO_4$ |
|---|---|---|---|
| Formal oxidation state of An | VIII | VIII | VI |
| Formal configuration $^{b}$) | $f^0$ | $f^1$ | $f^4 p^1_{O3} p^1_{O4}$ |
| Symmetry | $D_{4h}$ | $D_{4h}$ | $D_{2h}$ |
| $r(An-O^{1,2})$ | 1.753 | 1.742 | 1.747 |
| $r(An-O^{3,4})$ | ” | ” | 2.057 |
| $\omega_e(An–O^{1,2})$ | 954(2), 915, 779 | 952(2), 869, 758 | 935, 793 |
| $\omega_e(An–O^{3,4})$ | | | 485, 415 |
| $z^*(O^{1,2})$ | −0.72 | −0.68 | −0.72 |
| $z^*(O^{3,4})$ | ” | ” | −0.51 |
| $m^*(O^{1,2})$ | 0.05 | 0.21 | 0.28 |
| $m^*(O^{3,4})$ | ” | ” | 1.14 |
| **Actinyl superoxides** | $[PuO_2]^+(O_2)^-$ | $[AmO_2]^+(O_2)^-$ | $[CmO_2]^+(O_2)^-$ |
| Formal oxidation state of An | V | V | V |
| Formal configuration $^{b}$) | $f^3\pi^*_{O_2}$ | $f^4\pi^*_{O_2}$ | $f^5\pi^*_{O_2}$ |
| Symmetry | $C_{2v}$ | $C_{2v}$ | $C_{2v}$ |
| $r(An-O^{1,2})$ | 1.747 | 1.742 | 1.763 |
| $r(An-O^{3,4})$ | 2.279 | 2.292 | 2.276 |
| $r(O^3-O^4)$ | 1.306 | 1.309 | 1.309 |
| $\angle(O^1AnO^2)$ | 176.2 | 177.7 | 173.5 |
| $\omega_e(O^3–O^4)$ | 1273 | 1266 | 1266 |
| $\omega_e(An-(O^3O^4))$ | 425, 385 | 413, 386 | 421, 397 |
| $\omega_e(An–O^{1,2})$ | 968, 888 | 967, 858 | 908, 787 |
| $\mu$ | 1.78 | 1.89 | 1.65 |
| $z^*(O^{1,2})$ | −0.90 | −0.85 | −0.81 |
| $z^*(O^{3,4})$ | −0.32 | −0.33 | −0.33 |
| $m^*(O^{1,2})$ | 0.18 | 0.22 | 0.24 |
| $m^*(O^{3,4})$ | 0.54 | 0.54 | 0.53 |
| **Actinide diperoxide or peroxide-superoxide** | $Pu^{4+}(O_2^{2-})_2$ | $Am^{3+}(O_2^{2-})(O_2^-)$ | $Cm^{3+}(O_2^{2-})(O_2^-)$ |
| Formal oxidation state of An | IV | III | III |
| Formal configuration $^{b}$) | $f^4$ | $f^6\pi^*_{O_2}$ | $f^7\pi^*_{O_2}$ |
| Symmetry | $C_{2v}$ | $C_s$ | $C_1$ |
| $r_{min}(An\text{-}O)$ | 2.064 | 2.075 | 2.046 |
| $r_{max}(An\text{-}O)$ | ” | 2.238 | 2.298 |
| $r(O^1-O^2)$ | 1.437 | 1.443 | 1.483 |
| $r(O^3-O^4)$ | ” | 1.328 | 1.323 |
| $\omega_e(O^1-O^2)$ | 970, 941 | 915 | 882 |
| $\omega_e(O^3-O^4)$ | | 1168 | 1226 |
| $\omega_e(An–(O^1O^2))$ | 483,515,539,540 | 517, 498 | 558, 528 |
| $\omega_e(An–(O^3O^4))$ | | 423, 209 | 401,352 |
| $\mu$ | 2.19 | 2.29 | 2.95 |
| $z^*(O^{1,2})$ | −0.55 | −0.57 | −0.60,−0.62 |
| $z^*(O^{3,4})$ | ” | −0.37 | −0.36,−0.37 |
| $m^*(O^{1,2})$ | 0.13 | 0.16 | 0.06 |
| $m^*(O^{3,4})$ | ” | 0.53 | 0.51,0.55 |

$^{a}$) Ref.[11], $^{b}$) only open shells are indicated

**Table 2** Characteristic parameters of oxygen species in An·4O molecules: equilibrium interatomic distances $r$ (in Å), Bader charges per atom $z^*$, and characteristic stretching vibrations $\omega_e$ (in cm$^{-1}$)

| Species | $r$(An–O) | $r$(O–O) | $z^*$(O) | $\omega_e$(An-O) | $\omega_e$(O-O) |
|---|---|---|---|---|---|
| $=O^{2-}$ in $[AnO_2](O_2)$ | $1.75\pm0.01$ | | $-0.86\pm0.04$ | $890\pm75$ | |
| $=O^{2-}$ in $AnO_4$ | | | $-0.70\pm0.02$ | | |
| $-O^-$ | $2.06\pm0.01$ | | $-0.51$ | $450\pm50$ | |
| $(O_2)^{2-}$ | | $1.46\pm0.02$ | $-0.58\pm0.03$ | $525\pm25$ | $930\pm40$ |
| $(O_2)^-$ | $2.28\pm0.01$ | $1.32\pm0.01$ | $-0.34\pm0.02$ | $380\pm70$ | $1240\pm40$ |

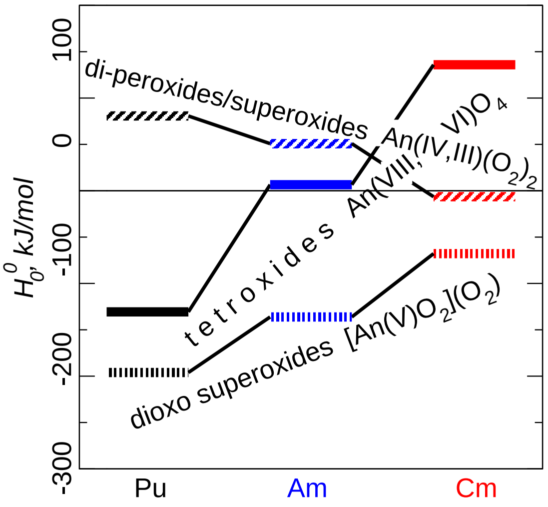

**Fig. 2** Calculated enthalpies $H_0^0$ of various An·4O isomers with respect to $H_0^0(AnO_2+O_2)$.

tential energy hypersurfaces corresponding to the isomers with two oxygen-oxygen bonds, $An(O_2)_2$. The relative stability of these isomers increases from An=Pu to An=Cm (Fig. 2). The equilibrium structure of $Pu(O_2)_2$ is symmetric ($C_{2v}$) and the two $O_2$ groups are identical (Fig. 1c), with O–O bond lengths typical for peroxide anions $(O_2)^{2-}$, slightly squeezed by the attracting An cation (1.44 Å); the spin magnetization density is localized essentially in the vicinity of the plutonium atom. In contrast, the $O_2$ subsystems in $Am(O_2)_2$ and $Cm(O_2)_2$ are not equivalent. One of them ($O^3O^4$ in Fig. 1d), has a shorter O–O bond and longer Pu–O separations, significant unpaired electron density, and small net charges of the oxygen atoms, and thus is readily identified as a superoxido group $(O_2)^-$, while ($O^1O^2$) seems to be a peroxido group (Table 1, 2). It is thus logical to assign the formal oxidation numbers +4 to Pu and +3 to Am and Cm for this kind of isomers, which are, by the way, also their most common oxidation states. The proposed interpretation of the nature of chemical bonding in An·4O is confirmed by the good correlation between the suggested integer formal oxidation states and the Bader net charges of the actinide atoms (Fig. 3). Also the magnetization densities, integrated over the atomic Bader basins ($m^*$ in Table 1), correlate well with the assigned numbers of unpaired spins. Closed shell oxidic atoms carry $m^* \approx 0.05$ to $0.28\ \mu_B$; correspondingly, monovalent oxygens carry $m^* \approx 1.14\ \mu_B$, and the half-valent superoxidic atoms carry $m^* \approx 0.51$ to $0.55\ \mu_B$.

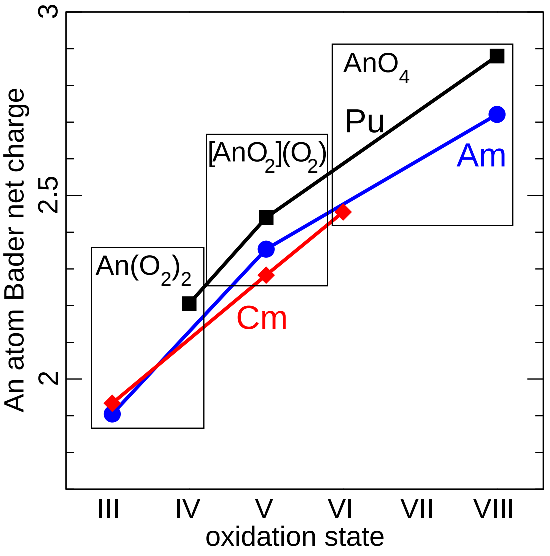

**Fig. 3** Bader net charges of actinide atoms in molecules of An·4O stoichiometry.

The effect of spin-dependent interactions (first of all, spin-orbit couplings) on various molecular properties is of certain interest because of the popularity of scalar relativistic methods of electronic structure theory. In the present case, these effects do not appear to be of critical importance for the qualitative description of the energetics of various isomers. For instance, the changes in the calculated $[AnO_2](O_2) \rightarrow AnO_4$ isomerization energies with switching off the effective spin-orbit interaction (i.e. passing to averaged relativistic pseudopotential model) do not exceed 25 kJ/mol.

The low-energy An·4O isomers with O–O bond(s) have considerable dipole moments (Table 1); this is obviously not an argument in favor of their high volatility. Further, it may also enhance the addition of polar ligands such as $H_2O$ at ambient temperatures. It might be worth underlining that the systems of An·4O stoichiometry discussed so far do not exhaust the multitude of oxygen-reach mononuclear compounds of Pu, Am, and Cm. For instance, the formation of a dioxo disuperoxido molecule ($[AnO_2](O_2)_2$) through the attachment of an oxygen molecule to $[AnO_2](O_2)$ can be accompanied by a small but (at least for An = Pu, Am) non-negligible energy lowering. According to our calculations, $\Delta H_0^0$ ($[AnO_2](O_2)$ + $O_2 \longrightarrow [AnO_2](O_2)_2$) amounts to −38, −44, and −19 kJ/mol for An = Pu, Am, and Cm, respectively. Thus one may expect that plutonium and americium dioxo disuperoxides can be stable at low temperatures.We note that, in contrast to all $[AnO_2](O_2)$ and $An(O_2)_2$ isomers, the $[AnO_2](O_2)_2$ molecules in their equilibrium configurations have zero dipole moments because of their high ($D_{2h}$) symmetry (Fig. 4). These species might be the lowest-energy isomers of the An·6O series, as is the case for U·6O[23].

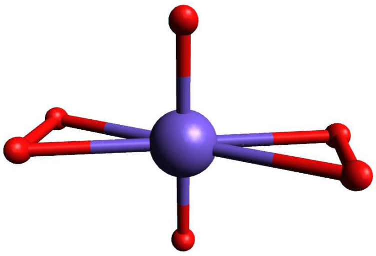

**Fig. 4** Equilibrium structure of $[AnO_2](O_2)_2$ molecules

## 4 Conclusions

Structures and energies of the low-lying An·4O isomers (An = Pu, Am, Cm) with none, one or two oxygen-oxygen bonds were determined at the two-component RDFT level, employing accurate shape-consistent small-core relativistic pseudopotentials. Going through the series of the actinide elements, the 5f shell energy decreases, thereby increasing its electron attracting power and stabilizing the lower versus the higher oxidation states. The different bonding and oxidation states of the various isomers are deduced on the basis of the geometric, vibrational and charge-density parameters. The "true" actinide(VIII) tetroxides $AnO_4$ may exist in principle as metastable species and might be verifiable at low temperatures, for instance if prepared in cold noble-gas matrices from An atoms and UV-irradiated $O_2$). However, the thermodynamical instability of the An(VIII) tetroxides with respect to the corresponding An(V) dioxido-superoxides increases significantly along the actinide series from Pu onwards. Even more, structural and magnetization-density features of the curium tetroxide clearly indicate that Cm is no longer octavalent but only hexavalent. The lowest-energy An·4O isomers from An = Pu through Cm are, however, the actinyl(V) (i.e. dioxido) superoxides $[AnO_2](O_2)$ with one short O–O bond and a significant spin magnetization density on the $(O_2)^-$ subsystem. This demonstrates the specific stability of the actinyl moieties, known from protactinium onwards, in the first half-period of the actinide elements. The lower-valent bis-dioxygen species are found at rather high energies, in particular for the earlier members An = Pu and Am. They exhibit tetravalency in the case of $Pu(IV)(O_2)_2$, and trivalency further on, $An(III)(O_2)(O_2)$ for An = Am and Cm. Extrapolating the energetic trends, one may expect that in the second half-period of the actinides, i.e. from berkelium onwards, the most stable tetraoxo molecules will derive from the An(III) oxidation state.

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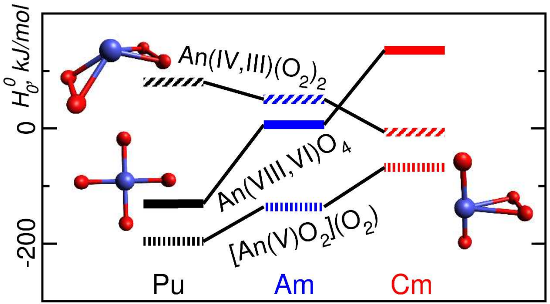
The most stable oxidation state of the tetra-oxo-actinides decreases from U(VI) to Pu(V), Np(V), Cm(V) preferentially forming actinyl-superoxides.


$H_0^0$, kJ/mol
0
-200
An(IV,III)$(O_2)_2$
An(VIII,VI)$O_4$
[An(V)$O_2$]($O_2$)
Pu
Am
Cm