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KOVÁCS, Attila, et al.

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Reference
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A theoretical study of AmO$_n$ and CmO$_n$ ($n = 1, 2$)

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1. Introduction

The current interest in transmutation of minor actinides (Np, Am and Cm), a nuclear process by which long-lived isotopes are converted into short-lived ones thus reducing the radioactive inventory of the high level waste from the nuclear fuel cycle, has stimulated extensive research for new nuclear fuel forms. For example (U, Pu, Am)O$_2$ has been proposed as fuel for next generation fast reactors and (Zr, Y, Am, Cm)O$_2$ has been proposed for dedicated transmutation devices, which in turn has led to a demand for a better understanding of the chemistry of minor actinide oxides at high temperatures, at typical operating temperatures (1500–2200 K) as well as more extreme conditions that can occur during abnormal situations, when mass transport via the vapor phase starts to become important. Vaporisation processes under these conditions can be described well by equilibrium thermodynamic models, but these models require fundamental knowledge of the properties of the condensed and gaseous phases that can be formed.

For the above reasons the molecular speciation in the gas phase and the molecular properties of the species are of key importance. As is known from the uranium and plutonium oxides, vapor species of the type AnO$_n$ can be formed with $n$ up to 3. Experimental results on CmO$_3$ demonstrated a rare-earth type of vaporization yielding primarily CmO(g) species. The number of experimental studies on the americium and curium oxides (AmO$_n$, CmO$_n$, where $n = 1, 2$) have been studied using relativistic, multi-configurational, quantum chemical methods.

2. Computational details

The calculations were performed using the software MOLCAS 6.4.$^5$ The complete active space (CAS) self-consistent field (SCF) method$^7$ was used to generate molecular orbitals and reference functions for subsequent multiconfigurational, second-order perturbation theory calculations of the dynamic correlation energy (CASPT2).$^8,9$ The active space consisted of 7s, 6d and 5f orbitals of the actinide elements as well as of the unoccupied 2p orbitals of oxygen. On the basis of preliminary SCF calculations on the closed-shell cations (lacking the unpaired electrons of the molecules) we constructed active spaces of 14 orbitals for AmO, AmO$^+$, AmO$_2$ and CmO, while an active space of 13 orbitals was used for CmO$_2$. Test calculations on AmO with 13 electrons in 16 active orbitals (13/16) gave results very similar to those obtained with the 13/14 active space. The orbital occupations within the active space were explored by 15-roots calculations.

All electron basis sets of atomic natural orbital type, developed for relativistic calculations (ANO-RCC) with the Douglas-Kroll-Hess Hamiltonian$^{10,11}$ were used for all the atoms. For americium and curium a primitive set of 26s23p17d13f5g3h was contracted to 9s8p6d5f2g1h, whereas for oxygen a primitive set of 14s3p2d1f was contracted to 4s3p2d1f achieving TZP quality. The

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Douglas–Kroll–Hess Hamiltonian was used in the CASSCF calculations in order to take into account scalar relativistic effects.

Our main goal was the analysis of the lowest-energy spin-free states of the target compounds. In addition, we performed spin–orbit test calculations on AmO and AmO+ to verify the effect of spin–orbit coupling on the computed relative energies. The spin–orbit effects were taken into account by using the CAS state interaction method (CASSI-SO), which allows CASSCF wave functions for different electronic states to interact under the influence of a spin–orbit Hamiltonian. The CASSCF/CASPT2/CASSI-SO methods and the basis sets used here have been successful in a number of studies on dimetal compounds.15–21

The potential energy curves of selected electronic states of the monoxide species were computed at the CASPT2 level of theory. The equilibrium bond distance, Re, the harmonic frequency, ωe, and other spectroscopic constants were determined by using the program VIBROT available in the MOLCAS package. The equilibrium structures of AmO2 and CmO2 were determined by numerical geometry optimizations at the CASPT2 level.

3. Results and discussion

3.1 AmO

The active space contained 13 electrons in 14 orbitals (13/14). Two possible spin multiplicities were considered, with five and seven unpaired electrons respectively. The lowest-energy electronic states of AmO designated by their multiplicity (m) and energy ordering are reported in Table 1.

The octet states are slightly more stable (consistently by ca. 0.4 eV) than the sextet ones. The computations show that all the four octet states have one dominant configuration, whereas the sextet ones consist of a mixture of 2–3 major configurations.

Characteristics of the presented low-energy states are three doubly-occupied orbitals of mainly O 2p in character with minor Am 6d and/or 6p contributions. These Am contributions (appearing in all three of the bonding orbitals) indicate the triple bond character of the Am–O bond. The third Am–O bond can be interpreted as one lone pair of O over-lapping with empty Am 6d/6z orbitals in a donor–acceptor type interaction. The triple bond character of the actinide–oxygen bond has been observed in several compounds.22–26

The seven unpaired electrons occupy six Am 5f orbitals and the Am 7s orbital (5f67s, 5F1/2). The consistently occupied 7s orbital in the low-energy states indicates its importance in the stabilization of the electronic configuration of AmO. The 6d orbitals of Am appear only as minor components in the bonding AmO orbitals.

The dissociation energy computed in the present study, D2(D0), is 4.68(4.62) eV. This value is lower than the estimate of Wang et al.,28 provides a clue to the reliability of our computed data. Hence we investigated the lowest-energy states of the AmO+ ion using the same active space (14 orbitals) as for AmO but with 12 electrons.

We considered two spin multiplicities with four and six unpaired electrons respectively. We found in all the presented low-energy states that the 7s orbital of Am is empty (in contrast to AmO, see above) indicating that this electron left at the formation of the AmO+ cation. Similarly to the case found for AmO, the septet states have one dominant configuration (5f6, 7F0), whereas the quintet ones have 2–3 dominant configurations. The ground state of AmO+ can be derived from the m8a ground state of AmO. The ground state of AmO+ has a multiplicity of seven with singly-occupied Am orbitals of 5f1+, 5f1−, 5f2+, 5f2−, 5f3+, 5f3−. The computed characteristics of this state are the bond distance of 1.758 Å, the bond dissociation energy D2(D0) of 4.17(4.11) eV and the harmonic vibrational frequency of 924 cm−1. The found lowest excited state lies higher than the ground state by 0.4 eV. The valence shell of Am in the low-energy states of AmO+ was found to include six singly-filled 5f orbitals with 5f0 being empty in all cases.

### Table 1

<table>
<thead>
<tr>
<th>States</th>
<th>T_e (eV)</th>
<th>Re (Å)</th>
<th>ω_e (cm⁻¹)</th>
<th>ω_ab (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m8</td>
<td>0.94</td>
<td>1.825</td>
<td>866</td>
<td>862</td>
</tr>
<tr>
<td>m6</td>
<td>0.45</td>
<td>1.800</td>
<td>891</td>
<td>886</td>
</tr>
</tbody>
</table>

The electronic states are designated by the multiplicity (m8 and m6) and energy ordering (a–b–c–d). The m8b state is degenerate with m8c, m6b is degenerate with m6c.
Using the absolute energies of the ground states of AmO and AmO\(^+\) we obtained an ionization energy of AmO of 6.2 eV from the spin-free calculations which changed slightly (to 6.3 eV) when the account for relativistic effects was extended to include spin–orbit couplings. The data are in good agreement with the experimental value of 5.9 ± 0.2 eV.\(^{28}\)

### 3.3 AmO\(_2\)

We used an active space with 9 electrons (9/14) considering two spin multiplicities with three and five unpaired electrons respectively. The lowest energy electronic states of AmO\(_2\) are compiled in Table 2.

All four sextet electronic states and the m4a and m4b quartet ones are essentially pure, having one dominant determinant, whereas the remaining two quartet states (m4c and m4d) consist of a mixture of 2–3 determinants of considerable magnitude. The ground state is m6a but the m6b state is only marginally higher. Our geometry optimizations indicate that AmO\(_2\) is linear in the presented electronic states. In general, the sextet states are somewhat more stable than the quartet ones.

In all the listed states the O 2p orbitals in the active space turned out to be doubly filled with minor contributions of the Am 6d0 or 5f0 orbitals. Together with the four AmO bonds in the inactive space, we have altogether six doubly filled orbitals with major O 2p contributions. Hence the triple bond character of the Am \(\equiv\) O bond appears also in AmO\(_2\), as proved previously in the analogous UO\(_2\).\(^{25}\) The unpaired electrons in the active space of AmO\(_2\) are distributed among the 5f orbitals. Both the 6d and 7s orbitals of Am placed in the active space remained unoccupied in the presented low-energy states.

The dissociation energy of AmO\(_2\) to AmO and O was computed to be 6.03 eV using active spaces of (13/11) for AmO and (4/3) for O.

### 3.4 CmO

The active space was constructed analogously to that of AmO, just containing one electron more (14) for CmO (14/14). We considered two spin multiplicities, those with six and eight unpaired electrons respectively. The computed data of the found lowest-energy states are given in Table 3.

The electronic ground state of CmO is m9a (5f\(^6\)7s\(^2\), \(^{9}\)S\(_0\)). The four nonet states as well as two of the septet states (the degenerate 7mb and 7mc) have one dominant configuration, whereas the other two septets (7ma and 7md) consist of a mixture of several major electron configurations. The triple bond character of the Cm \(\equiv\) O bond appears in six of the eight investigated states. In the m9c and m9d states, however, the lowest-energy configurations contain a doubly-occupied 7s orbital of Cm, while we found molecular orbitals with singly-populated O 2p y and O 2p x orbitals (in m9c and m9d respectively) containing minor contributions from 5f1 and 5f3.

The computed dissociation energy \(D_1(D_0)\), of 7.12(7.07) eV, agrees well with the value of 7.5 eV \((D_0)\) derived from vaporization measurements on CmO\(_2\),\(^1\) and is close to the lanthanide equivalent GdO, 7.36 eV \((D_0)\).\(^{29}\)

### 3.5 CmO\(_2\)

Our preliminary SCF computations indicated that the electronic structures of AmO\(_2\) and CmO\(_2\) differ considerably. Therefore, in contrast to the (9/14) active space of AmO\(_2\), we used an active space of 13 orbitals in the case of CmO\(_2\). We considered two spin multiplicities with four and six unpaired electrons respectively. The lowest-energy electronic states which were found are compiled in Table 4.

The four heptet states and two of the quintet ones (m5b and m5c) have one dominant electron configuration, whereas m5a and m5d consist of a mixture of several major configurations. The ground state is the linear m7a. Except for m7b, the excited states are quite high in energy (over 2.5 eV). In contrast to our former results on AmO\(_2\), we also found bent structures among the low-lying electronic states of CmO\(_2\) (m7b and m7d).

### Table 2 Relative energies \((T_c, \text{eV})\), bond distances (Å) and singly-occupied Am orbitals for the lowest electronic states of AmO\(_2\) from CASPT2 computations

<table>
<thead>
<tr>
<th>States(^a)</th>
<th>(T_c)</th>
<th>Am (\equiv) O</th>
<th>Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>m6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>0.00</td>
<td>1.832</td>
<td>5f1+, 5f2+, 5f2–, 5f3+, 5f3–</td>
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<tr>
<td>b</td>
<td>0.02</td>
<td>1.832</td>
<td>5f1–, 5f2+, 5f2–, 5f3+, 5f3–</td>
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<tr>
<td>c</td>
<td>1.09</td>
<td>1.859</td>
<td>5f1+, 5f1–, 5f2+, 5f3+, 5f3–</td>
</tr>
<tr>
<td>d</td>
<td>1.12</td>
<td>1.854</td>
<td>5f1–, 5f1+, 5f2+, 5f3+, 5f3–</td>
</tr>
<tr>
<td>m4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>1.69</td>
<td>1.809</td>
<td>5f2–, 5f3+, 5f3–</td>
</tr>
<tr>
<td>b</td>
<td>1.69</td>
<td>1.809</td>
<td>5f2–, 5f3+, 5f3–</td>
</tr>
<tr>
<td>c</td>
<td>2.42(^a)</td>
<td>1.809</td>
<td>Strongly mixed</td>
</tr>
<tr>
<td>d</td>
<td>2.42(^a)</td>
<td>1.809</td>
<td>Strongly mixed</td>
</tr>
</tbody>
</table>

\(^a\) The electronic states are designated by the multiplicity (m6 and m4) and energy ordering (a–b–c–d). The m6c state is degenerate with m9a, m7b is degenerate with m7c.

### Table 3 Relative energies \((T_c, \text{eV})\), bond distances (Å), harmonic \((\omega_h)\) and anharmonic vibrational frequencies \((\omega_{ah}, \text{cm}^{-1})\) and singly-occupied orbitals for the lowest electronic states of CmO from CASPT2 computations

<table>
<thead>
<tr>
<th>States(^a)</th>
<th>(T_c)</th>
<th>Cm (\equiv) O</th>
<th>(\omega_h)</th>
<th>(\omega_{ah})</th>
<th>Orbitals</th>
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<tr>
<td>m9</td>
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<td></td>
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</tr>
<tr>
<td>a</td>
<td>0.00</td>
<td>1.824</td>
<td>858</td>
<td>843</td>
<td>7s, 5f0, 5f1+, 5f1–, 5f2+, 5f2–, 5f3+, 5f3–</td>
</tr>
<tr>
<td>b</td>
<td>1.79</td>
<td>1.846</td>
<td>802</td>
<td>798</td>
<td>7s, 5f0, 5f1+, 5f1–, 5f2+, 5f2–, 5f3+, 5f3–</td>
</tr>
<tr>
<td>c</td>
<td>2.87</td>
<td>2.090</td>
<td>578</td>
<td>568</td>
<td>5f0, 5f1+, 5f2+, 5f2–, 5f3+, 5f3–</td>
</tr>
<tr>
<td>d</td>
<td>2.87</td>
<td>2.090</td>
<td>578</td>
<td>568</td>
<td>5f0, 5f1+, 5f2+, 5f2–, 5f3+, 5f3–</td>
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<tr>
<td>m7</td>
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<tr>
<td>a</td>
<td>0.44</td>
<td>1.828</td>
<td>827</td>
<td>816</td>
<td>5f0, 5f1+, 5f2+, 5f2–, 5f3+, 5f3–</td>
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<tr>
<td>b</td>
<td>2.62</td>
<td>2.046</td>
<td>558</td>
<td>548</td>
<td>5s, 5f1+, 5f2+, 5f2–, 5f3+, 5f3–</td>
</tr>
<tr>
<td>c</td>
<td>2.62</td>
<td>2.046</td>
<td>558</td>
<td>548</td>
<td>5s, 5f1–, 5f2–, 5f3+, 5f3–</td>
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<tr>
<td>d</td>
<td>2.80</td>
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<td>799</td>
<td>795</td>
<td>5s, 5f1–, 5f2, 5f2–, 5f3+, 5f3–</td>
</tr>
</tbody>
</table>

\(^a\) The electronic states are designated by the multiplicity (m9 and m7) and energy ordering (a–b–c–d). The m9c state is degenerate with m9d, m7b is degenerate with m7c.

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The electronic ground states of the investigated oxides contain actinide–oxygen triple bonds formed by 2p orbitals of oxygen with minor contributions of 6d/6p orbitals of the actinide atom. The unpaired electrons are distributed in the 5f orbitals of Cm; the 7s orbital remained unoccupied in the presented electronic states. The dissociation energy of CmO2 to CmO and O was computed to be 4.62 eV using active spaces of (13/13) for CmO2 generally populate the 5f orbitals of Cm; the 7s orbital is occupied only in m7c. The 6d orbitals of Cm remained unoccupied in the present electronic states.

Similarly to AmO2, the O 2p orbitals in the active space (accompanied by minor contributions of the Am 6d or 5f0 orbitals) are doubly filled, forming in this way the third bond in the CmO bonding. The unpaired electrons in the active space of CmO2 generally populate the 5f orbital of Cm; the 7s orbital is occupied only in m7c. The 6d orbitals of Cm remained unoccupied in the present electronic states.

The dissociation energy of CmO2 to CmO and O was computed to be 4.62 eV using active spaces of (13/13) for CmO and (4/3) for O. Note that we preferred this active space for CmO over (13/11), because the latter one converged rather poorly in the absolute energy. An overview of the dissociation energies of the target compounds is given in Table 5.

<table>
<thead>
<tr>
<th>States</th>
<th>T_e (eV)</th>
<th>Geometry</th>
<th>Orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>m7a</td>
<td>1.833 (180.0)</td>
<td>5f1+, 5f1−, 5f2+, 5f2−, 5f3+, 5f3−</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>1.847 (104.7)</td>
<td>5f0, 5f1+, 5f2+, 5f3+, 5f3−</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>1.736 (180.0)</td>
<td>7s, 5f1−, 5f2+, 5f3+, 5f3−</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>1.835 (115.3)</td>
<td>5f0, 5f1−, 5f2+, 5f3+, 5f3−</td>
<td></td>
</tr>
<tr>
<td>m5a</td>
<td>1.808 (180.0)</td>
<td>Strongly mixed</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>1.794 (180.0)</td>
<td>5f1−, 5f2−, 5f3+, 5f3−</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>1.794 (180.0)</td>
<td>5f1−, 5f2−, 5f3+, 5f3−</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>1.815 (180.0)</td>
<td>Strongly mixed</td>
<td></td>
</tr>
</tbody>
</table>

* The electronic states are designated by the multiplicity (m7 and m5) and energy ordering (a–b–c–d).

4. Conclusions

In the present study a theoretical analysis of the electronic structure of four actinide oxides, AmO, AmO2, CmO, and CmO2, as well as that of the AmO+ ion has been performed. The good agreement between the computed and experimental ionization energy of AmO (6.3 and 5.9 ± 0.2 eV respectively) justified the reliability of the theoretical level used in the present study.

The electronic ground states of the investigated oxides contain actinide–oxygen triple bonds formed by 2p orbitals of oxygen with minor contributions of 6d/6p orbitals of the actinide atoms. The unpaired electrons are distributed in the 5f sub-shell, the 7s orbital being occupied only in the case of AmO and CmO. Both dioxides are linear in the ground electronic state.

The computed dissociation energies of AmO and CmO can be used to assess the reliability of available estimates based on experimental data. The theoretical dissociation energy of CmO (7.1 eV) confirmed the value of 7.5 eV obtained by Smith et al., while, in contrast, a considerable difference between the theoretical and estimated dissociation energy of AmO (4.6 and 5.73 ± 0.37 eV respectively) exists. However, our calculated values are close to the dissociation energies of the lanthanide equivalents EuO and GdO.29

Altogether, the molecular parameters obtained form a solid basis to evaluate reliable thermodynamic data for these species.

Acknowledgements

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