DFT Study of the Uranium and Plutonium Oxides in Gas Phase: Structures and Thermodynamic Properties

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ABSTRACT

The aim of this paper is to investigate the equilibrium structures and the thermodynamic properties of uranium and plutonium oxides in the gas phase, which can be considered as a first step towards the study of fuel-coolant interaction in IV Generation Lead-cooled Fast Reactors (LFR). An innovative approach based on Density Functional Theory (DFT) combined with the Generalized Gradient Approximation (GGA) has been employed, thus exploiting the recent advances in computational methods applied to actinide chemistry. Calculations have been performed in order to determine the minimum energy configuration of the considered molecules starting from several initial geometrical configurations and considering all the possible spin multiplicities. The vibrational harmonic frequencies obtained for UO, UO\textsubscript{2}, UO\textsubscript{3}, PuO, PuO\textsubscript{2}, and PuO\textsubscript{3} are in good agreement with the available experimental data, as well as with the related thermodynamic properties, i.e. entropy and specific heat capacity. A reasonable agreement with experimental data was found also for the calculated formation enthalpies and the bond dissociation energies.

1 INTRODUCTION

Gen IV reactor system concept has been developed with some precise guidelines: sustainability, cost reduction, safety & reliability. By adopting high burn-up rate and advanced closed fuel cycle, Gen IV systems will be able to strongly reduce the amount of radioactive waste heading to the permanent disposal [1] and increasing the output energy by a factor 100, given a fixed amount of uranium (\textsuperscript{238}U) [2]. Similar attention has been placed in reactor structures engineering, in order to limit the use of expensive and exotic materials and to reduce costs during the entire reactor lifetime. A complete understanding of the
physicochemical interaction between materials routinely or accidentally being in contact, such as piping-coolant or fuel-coolant, is therefore required in order to guarantee safety & reliability. As some GEN IV systems depart from the classical H₂O coolant in favour of liquid sodium or lead, it becomes even more important evaluating fuel behaviour and performance in normal and abnormal operation regimes. Several types of fuel have been proposed for the Gen IV reactors, but the most common choice is uranium and plutonium Mixed OXides (MOX) with the 80wt% of uranium dioxide and 20wt% of plutonium dioxide. Unfortunately, experimental data on chemical compatibility and inter diffusivity among fuel/cladding constituents and coolant, fission gas release, and fission gas-driven fuel swelling are relatively scarce. The same lack of data stands for cladding strength, creep resistance and geometric stability of available and prospective cladding materials under the coolant influence [3].

Knowledge of uranium and plutonium oxides properties is therefore important to correctly evaluate fuel behaviour and potential interaction with cladding and coolant during the entire reactor operating envelope, and especially during abnormal operation when the reactor core can reach high temperatures. Recent significant advances in computational methods have allowed the actinides chemistry to be modelled with satisfactory accuracy, suggesting the possibility to circumvent expensive experimental studies [4-9]. Nuclear materials research and fast-moving projects, such as tomorrow reactor systems, could especially benefit from these powerful tools, enabling fast and reliable assessments on materials being used without the burden of a full experimental setup. The theoretical approach allows to evaluate molecular structures and to estimate the thermodynamic data for uranium and plutonium oxides, thus helping establishing the system safety from the chemical hazard viewpoint. Despite these advances, the study of uranium and plutonium molecules still represents a challenge for researchers, due to specific characteristics of actinides, such as the relatively large atomic number, due to the relativistic effects and the 5f, 6d, 7s and 7p orbitals, whose presence give rise to a multitude of possible configurations [5]. Notwithstanding these difficulties, some important and innovative works have already been published on the application of the Density Functional Theory with the Generalized Gradient Approximation (DFT-GGA) to study the electronic and geometric structures of UO₂ [6] and bulk PuO₂ [7], while other authors [8,9] examined the electronic structure of UO₂ and uranyl and plutonyl ions using multi-configurational wave functions (e.g. CASSCF/CASPT2), taking into account spin-orbit coupling. However, comparatively less work has been done on the thermodynamic properties of AnO₃ molecules (An = Th, Pa, U, Np, Pu, Am, Cm and y= 1, 2) [10].

As a first step towards the development of a comprehensive thermodynamic database for uranium and plutonium oxides, in this work, we present a theoretical study on gaseous UO, UO₂, UO₃, PuO, PuO₂, and PuO₃ molecules, focusing the attention on two main aspects: (i) finding out the minimum energy configuration and (ii) deriving some thermodynamic properties. The computational approach is described in section 2, while the results are reported in section 3. The times of computation were not reported, but amounted to the order of hours on a reasonable powerful HPC facility like the one employed in the course of this work.

## 2 COMPUTATIONAL METHOD

All calculations were performed using DFT [11,12] and the Gaussian09 suite of programs [13]. On the basis of some preliminary simulations and of results reported in several papers [11,14], the B3PW91 [15,16] hybrid functional was selected to perform all the simulations of this work. For oxygen atoms the well-known basis set 6-311+G(d,p) was used.
For uranium and plutonium atoms the STUTTGART small-core Effective Core Potentials (ECP) [13,17] and the ECP60MWBSEG valence basis sets were employed, as it is known that for these systems the best performances are obtained using small-core ECPs [4]. DFT calculations were performed to obtain the optimized geometries and the vibrational frequencies of gaseous UO, UO$_2$, UO$_3$, PuO, PuO$_2$, and PuO$_3$ molecules, starting from a wide selection of possible initial geometric configurations and considering all possible spin multiplicities. Subsequently, entropies and specific heat capacities were evaluated using statistical thermodynamics and the harmonic approximation. Formation enthalpies (at 298 K) and bond dissociation energies (at 0 K) were computed from atomization energies including Zero Point Energy corrections [18]. The computed data were compared with the available experimental data.

3 RESULTS AND DISCUSSION

3.1 Uranium oxides

Multiplicities and selected geometrical parameters for the minimum energy structures of gaseous UO, UO$_2$, and UO$_3$ calculated using DFT simulations are shown in Table 1. All the experimental data reported in the paper are from specific database [19-22].

Table 1: Multiplicities and selected geometrical parameters of the minimum energy structures of gaseous UO, UO$_2$, and UO$_3$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Multiplicity</th>
<th>Distance U-radial O [nm]</th>
<th>Distance U-axial O [nm]</th>
<th>Calculated Angle O-U-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO</td>
<td>5</td>
<td>0.1830</td>
<td>0.1839</td>
<td></td>
</tr>
<tr>
<td>UO$_2$</td>
<td>3</td>
<td>0.1779</td>
<td>0.1800</td>
<td>179.992°</td>
</tr>
<tr>
<td>UO$_3$</td>
<td>1</td>
<td>0.1785</td>
<td>0.1835</td>
<td>161.557°</td>
</tr>
</tbody>
</table>

Table 1 shows the calculated ground states of UO, UO$_2$, and UO$_3$. For UO$_2$, the U-O bond lengths are identical and collinear, so that the molecule has $D_{\infty h}$ symmetry as expected from experimental evidence [7]. In the UO$_3$ molecule, which has $C_2v$ symmetry, the distances between the two radial oxygen atoms and U are identical, while the third O atom has a longer bond length, in accordance with the computational works performed by Grenthe [23] and Peng [11]. As shown in Table 1, the estimated U-O distances of UO and UO$_2$ slightly underestimate the experimental values. Figure 1 reports the geometric configurations obtained for the U oxides in the minimum energy configuration. The obtained equilibrium structures of UO, UO$_2$, and UO$_3$ are consistent with the structures reported in the literature [6].

Figure 1: Minimum energy structures of UO, UO$_2$, and UO$_3$. 
Subsequently, considering only the minimum energy configuration of UO, UO₂, and UO₃, the thermodynamic properties were evaluated as described in section 2. The calculated vibrational frequencies, the entropies, the specific heats and the formation enthalpies are reported in Table 2.

Table 2: Thermodynamic properties of gaseous UO, UO₂, and UO₃ at 298.15K and 1 bar.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>UO(g)</td>
<td>834.1³</td>
<td>820.0³</td>
<td>253.6</td>
<td>252±0.1</td>
</tr>
<tr>
<td>UO₂(g)</td>
<td>145.2, 786.3³, 807.8³</td>
<td>771.0³, 776.1³</td>
<td>251</td>
<td>266±4</td>
</tr>
<tr>
<td>UO₃(g)</td>
<td>152.1, 194.7³, 208.8, 786.0², 897.6³, 904.7³</td>
<td>740.7³, 843.5³, 852.5³</td>
<td>309.6</td>
<td>309.5 ± 2.0</td>
</tr>
</tbody>
</table>

³ is used to indicate the stretching vibrational frequencies.

As shown in Table 2, the computed symmetric and asymmetric (the highest value) stretching vibrational frequencies of UO, UO₂, and UO₃ are in reasonable agreement with the experimental values [17] while the entropy values are in good agreement with the experimental data. The computed specific heat capacities are, in general, slightly underestimated, with the exception of UO₃ that closely matches the experimental data. The calculated formation enthalpies underestimate systematically by about 100 kJ/mol the experimental values.

The bond dissociation energies (BDE), with the relative reactions and the experimental values, are listed in Table 3, showing how the calculated values for UO and UO₂ tend to overestimate the experimental ones, while for UO₃ it is the opposite.

Table 3: Bond Dissociation Energies of gaseous UO, UO₂ and UO₃ molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond dissociation energy [kcal/mol]</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calc.</td>
<td>Exp.</td>
</tr>
<tr>
<td>UO</td>
<td>205.964</td>
<td>181.769</td>
</tr>
<tr>
<td>UO₂</td>
<td>171.3</td>
<td>175.2 ±62.3</td>
</tr>
<tr>
<td>UO₃</td>
<td>134.843</td>
<td>153.864</td>
</tr>
</tbody>
</table>

The availability of experimental BDE data for the compounds of interest permits a comparison with the calculated values. The averaged percent deviation between the calculated values and the experimental ones has been calculated and it is equal to 9.30%. This value suggests a satisfactory agreement between the experimental and calculated values.

3.2 Plutonium oxides

The theoretical approach used for uranium oxides was applied similarly to study PuO, PuO₂, and PuO₃. DFT simulations were thus used to determine the minimum energy configurations. The calculated spin multiplicities and several selected geometrical parameters are reported in Table 4.

Table 4: Multiplicities and selected geometrical parameters of the minimum energy structures of gaseous PuO, PuO₂, and PuO₃.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Multiplicity</th>
<th>Distance Pu– radial O [nm]</th>
<th>Distance Pu- axial O [nm]</th>
<th>Calculated Angle O-Pu-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuO</td>
<td>7</td>
<td>0.1818</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PuO₂</td>
<td>5</td>
<td>0.1802</td>
<td>-</td>
<td>179.996°</td>
</tr>
<tr>
<td>PuO₃</td>
<td>3</td>
<td>0.1751</td>
<td>0.1888</td>
<td>171.842°</td>
</tr>
</tbody>
</table>
The calculated geometrical parameters reported in Table 4 are related to the minimum energy configurations displayed in Figure 2. It can been noted that the calculated ground states of PuO, PuO$_2$, and PuO$_3$ are a septet, a quintet, and a triplet, respectively. The bond lengths cannot be compared with the experimental values because no reference data were found. Anyway it can be noted that, as it was the case for UO$_2$, also PuO$_2$ has D$\infty$h symmetry since the Pu-O distances are identical and the bonds are collinear. Furthermore, as for UO$_3$, also in PuO$_3$ the distances between two radial oxygen atoms and Pu are identical, while the third O atom has a longer bond, so that the geometry has C$2v$ symmetry.

Figure 2: Minimum energy structures of PuO, PuO$_2$, and PuO$_3$.

The thermodynamic properties of PuO, PuO$_2$, and PuO$_3$ molecules have been evaluated as described in section 2 and the values of the vibrational frequencies together with the calculated entropies, specific heats, and formation enthalpies are listed in Table 5.

Table 5: Thermodynamic properties of gaseous PuO, PuO$_2$, and PuO$_3$ at 298.15K and 1bar.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PuO</td>
<td>814.6$^a$, 822.0$^a$</td>
<td>256.6</td>
<td>248.1</td>
<td>-18.952 -60 ± 10</td>
</tr>
<tr>
<td>PuO$_2$</td>
<td>170.5, 784.1$^b$, 832.6$^a$ (asym)</td>
<td>275.9</td>
<td>278.0</td>
<td>-373.218 -410 ± 24</td>
</tr>
<tr>
<td>PuO$_3$</td>
<td>224.2, 240.8, 252.5, 385.8$^c$, 821.1$^c$, 918.8$^c$</td>
<td>-</td>
<td>322.0</td>
<td>316.1</td>
</tr>
</tbody>
</table>

$^a$ is used to indicate the stretching vibrational frequencies.

Taking into account the limited experimental data, the adopted computational method underestimates the vibrational frequency in the case of PuO, while a slight overestimation was found for the PuO$_2$ asymmetric stretching. The same observation can be made for entropy values, even if the computed results can be considered in good agreement with the experimental data. Concerning the specific heat, the experimental value is available only for PuO$_3$ and, in this case, the computed value is slightly underestimated with respect to the experimental one.

Table 5 shows that the calculated formation enthalpies of plutonium oxides overestimate the experimental values by about 40 kJ/mol, thus giving an agreement with experimental data that is significantly better than that found for U oxides. The formation enthalpies of PuO and PuO$_2$ molecules are coherent with the data available in literature coming from other calculations.
The BDE of PuO, PuO₂, and PuO₃ molecules and their relative reactions are listed in Table 6.

Table 6: Bond Dissociation Energy of gaseous PuO, PuO₂, and PuO₃.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond Dissociation Energy [kcal/mol]</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PuO</td>
<td>Calc. 145.1 Exp. 164.9 ± 58.3 % deviation -12.01%</td>
<td>PuO → Pu + O</td>
</tr>
<tr>
<td>PuO₂</td>
<td>Calc. 142.6 Exp. 145.6 ± 30.1 % deviation -2.06%</td>
<td>PuO₂ → PuO + O</td>
</tr>
<tr>
<td>PuO₃</td>
<td>Calc. 81.2 Exp.  -  % deviation -</td>
<td>PuO₃ → PuO₂ + O</td>
</tr>
</tbody>
</table>

The computed values listed in Table 6 are in good agreement with the literature ones for both PuO and PuO₂. As further proof of a satisfactory agreement between literature and calculated data, the averaged percent deviation between the estimated values and the experimental ones was again evaluated and it is equal to 7.03%.

The thermodynamic properties evaluated for plutonium oxides are in fair agreement with the scarce experimental or literature data. This result contributes to confirm the validity of the theoretical approach also for the study of Pu oxides.

4 CONCLUSION

The minimum energy structures of UO, UO₂, UO₃, PuO, PuO₂, and PuO₃ were systematically investigated by DFT within the GGA approximation using a hybrid functional. The equilibrium structures of molecules at the minimum energy configuration have been determined considering several initial geometric configurations and varying the spin multiplicities. The thermodynamic properties have been evaluated for the minimum energy configuration obtained for uranium and plutonium oxides. For UO, UO₂, and UO₃ the results show that bond lengths, vibrational frequencies, and thermodynamic parameters at the ground state are in fair agreement with the experimental data. This result implies that the theoretical approach could be applied to investigate also U and Pu more complex oxides whose experimental data are not fully available (for example U₂O₃ and Pu₂O₃). Thermodynamic parameters obtained for plutonium oxides are in agreement with the available literature data. The relatively short calculation times of the DFT approach, along with the good results obtained for uranium oxides compared with the available experimental data, suggest that a fully theoretical investigation, like the one performed on plutonium oxides, could be a reliable alternative to the experimental approach, at least as long as experimental data remain scarce or too expensive. Furthermore, with the researcher freed by difficulties, such as the handling of hazardous and nuclear proliferation materials, this approach could be viable, especially when answers are requested at fast pace by the engineering designers of advanced nuclear facilities.

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REFERENCES


