Electronic structure and spectroscopic properties of mixed sodium actinide oxides Na\textsubscript{2}AnO\textsubscript{4} (An = U, Np, Pu, Am)

Attila Kovács

European Commission, Joint Research Centre, P. O. Box 2340, 76125 Karlsruhe, Germany

A R T I C L E  I N F O

Article history:
Received 29 June 2016
Received in revised form 19 September 2016
Accepted 22 September 2016
Available online 22 September 2016
Dedicated to Prof. Georgiy V. Girichev on the Occasion of his 70th birthday.

Keywords:
Actinides
Relativistic multireference calculations
DFT
Electronic structure
Molecular geometry
Vibrational frequencies

A B S T R A C T

Multireference relativistic post-HF and DFT calculations have been performed on four Na\textsubscript{2}AnO\textsubscript{4} (An = U, Np, Pu, Am) molecules. Beyond the electronic characteristics of the ground and excited electronic states, the molecular geometries and vibrational frequencies have been determined.

© 2016 The Author. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

In order to reduce the radioactive waste of nuclear reactors, the reactors under recent development are planned to operate in a closed fuel cycle, in which the highly radioactive minor actinides are re-used for energy generation. One of the new designs is the Sodium cooled Fast Reactor (SFR). The main advantages of the sodium melt as coolant are the high heat capacity resulting in a high margin to overheating and the high boiling point (T = 1156 K) being well above the reactor’s planned operating temperature (around 850 K).

The nuclear reactors have to obey to very high safety standards, therefore possible accidents have to be carefully explored. Such an accident can be the breach of the fuel clad, in which case the sodium coolant and fuel can react with each other forming mixed sodium actinide oxides. Beside U and Pu (components of the MOX fuel) the most relevant actinides in these fuels are Np and Am. From the Na-An-O systems the An = U and Pu ones have been studied extensively in the literature. The published properties include the crystal structures [1,2], thermodynamic [3–5], magnetic [6,7], and spectroscopic properties of the solids [8–10]. In the solid phase numerous compositions were reported: Na\textsubscript{3}UO\textsubscript{4}, NaUO\textsubscript{3}, Na\textsubscript{2}UO\textsubscript{4}, Na\textsubscript{2}PuO\textsubscript{3}, Na\textsubscript{2}PuO\textsubscript{4}[1], Na\textsubscript{2}NpO\textsubscript{3}, Na\textsubscript{2}NpO\textsubscript{4}, Na\textsubscript{3}NpO\textsubscript{5}, Na\textsubscript{3}NpO\textsubscript{6}, Na\textsubscript{2}NpO\textsubscript{5}[11,12], and Na\textsubscript{2}PuO\textsubscript{3}, Na\textsubscript{3}PuO\textsubscript{4}, Na\textsubscript{4}PuO\textsubscript{4} or Na\textsubscript{4}PuO\textsubscript{5}, Na\textsubscript{3}PuO\textsubscript{4}, Na\textsubscript{4}PuO\textsubscript{5}, Na\textsubscript{4}PuO\textsubscript{5} [1,2,12,13]. For the gaseous phase scarce data indicate the possible appearance of Na\textsubscript{2}NpO\textsubscript{4} as evaporation product on the basis of mass spectrometric measurements [14].

In the present paper we are dealing with Na\textsubscript{2}AnO\textsubscript{4} species, which can form in the vapour at severe accident situations. In order to simulate their formation and behaviour, the knowledge of their thermodynamic characteristics is required. These data can be calculated from reliable structural and spectroscopic parameters obtained conveniently by means of advanced quantum chemical calculations [15–20]. In the following we present the electronic structure of the four Na\textsubscript{2}AnO\textsubscript{4} (An = U, Np, Pu, Am) molecules determined by relativistic multireference calculations as well as some other structural and spectroscopic properties of the ground electronic states determined by B3LYP density functional theory (DFT) calculations.

2. Computational details

The calculations were performed using the software MOLCAS
The complete active space (CAS) SCF method [22] was used to generate molecular orbitals and reference functions for subsequent multiconfigurational second-order perturbation theory calculations of the dynamic correlation energy (CASPT2) [23,24]. The Douglas-Kroll-Hess Hamiltonian was used in the CASSCF calculations in order to take into account scalar relativistic effects.

All electron basis sets of atomic natural orbital type, developed for relativistic calculations (ANO-RCC) with the Douglas-Kroll-Hess Hamiltonian [25,26] were used for all the atoms. For the actinides a primitive set of 26s23p17d13f5g3h basis functions was contracted to 9s8p6d5f2g1h [27] achieving TZP quality. Analogous contracted basis sets were applied for O (14s9p4d3f2g4s3p2d1f) [28] and for Na (17s12p5d4f2g5s4p2d1f) [29].

To determine the optimal size of the active space, preliminary state-averaged calculations using five roots (i.e. considering five electronic states in CASSCF) were performed in C1 symmetry with various number of inactive electrons. We found for all the four actinides that only two 2-electron orbitals had populations below 1.96 e, hence only these two orbitals were included beyond the unpaired An valence electrons in the active spaces [30]. Accordingly, in the subsequent calculations the active spaces contained 4, 5, 6, 7 electrons on 16 orbitals for the U, Np, Pu, and Am derivatives, respectively.

The electronic structures of the title molecules were investigated using D2h symmetry, in which the eight symmetry species of the point group were treated separately. For the lowest-energy symmetry species (within 20 kJ/mol) geometry optimizations were performed in order to ensure the ground electronic states and the respective global minimum geometries of the four title compounds. The vertical excited electronic states were calculated on the optimized geometries of the ground electronic states. Beyond the ground-state spin multiplicities were calculated. The ground-state characters of the results were confirmed by evaluating the STABLE keyword of Gaussian 09, which checks for eventual lower-energy solutions of the wavefunction. The geometry optimizations were followed by the frequency calculations confirming the minimum characters of the obtained geometries. The anharmonic frequencies were calculated by evaluation of the quartic force field by means of numerical derivation (Freq = Anharmonic keyword in Gaussian 09). The assignment of the fundamentals was done on the basis of visual observation by means of the GaussView software [69], facilitating the recognition of their main vibrational components. The study of the bonding properties was based on atomic charges and orbital population obtained by natural bond orbital analysis [70] using the NBO5.9 [71] code.

3. Results and discussion

3.1. Electronic structure

The electronic structure of the Na2AnO4 species was investigated on the double bidentate NaO2AnO2Na coordination structure, characteristic on hexavalent alkali transition metal mixed oxides [20,72–76]. However, the D2d geometry formed by the transition metal compounds proved to be a saddle-point for actinides according to our calculations. The minimum structure for all the four Na2AnO4 molecules is the planar D2h one (presented in Fig. 1), hence we optimized these structures at the SF CASPT2 level. The optimized geometries of the ground electronic states (except where noted) were used to evaluate the characteristics of the electronic structures.

The lowest-energy electronic states of Na2UO4 from SF- and SO-CASPT2 calculations are given in Table 1. In agreement with general experience on closed-shell hexavalent uranium-containing molecules [15,77–79], the ground state of Na2UO4 is 1A1g. This SF state forms exclusively the SO ground state. We note that contributions from another configurations (also in most low-lying excited states)
The electronic state is a doublet $^{2}B_{3u}$ state, in which the unpaired electron is located on a hybrid 5f (5f$_{3}$, 5f$_{1}$) molecular orbital. The lowest excited states are formed by doublet states, having the unpaired electron on various 5f orbitals. The quartet SF excited states start from 185 kJ/mol with unpaired electrons generally on 5f- and 1-electron bonding orbitals (as exception, the $^{4}B_{3u}$ state has only 5f electrons as major contributions). The states with $B_{3u}$-type symmetry have very high energies, they are beyond the energy window considered in the present study. We note that nearly all the states have a major electron configuration with contribution above 90%, hence single-determinant methods can be expected to be suitable for modelling Na$_2$NpO$_4$.

The SO ground state is dominated by 75% by the SF ground state $^{2}B_{3u}$. The SO excited states start at 69 kJ/mol with the doublet states, while the quartets appear from 185 kJ/mol. Most SO states have one major contribution. From the available (low-energy) SF states the $B_{3u}$-types have a larger propensity for mixing.

The lowest-energy electronic states of Na$_2$PuO$_4$ from SF- and SO-CASPT2 calculations are given in Table 3. The SF ground electronic state is a triplet $^{3}A_{2g}$ state, in which the two unpaired electrons are located on two 5f (5f$_{3}$ and 5f$_{1}$) Pu orbitals. The three lowest-energy excited states are formed similarly by triplet states. The energy differences from the ground state are considerably smaller than observed in the case of Na$_2$NpO$_4$ and Na$_2$UO$_4$: e.g. the first excited state lies only by 5 kJ/mol higher vs the 38 kJ/mol in Na$_2$NpO$_4$. In order to treat more accurately the very close (within 11 kJ/mol) lying first two excited ($^{3}B_{1g}$ and $^{3}B_{2g}$) states, we optimized their geometries and the obtained adiabatic energies were used in the present study.

The lowest-energy singlet ($^{1}A_{2g}$) state has a closed-shell electronic structure, hence no unpaired electrons. It appears higher in energy by 50 kJ/mol above the triplet ground state. The other singlet states (from 83 kJ/mol) have open-shell electronic structures, one of the two unpaired electrons with a switched spin. In these low-energy triplet and singlet states the unpaired electrons occupy only non-bonding 5f orbitals of Pu. Single population of bonding and anti-bonding orbitals appears in the first quintet state ($^{5}B_{1g}$), which is formed by excitation of a bonding electron from the (5f$_{3}$, 2p$_{y}$) bonding orbital to an anti-bonding one. The quintet states lie quite high in energy above the ground state, thus our energy window contains only $^{3}B_{1g}$. Very high relative energies have the ungerade states (A$_{2u}$, B$_{2u}$) too, being beyond the energy window considered in the present study. We note that most of the SF states listed in Table 3 (including the ground state) have the main electron configurations with contributions above 85%, suggesting that single-determinant methods can work for the ground and low-lying excited SF states of Na$_2$PuO$_4$.

In contrast to the previously discussed U and Np derivatives, the SO ground state of Na$_2$PuO$_4$ is considerably mixed (cf. Table 3). Moreover, the $^{3}A_{2g}$ SF ground state does not have any contribution in

---

**Table 1**

<table>
<thead>
<tr>
<th>No.</th>
<th>Term symbol</th>
<th>E$^a$</th>
<th>Character$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF</td>
<td>$^{1}A_{2g}(1)$</td>
<td>0.0</td>
<td>100% $^{1}A_{2g}(1)$</td>
</tr>
<tr>
<td>2</td>
<td>$^{2}B_{2u}$</td>
<td>21274</td>
<td>96% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
<tr>
<td>3</td>
<td>$^{3}A_{2g}(2)$</td>
<td>22996</td>
<td>74% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
<tr>
<td>4</td>
<td>$^{4}B_{1g}$</td>
<td>24501</td>
<td>96% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
<tr>
<td>5</td>
<td>$^{5}B_{2g}$</td>
<td>24935</td>
<td>96% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
<tr>
<td>6</td>
<td>$^{6}A_{1u}$</td>
<td>25395</td>
<td>94% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
<tr>
<td>7</td>
<td>$^{7}B_{3g}$</td>
<td>25470</td>
<td>98% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
<tr>
<td>8</td>
<td>$^{8}A_{1g}(1)$</td>
<td>25554</td>
<td>95% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
<tr>
<td>9</td>
<td>$^{9}B_{1g}$</td>
<td>25805</td>
<td>97% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
<tr>
<td>10</td>
<td>$^{10}B_{2g}$</td>
<td>26037</td>
<td>99% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
<tr>
<td>11</td>
<td>$^{11}A_{2g}(2)$</td>
<td>27811</td>
<td>85% $^{3}f_{u}(2p_{y},6p_{z})$</td>
</tr>
</tbody>
</table>

$^a$ Vertical excitation energies obtained on the geometry of the $^{1}A_{2g}(1)$ ground state. Additional (higher-energy) SO states are given in the Supplementary Material.

$^b$ SF section: Character of the unpaired electrons in the main electron configuration. The primary spin of the unpaired electrons is $\sigma$, $b$ means electrons with opposite spin according to the singlet spin multiplicity of the given states; SO section: composition in terms of SF states.

---

**Table 2**

<table>
<thead>
<tr>
<th>No.</th>
<th>Term symbol</th>
<th>E$^a$</th>
<th>Character$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF</td>
<td>$^{2}B_{2u}(1)$</td>
<td>0.0</td>
<td>92% (5f$<em>{3}$, 5f$</em>{1}$)</td>
</tr>
<tr>
<td>2</td>
<td>$^{2}B_{2g}$</td>
<td>3202</td>
<td>83.8% 5f$_{u}$</td>
</tr>
<tr>
<td>3</td>
<td>$^{3}B_{1u}$</td>
<td>5057</td>
<td>91% 5f$_{u}$</td>
</tr>
<tr>
<td>4</td>
<td>$^{4}B_{2u}(2)$</td>
<td>8133</td>
<td>90% (5f$<em>{3}$, 5f$</em>{1}$)</td>
</tr>
<tr>
<td>5</td>
<td>$^{5}A_{u}$</td>
<td>9872</td>
<td>86% 5f$_{u}$</td>
</tr>
<tr>
<td>6</td>
<td>$^{6}B_{1u}$</td>
<td>15439</td>
<td>86% 5f$<em>{u}$, (2p$</em>{y},6p_{z}$)</td>
</tr>
<tr>
<td>7</td>
<td>$^{7}A_{u}$</td>
<td>16050</td>
<td>90% (6d$_{z^2}$, 7s)</td>
</tr>
<tr>
<td>8</td>
<td>$^{8}A_{1u}$</td>
<td>16576</td>
<td>93% 5f$<em>{u}$, 5f$</em>{z}$, (2p$<em>{y},6p</em>{z}$)</td>
</tr>
<tr>
<td>9</td>
<td>$^{9}B_{1u}$</td>
<td>17061</td>
<td>94% 5f$<em>{u}$, 5f$</em>{z}$, 5f$_{z}$</td>
</tr>
</tbody>
</table>

$^a$ Vertical excitation energies obtained on the geometry of the $^{2}B_{2u}(1)$ ground state.

$^b$ SF section: Character of the unpaired electrons in the main electron configuration; SO section: composition in terms of SF states. Each SO state is doubly degenerated.
the SO ground state, it forms the main contribution of the first excited state. Apparently, the SO coupling between the $^3\text{B}_g$ and $^3\text{B}_2g$ states is very advantageous and decreased considerably the energy of the formed SO state. The strong mixing is characteristic on the low-energy excited SO states (dominated by the triplet SF states below 200 kJ/mol) as well. Hence, for the electronic properties of Na$_2$PuO$_4$ the SO coupling is very important.

The lowest-energy electronic states of Na$_2$AmO$_4$ from SF- and SO-CASPT2 calculations are given in Table 4. The SO ground electronic state at the level of our calculations is a quartet $^4\text{A}_g$ state, in close in energy (1.6 kJ/mol). Because of the energetic proximity we and antibonding orbitals appear from 59.6 kJ/mol ($^6\text{B}_2u$), while the similar by quartet states. Sextet SF states with 1-electron bonding these three lowest-energy states.

In order to ensure the ground state and accurate relative energies of SO-CASPT2 calculations are given in Table 4. The SF ground state is considerably mixed (cf. Supplementary Material). The low-energy excited SF states up to 59 kJ/mol are formed according to the singlet spin multiplicity of the given states; SO section: composition in terms of SF states.

We note that most of the SF states considered in the present study (cf. Supplementary Material), below 100 kJ/mol dominated by the quartet SF states.

3.2. DFT calculations on the molecular properties

The first question in our DFT calculations was: how can they reproduce the ground state electronic structures of the title molecules? From the SF-CASPT2 results above we concluded that, due to the very large contributions of the main electron configurations, the ground states of all the four molecules may reliably be modelled by single-determinant methods.

The term symbols of the ground electronic states together with some natural bond orbital characteristics (natural atomic charges and actinide valence populations) from our B3LYP calculations are compiled in Table 5. They support the mentioned conclusion, as B3LYP predicted correctly the $^1\text{A}_g$, $^2\text{B}_3u$, and $^4\text{A}_g$ SF ground states of Na$_2$UO$_4$, Na$_2$NpO$_4$ and Na$_2$AmO$_4$, respectively. We recall, that these SF ground states form the main contributions of the respective SO ground states. Only the $^3\text{B}_g$ DFT ground state of Na$_2$PuO$_4$ seems to be in contradiction with the $^4\text{A}_g$ SF ground state of Na$_2$PuO$_4$. However, as shown above, in the SO ground state of Na$_2$PuO$_4$ the main contributor is $^1\text{Ag}$, while $^4\text{A}_g$ is the main contributor of the first excited SO state. Though in our B3LYP calculations no SO coupling was taken into account, they provide a reasonable estimate of the real ground state of Na$_2$PuO$_4$. The good performance of advanced DFT methods in the prediction of the ground states of actinide oxides has been shown earlier [47,57,58].

They proved to be reliable for species with considerable energy gap between the ground and first excited states. Discrepancies were found only in a few cases with very close lying first excited state. This happens apparently in the B3LYP treatment of Na$_2$PuO$_4$ too, but the neglect of SO coupling seems to compensate for the error on the SF state.

The natural atomic charges given in Table 5 reflect the strong
Na2UO4 as a studies used [47,57,58] B3LYP level predicted the D2h structure of the B3LYP optimizations. In the view of our previous good experi-
table 5). We note the larger change between U and Np in agree-

electrons. From U to Am the 5f population shows a gradual increase.

positive charge of An is formed mainly by the leave of the 7s

in agreement with the trends found in actinide dioxides: the partial

importance of 5f orbitals in bonding) while the 6d orbitals prefer a

largest 6d population supporting the important role of these or-

bitals in the formation of the molecular geometry of Na2UO4.

We start the discussion of the geometry with a peculiar result of

surface, being in contrast with the D2h CASPT2 minimum. The

B3LYP minimum is a slightly (by 13°) twisted D2 geometry. We

investigated this problem in more detail: Computations with
different parameters (basis set, grid size) resulted likewise in a D2

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,

B2LYP, PBE0 in conjunction with the same basis set agreed with

B3LYP minimum. However, all other theories, CCSD(T), MP2,
of CCSDT(T), MP2, CASPT2 (as post-HF) and B3LYP, B2LYP and PBE0 (DFT). While the CASPT2 and B3LYP results for the U-O bond distance are in very good agreement with the CCSDT(T) one, the Na-O bond distances are somewhat underestimated. MP2 and B2LYP predict somewhat longer U-O bonds, but again shorter Na-O bonds. We note that these two latter methods produce exactly the same geometrical parameters, hence B2PLYP can replace effectively MP2 geometry, due probably to the overestimated 6d contribution in the contributing 5f actinide orbitals in the bonding. We found a minor failure of the B3LYP exchange-correlational functional for the geometry, due probably to the overestimated 6d contribution in the Na2UO4 molecule.

We determined the low-lying electronic states of the title molecules by means of SO-CASPT2 calculations. Except for Na2PuO4, the SO ground states consist of mainly (in Na2UO4 entirely) the SF ground state. In Na2PuO4 the SO coupling between the first and second SF excited states lowers the energy considerably, forming in this way the SO ground state. From the four molecules Na2AnO4 is practically a single-reference species with 97% contribution of the main electron configuration. Going towards Na2AmO4 this decreases gradually to 82%, which facilitates the modelling of the spin-free electronic structure of these species with single-determinant quantum chemical methods. Indeed, our B3LYP calculations reproduced the ground electronic states of the title Na2AnO4 molecules and predicted geometries in good agreement with the spin-free CASPT2 one.

Acknowledgement

The author thanks Prof. R. J. M. Konings for advice.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.09.065.

References


Table 6
Computed geometrical parameters of M2AnO4 molecules.a

<table>
<thead>
<tr>
<th>Na2AnO4</th>
<th>An-O</th>
<th>Na-O</th>
<th>OAn-O</th>
<th>(OAnO)</th>
<th>Na-OAnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2UO4</td>
<td>1.936</td>
<td>2.216</td>
<td>93.9</td>
<td>86.1</td>
<td>73.2</td>
</tr>
<tr>
<td>CASPT2</td>
<td>1.938</td>
<td>2.183</td>
<td>93.9</td>
<td>86.1</td>
<td>74.6</td>
</tr>
<tr>
<td>MP2</td>
<td>1.953</td>
<td>2.193</td>
<td>94.0</td>
<td>86.0</td>
<td>74.8</td>
</tr>
<tr>
<td>B2LYP</td>
<td>1.953</td>
<td>2.193</td>
<td>94.0</td>
<td>86.0</td>
<td>74.8</td>
</tr>
<tr>
<td>B3LYP D2h</td>
<td>1.930</td>
<td>2.177</td>
<td>94.2</td>
<td>85.8</td>
<td>74.3</td>
</tr>
<tr>
<td>D2</td>
<td>1.932</td>
<td>2.180</td>
<td>95.4</td>
<td>86.1</td>
<td>74.5</td>
</tr>
<tr>
<td>PBE0</td>
<td>1.910</td>
<td>2.173</td>
<td>93.9</td>
<td>86.1</td>
<td>73.7</td>
</tr>
<tr>
<td>Na2PuO4</td>
<td>1.904</td>
<td>2.181</td>
<td>93.5</td>
<td>86.1</td>
<td>74.6</td>
</tr>
<tr>
<td>CASPT2</td>
<td>1.919</td>
<td>2.172</td>
<td>93.5</td>
<td>86.1</td>
<td>74.6</td>
</tr>
<tr>
<td>B2LYP</td>
<td>1.912</td>
<td>2.175</td>
<td>93.8</td>
<td>86.2</td>
<td>73.9</td>
</tr>
<tr>
<td>B3LYP</td>
<td>1.889</td>
<td>2.169</td>
<td>93.5</td>
<td>86.3</td>
<td>73.6</td>
</tr>
<tr>
<td>PBE0</td>
<td>1.885</td>
<td>2.163</td>
<td>94.2</td>
<td>85.8</td>
<td>72.8</td>
</tr>
</tbody>
</table>

a Bond distances are given in angstroms, bond angles in degrees, the moments of inertia in kg m². The angle (OAnO) corresponds to the one in the Na2O3An rings.

Table 7
Calculated anharmonic frequencies (cm⁻¹) of the fundamentals.

<table>
<thead>
<tr>
<th>Sym</th>
<th>Na2UO4</th>
<th>Na2PuO4</th>
<th>Na2AmO4</th>
<th>Na2AmO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Az</td>
<td>749</td>
<td>746</td>
<td>722</td>
<td>648</td>
</tr>
<tr>
<td>Az</td>
<td>642</td>
<td>442</td>
<td>470</td>
<td>453</td>
</tr>
<tr>
<td>Bz</td>
<td>248</td>
<td>242</td>
<td>251</td>
<td>247</td>
</tr>
<tr>
<td>Bz</td>
<td>683</td>
<td>705</td>
<td>710</td>
<td>670</td>
</tr>
<tr>
<td>Bz</td>
<td>238</td>
<td>250</td>
<td>463</td>
<td>463</td>
</tr>
<tr>
<td>Bz</td>
<td>273</td>
<td>271</td>
<td>277</td>
<td>265</td>
</tr>
<tr>
<td>Bz</td>
<td>653</td>
<td>676</td>
<td>665</td>
<td>658</td>
</tr>
<tr>
<td>Bz</td>
<td>362</td>
<td>382</td>
<td>392</td>
<td>398</td>
</tr>
<tr>
<td>Bz</td>
<td>121</td>
<td>131</td>
<td>133</td>
<td>148</td>
</tr>
<tr>
<td>Bz</td>
<td>190</td>
<td>219</td>
<td>229</td>
<td>242</td>
</tr>
<tr>
<td>Bz</td>
<td>43</td>
<td>57</td>
<td>60</td>
<td>37</td>
</tr>
<tr>
<td>Bz</td>
<td>145</td>
<td>156</td>
<td>154</td>
<td>147</td>
</tr>
<tr>
<td>Bz</td>
<td>518</td>
<td>529</td>
<td>475</td>
<td>473</td>
</tr>
<tr>
<td>Bz</td>
<td>301</td>
<td>302</td>
<td>313</td>
<td>304</td>
</tr>
<tr>
<td>Az</td>
<td>175</td>
<td>142</td>
<td>127</td>
<td>142</td>
</tr>
<tr>
<td>Az</td>
<td>142</td>
<td>75</td>
<td>127</td>
<td>142</td>
</tr>
</tbody>
</table>

The symbols v, β, γ, s, as mean stretching, in-plane bending, out-of-plane bending, symmetric, asymmetric, respectively. The angle (OAnO) corresponds to the one in the Na2O3An rings.

According its D2 symmetry, the symmetry species of Na2UO4 do not have the g/u (gerade/ungerade) symbols.

Harmonic frequencies, because the calculation of the anharmonic frequencies was erroneous.

4. Conclusions

In the current study the molecular properties of Na2AnO4 (An = U, Np, Pu, Am) compounds have been predicted by multi-reference post-HF and DFT calculations. The computations support