Studie on transuranic oxides provide a particularly valuable insight into chemical bonding in actinide compounds, in which subtle differences between metal ions and oxygen atoms are of fundamental importance for the stability of these compounds as well as their existence. In the case of neptunium, it is still mainly limited to specific Np oxide compounds without periodicity in the formation of stable structures or different oxidation states. Here, we report a systematic global minimum search of Np2Ox (x = 1−7) clusters and the computational study of their electronic structures and chemical bonding. These studies suggest that Np(x) ion could play the structure-directing role, and thus the mixed-valent Np(II/IV) in Np2O4 is predicted accessible. In comparison with lower oxidation state Np analogues, significant 5f-orbital covalent interactions with Np(v)=O bonding are observed, which shows that these model neptunium oxides can provide new understandings into the behavior of 5f-electrons in chemical bonding and structural design.

1. Introduction

Nanoscience sometimes produces results that are more mystifying than in any other discipline. Acceptably, neptunium is one of the most complex and fascinating chemical elements in the periodic table. Changes in neptunium dioxide (NpO2) particle size from bulk to nanoparticles (NPs) could have a dramatic effect on NpO2 properties. In different solution environments, Np has been known to exist and even co-exist in several oxidation states, from Np(III) to Np(VI). Among those oxidation states, the pentavalent neptunium within the NpO2+ cation is the most widely concerned neptunium species both in nuclear reprocessing technology and under environmentally relevant conditions. Recently, it was repeatedly found that neptunium oxide NPs are produced during nuclear waste processing under oxidizing conditions, and formed in interfacial processes between neptunium of different initial oxidation states and various mineral surfaces, and found as bonded to mineral or organic colloids in the groundwater. All these results indicate the high importance of neptunium oxide NPs in the context of the environmental behavior of neptunium. A complete understanding of neptunium oxides at a fundamental level is therefore essential if one is to design future nuclear waste remediation and separation cycles, as well as to develop advanced fuel cycles. Quantum chemistry methods can be used to study radioactive neptunium safely via the geometry structure and the electronic structure of such NPs.

Small neptunium oxide clusters can be prepared by laser ablation of neptunium metal in the presence of an oxygen-saturated atmosphere. In the presence of oxygen gas, neptunium oxide clusters such as NpO2 and Np2O5 have already been generated and detected. Several experimental studies have already been applied to study the structural, energetic, vibrational, electronic, and magnetic properties of neptunium oxide clusters. For example, the photoionization spectra of NpO2 were measured and strongly size-dependent ionization potentials were observed. For the NpO2 molecule, the electron–spin resonance and optical spectroscopy in neon and argon matrices revealed that its ground state is a 3Δ state, and the molecular bond length and vibrational frequency have been predicted to be 1.761 Å and 942 cm−1, respectively. Accompanying these experimental results, several theoretical calculations were also performed to explore the ground-state electronic structures of neptunium oxide clusters, however, most of those studies were mostly focused on the monomer neptunium oxide clusters. In this paper, we systematically study the atomic and electronic structures of neutral dimer Np oxide clusters, which provide more conclusive properties of Np materials with a systematic oxidation state than the monomer species.

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2. Results and discussion

2.1. Electronic structure and oxidation state in new neptunium complexes

The most intriguing question concerning \( \text{NP}_2\text{O}_3 \) nanoparticles is the potential presence of various oxidation states of neptunium. Global minimum searching by using particle-swarm optimization methodologies based Crystal Structure Analysis in Particle Swarm Optimization (CALYPSO) code\(^{12}\) combined with full geometry optimization performed at DFT levels (GGA+U and PBE/TZ2P)\(^{13}\) were firstly carried out and followed by DLPNO-CCSD(T)\(^{14}\) energy corrections to predict the ground-state structures corresponding to each potential energy profiles. Based on the most stable structure, which is shown in Fig. 1, the electronic structure, and chemical bonding analyses were further explored. The series of \( \text{NP}_2\text{O}_x \) molecules are fascinating for at least three reasons: (1) each lowest-energy structure appears to be the primary product of the reaction between two \( \text{NP} \) atoms and the oxygen atoms. (2) They are the simplest examples of a series of complexes with fully distributed oxidation states of \( \text{NP} \), e.g. \( \text{NP}^0 \), \( \text{NP}^+ \) or \( \text{NP}^{+\text{II}} \) is a highly unusual oxidation state of \( \text{NP} \).\(^{15}\) (3) One more interesting aspect of this work are the apparent production of several fundamental new molecules of \( \text{NP} \), including the \( \text{NP}^+ \) complex \( \text{NP}_2\text{O}_2 \) in addition to the mix-valent \( \text{NP}^{+\text{V/III}} \) complex \( \text{NP}_2\text{O}_3 \), and the heptavalent \( \text{NP} \) oxide \( \text{NP}_2\text{O}_7 \). To address some of these matters, we have delved more deeply into the electronic structure of and bonding in these \( \text{NP}_2\text{O}_x \) complexes.

The ground electron configuration of an \( \text{NP} \) atom is \([R_n]7s^56d^15f^4\). As known, neptunium could exhibit six oxidation states in molecular complexes, from +2 to +7, with +5 being the most common in aqueous media, although the accessibility of divalent oxidation state requires skillful efforts. An \( \text{NP}^0 \) complex could, in principle, retain its two metal-based electrons in an \( s^2f^4 \), an \( s^1f^5 \), or an \( s^1d^1f^4 \) configuration. The relative energies of the \( 7s \), \( 6d \), and \( 5f \) orbitals in a low-valent early-actinide complex will be sensitive to the ligands present. For example, the ligand field provided by three substituted cyclopentadienyl ligands causes \( \text{U}^{\text{II}} \) complexes [\( \text{U} \{\text{An,ArO},\text{mes}\}^- \)] to have an \( f^4 \) configuration,\(^{16}\) in contrast to the \( 5f^6d^1 \) configuration for the \( \text{U}^{2+} \) ion in [\( \text{U} \{\text{Cp}^\text{″}\},\text{Cp}^\text{″} = \text{C}_3\text{H}_5\text{SiMe}_3\}] \) complex.\(^{17}\) In both of these cases, the ligand field is strong enough and isotropic enough to destabilize the \( 7s \) orbitals well above the \( 6d \) orbitals, and the \( 5f \) orbitals are still as high in energy as \( 6d \) orbitals to be used to host the metal-based electron. A further complication in determining the electronic structures of the low-valent early actinides is expected to arise because when valence orbitals’ energy levels of low-valent \( \text{NP} \) are in a narrow range and are not fully filled, there is usually obvious destruction of the Aufbau principle in any DFT method. For example, in the case of low oxidation state \( \text{NP} \), placing the added electrons in the \( f_0 \) orbital will result in the unoccupied \( f_{+3} \) orbital below the \( f_0 \) orbital. Contrary to expectations, if the electron is placed in the \( f_{+3} \) orbital, the unoccupied \( f_0 \) orbital is below the \( f_{+3} \) orbital.\(^{18}\) To avoid these problems and to give a quantitative description in the \( 7s \), \( 6d \) and \( 5f \) orbital energies, we have used the approximation of “smearing” in which the electrons that lie around the Fermi level and that are close in energy are smeared out over the orbitals, which are fractional occupations and mainly depends on the major quantum and angular momentum. The calculated energies of \( 5f \), \( 6d \) and \( 7s \) atomic orbitals of \( \text{NP}^0 \) to \( \text{NP}^{+\text{II}} \) are displayed in Scheme 1, which shows regular periodic trends in the valence orbitals of \( \text{NP}^{n+} \) as \( n \) proceeds from 0 to 7.

In \( \text{NP}^0 \) and \( \text{NP}^+ \), in essence, the three orbitals are almost degenerate with the \( 6d \) being the highest energy level. Thus, our calculation of the \( s^1f^5 \) state for the \( \text{NP}^+ \) molecule \( \text{NP}_2\text{O} \) is reasonable. Starting from \( \text{NP}^+ \), the \( 5f \) level has declined below of \( 7s \) and still degenerated to the \( 7s \) level, where the \( 6d \) orbitals retain higher energy than the \( 7s \) orbitals. Thus, \( \text{NP} \) has the electronic configuration of \( s^1f^4 \) or \( f^5 \) in \( \text{NP}_2\text{O}_4 \).\(^{19}\) At \( \text{NP}^{+\text{III}} \), the \( 6d \) and \( 7s \) switched energetic levels, however, their energies are still near-degenerated, both being higher than \( 5f \) levels. Consequently, \( \text{NP}_2\text{O}_3 \) has the \( \text{NP} \) \( (f^4) \) configuration. As \( \text{NP} \) oxidation proceeds through the series, the valence orbitals drop in energy with the dropping in the range of \( 5f > 6d > 7s \). This decreasing extent in the energy for different angular momentum enlarges the range of \( 7s \), \( 6d \), and \( 5f \) energy levels, and makes the

![Scheme 1](https://example.com/scheme1.png)

**Scheme 1** Smeared energies of the valence atomic orbitals of \( \text{NP}^{n+} \) (\( n = 0 \) to 7).

**Fig. 1** The global minimum structure of \( \text{NP}_2\text{O}_x \) (\( x = 1 \) to 7).
5f orbitals much inert for the higher oxidation state. Therefore, more electron-transfer from neptunium to the ligand becomes more difficult, thus making the unpaired electrons largely located on the nonbonding 5f AO's with increasing formal charge, with the number of electrons decreasing.

For instance, our calculations indicate that the ground state electronic configuration of the Np\(^{+V}\) ion in Np\(_2\)O\(_3\) is \(5f^47s^1\), which differs from the Np\(^{+V}\) \(5f^6d^1\) electronic configuration in the [Np(Cp\(_3\))\(^+\)]\(^-\) complex,\(^{17}\) in contrast to the \(5f^6d^1\) configuration for the U\(^{+V}\) ion in [U(Cp\(_3\))\(^-\)]\(^2\),\(^{20}\) or the configuration of the \(5f^6\) state for Pu\(^{+V}\) in the [Pu(Cp\(_3\))\(^-\)]\(^-\).\(^{21}\) This is ascribed to the short Np–O bond length arouses strong interaction to destabilize the 6d orbital above the 7s orbitals. As traversing the series of oxidation states, the Np 5f orbitals gradually decrease in energy levels and become less chemically accessible, thereby the \(5f^{n+1}\) configuration for trivalent Np has been presumed to have more stability. Thus, the predicted Np\(^{+V}\) ion with a 5f\(^4\) electronic configuration in Np\(_2\)O\(_3\) is reasonable. Remarkably, Np\(_2\)O\(_4\) consists of a 5f\(^2\) electronic configuration of one of the neptunium centers as well as a 5f\(^4\) electronic configuration of the other neptunium, being capable of indicating the formation of the first mixed-valent Np\(^{+V}/\)Np\(^{+V}\)\(^{+V}\) oxide compound. The reason for the formation of such an electronic structure is that Np\(^{+V}\) with double-degenerated \(f^2\) configuration has extreme stability over that of Np\(^{+V}\) with triple-degenerate \(f^3\) configuration, due to the lower energy levels of Np\(^{+V}\) with 5f orbitals having stronger covalence with O 2p orbitals, which is necessary for forming Np(\(v\))=O multiple bonds. Therefore, Np\(_2\)O\(_4\) has a \((5f\text{Np}_1)^2(5f\text{Np}_2)^2\) valence configuration with two pentavalent Np, which could be considered as the fifth oxygen atom consequently oxidizing the Np2(m) atom in Np\(_2\)O\(_4\) into Np(\(v\)). This mechanism is evocative of the stabilization of Np(\(v\)). The ground state Np\(_2\)O\(_4\) is a triplet \(^3B_{2u}\) state with the electronic structure of \(5f^1\)–\(5f^4\) on Np atoms, thus each Np has a hexavalent oxidation state. For Np\(_2\)O\(_7\), the lowest stable isomer is a closed-shell singlet \(^1\Lambda\) with the valence electronic structure of \(5f^0\) on Np, thus a compound featuring heptavalent Np has been predicted. In addition, the series of Np\(_2\)O\(_x\) considered currently is in a neutral state and the valent state of the Np\(_2\)O\(_x\) compound indeed significantly affect the electronic structure of the Np atom, which will be discussed in our further works.

The effective charge analyses (Table S10\(^{19}\)) show that the charge value on Np in Np\(_2\)O\(_x\) compounds increases gradually, implying that the increased oxidation state along with the increased number of oxygen atoms, agrees well with the decreasing spin population values in this series. As detailed in Table 1, the 5f population for both Np in Np\(_2\)O\(_5\) is 5.45|e, which generally decreases when \(x\) increases and becomes 5.14|e in Np\(_2\)O\(_3\) (f\(^3\)), 4.16|e in Np\(_2\)O\(_5\) (f\(^3\)), 2.53|e (f\(^2\)) and 3.92|e (f\(^1\)) for Np\(_2\)O\(_4\), 2.23|e for Np\(_2\)O\(_6\), 1.15|e for Np\(_2\)O\(_7\) (f\(^1\)) and 0.00|e in Np\(_2\)O\(_7\) (f\(^0\)). This is a piece of evidence that the oxidation state of Np has increased from \(+I\) to \(+VII\), as expected. Obviously, Np atoms in Np\(_2\)O\(_4\) exhibits two oxidation states, \(+V\) in Np1 and \(+III\) in Np2, ascribed to the stable Np(\(v\)) electronic state. In addition, the trend of Bader charges on Np in Np\(_2\)O\(_x\) compounds exhibit a decreasingly enlarging trend, from 0.63|e in Np\(_2\)O\(_2\) to 2.79|e in Np\(_2\)O\(_7\), and not linearly correlated with the oxidation state of Np, which is because a very high OS metal cation in compounds would spontaneously oxidize its ligands by self-reduction. The stabilities of the various oxidation states of Np along the series are shown in Fig. 2, where the formal oxidation states, are plotted together with the corresponding values for the HOMO–LUMO gaps.

### 2.2. \(f-f\) bond in Np\(_2\)O\(_3\)

Fig. 3 illustrates the linear synchronous transit (LST) potential energy surfaces of Np\(_2\)O\(_3\) species upon converting a \(^5\Sigma^+\) to the \(^7\Sigma^+\) state as a function of the distance (\(R_o\)) from two Np centers.

### Table 1  Optimized structures (bond length in Å and bond angle in °), the oxidation state of Np (OS), Mayer bond order (BO) for Np1–Np2, Bader charges (Q\(_{\text{Bader}}\)) as well as Mulliken spin (S\(_{\text{Mulliken}}\)) on Np atoms of the global minimum isomer for Np\(_2\)O\(_x\) (\(x = 1\) to 7)

<table>
<thead>
<tr>
<th>Species</th>
<th>(2\text{,v}^1)A (symm.)</th>
<th>Elec. conf.</th>
<th>OS</th>
<th>Geometry</th>
<th>BO</th>
<th>Q(_{\text{Bader}})</th>
<th>S(_{\text{Mulliken}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Np(_2)O</td>
<td>(1\text{A}<em>2) (C(</em>{2v}))</td>
<td>f(^3)s(^1)–f(^3)s(^1)</td>
<td>+I</td>
<td>Np–O = 2.063</td>
<td>1.51</td>
<td>0.63</td>
<td>5.45</td>
</tr>
<tr>
<td>Np(_2)O(_2)</td>
<td>(1\text{B}<em>{2g}) (D(</em>{2h}))</td>
<td>f(^1)f(^5)s(^1)</td>
<td>+II</td>
<td>Np–O = 2.086</td>
<td>0.77</td>
<td>1.20</td>
<td>5.14</td>
</tr>
<tr>
<td>Np(_2)O(_3)</td>
<td>(9\text{E}) (D(_{3h}))</td>
<td>f(^4)f(^4)</td>
<td>+III</td>
<td>Np–O = 1.255, 2.052</td>
<td>0.55</td>
<td>1.75</td>
<td>4.16</td>
</tr>
<tr>
<td>Np(_2)O(_4)</td>
<td>(1\text{A}) (C(_{2v}))</td>
<td>f(^2)f(^2)</td>
<td>+V</td>
<td>Np–O = 1.802, 2.013</td>
<td>0.72</td>
<td>2.39</td>
<td>3.25</td>
</tr>
<tr>
<td>Np(_2)O(_5)</td>
<td>(5\text{A}) (C(_{2v}))</td>
<td>f(^1)f(^1)</td>
<td>+VI</td>
<td>Np–O = 2.013, 2.192</td>
<td>0.31</td>
<td>2.42</td>
<td>2.23</td>
</tr>
<tr>
<td>Np(_2)O(_6)</td>
<td>(3\text{B}<em>{2u}) (D(</em>{2h}))</td>
<td>f(^1)f(^1)</td>
<td>+VII</td>
<td>Np–O = 2.100, 2.100</td>
<td>1.02</td>
<td>2.62</td>
<td>1.15</td>
</tr>
<tr>
<td>Np(_2)O(_7)</td>
<td>(1\text{A}) (C(_{2v}))</td>
<td>f(^0)f(^0)</td>
<td>+VII</td>
<td>Np–O = 3.843</td>
<td>0.13</td>
<td>2.79</td>
<td>0.00</td>
</tr>
</tbody>
</table>
[Np-core yellow and O-cores red] with $R_0 = R_0 - 0.05n$ ($n = 1$–$9$). The starting point with $R_0 = 2.943$ pm corresponds to the $D_{3h}$ structure, and the reduced ending point with $R_9 = 2.500$ pm, corresponds to the $D_{3h}$ structure. Along both the potential energy surfaces, energies increase sharply before $R_0$ and also gradually increase after $R_0$, indicating that $R_0 = 2.943$ is the local minimum. The nonet state is generally lower in energy than the septet, while the $^7E^*$ structure with proposed f-f bonding is only slightly lower energy at $R_9 = 2.500$ about 0.013 eV compared to the $^9E^*$ one. Therefore, the $^7E^*$ structure is significantly less stable than the $^9E^*$ one, giving the $^9E^*$ without the f-f bond for the ground state of Np$_2$O$_3$. The intrinsic bonding mechanism in Np$_2$O$_3$ between Np and O atoms has been revealed by analyzing the Kohn–Sham molecular orbitals of Np$_2$O$_3$ and their MO energy levels with correlation to the atomic orbitals (AOs).

As illustrated in Fig. 4, the fragment molecular orbital (FMO) analysis of the Np$_2$O$_3$ ($D_{3h}$) $^9E^*$ ground state can be interpreted base on the orbital interactions between Np$_2$ and O$_3$ fragments. For O$_3$ ligands, the O 2p-based $\pi^*$ MOs 2b$_1$, 5a$_1$, and 4b$_2$ play as electron acceptors when inserted into Np$_2$, and transformed into group orbitals 7a'$_1$ + 6a''$_2$ + 1a'$_2$ of the Np$_2$O$_3$. According to the frontier occupied MOs shown in Fig. 3, the splitting of Np valence orbitals upon interacting with O 2p is consistent with the conventional crystal-field theory. Without spin–orbit coupling, firstly, the 7s orbitals as doubly-occupied orbitals are $\sigma_u$ in a $D_{2h}$ field in Np$_2$ dimer species that is considerably further destabilized by the strong interaction with the O 2p orbitals to be unoccupied 10a' orbital. Similarly, Np 5f orbitals are split as $\phi_u$ ($f\delta$) $\sim$ $\delta_u$ ($f\delta$) $\ll$ $\pi_u$ ($f\pi$) $< \sigma_u$ ($f\sigma$) in Np$_2$ species, where the strong destabilization of the $f_u$, $f_8$ and $f_6$ orbitals from the f-manifold is an indication of their strong interaction with the unfilled O 2p orbitals. Several MOs with the low orbital energies shown in the plot reflect the strong bonding interaction between the central Np 5f hybrid orbitals and O 2p orbitals; the $\sigma_u$ of Np$_2$ overlaps with the corresponding two O 2p orbitals, forming 8a', bonding orbitals and 8a'' anti-bonding orbital of Np$_2$O$_3$. The $\pi_u$ group orbitals of Np$_2$ transform into 8e' and 6e'' orbitals of

![Fig. 2](image1.png) The formal oxidation state of Np along with the series together with the corresponding values for the HOMO–LUMO gaps of Np$_2$O$_x$ ($x = 1$ to 7).

![Fig. 3](image2.png) Linear transit (LT) potential energy curves of Np$_2$O$_3$ calculated at the SR-DFT/PBE level.
2.3. Mixed-valent in Np2O4

The mixed-valence has been encountered in a number of scientific areas, and it has been considered relying on ligand field theory and qualitatively related to the extent of delocalization of the valence shell electrons. Especially in the transition-metal-containing compounds, the ligand field affects the local spin of metal atoms. The Np2O4 is a mixed-valent compound that could be ensured by structural and electronic structures that support the delocalization of 5f electrons in Np5+/Np5+, however, it depends less on the ligand field. Firstly, Np(v) cation Np(III) has a quasi-tetrahedral type with the three Np–O single bonds of ca. 2.00 Å, while Np(v) exists in a [O=Np(v)=O] fragment, where Np(v) presents an octahedral coordination type, e.g. O=Np bond lengths of 1.811 Å and 1.972 Å, and the bond angle O1–Np1–O2 of 178.3 deg. as well as the bond angle O2–Np1–O3 of 105.4 deg., known as an Np( V) structural feature. In addition, Np–O6 distances are shorter at the Np(v) site than at the Np(III). Thus, this mixed-valent cluster could be classified into a class II system, which has three bridging O6 between two Np ions of differing valences. In this bonding feature, two Np atoms are at a very close distance of 2.994 Å, which is of unprecedented structure and the oxidation state of Np. This structure identifies the stable geometry of anion compounds Hf2O4+ and Zr2O4−, where the C3v isomer has typical M–O and M=O stretching modes in IR spectra. Secondly, the atomic free valence and spin and orbital populations (Table 1) indicate two unpaired 5f-electrons on Np(v) atom and four unpaired 5f-electrons on Np(III). We also chose the localized singly occupied molecular orbital (SOMO, Fig. 5) pictures to sketch the correlated oxidation states in Np2O4. That the lowest two SOMOs are from Np(v) atom and the rest four are from Np(III), reflects that the higher oxidation state of Np has lower valence orbitals, due to the enlarging difference of spin-polarization of Np(v) and Np(III).

Fig. 4  Kohn–Sham MO analysis of the Np2O3 based on SR-ZORA PBE/TZ2P calculations. The left side is the frontier energy levels, including 6s and 5d bands; the inset on the right side is the O3 π*-type pairs, which are strongly localized on O and lead to its effective negative charge.

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the chemical bonding of Np–O.24 Such as one of the Np=O bonding MO in 4A was composed of 24.85% of Np 5f orbitals into the bonding, 6.05% larger in contribution compared to 18.80% of Np 5f orbitals in the counterpart MO in 4C. This phenomenon has been found as the unique feature for f-orbitals that the participation of f orbitals in chemical bonding could direct the structure of a compound.24 As is known, the most stable oxidation state is Np(V) and several neptunium oxidation states could exist simultaneously in the solution, thus we could provide evidence for the co-existence of two different cations (Np3+, Np5+) in Np2O4 compounds.

2.4. Heptavalent Np in Np2O7

In the ground 1A’ state for Np2O7, Np1 is bounded by three-terminal oxygen atoms with the Np1–O3 bond length of 1.787 Å, by one actinyl oxygen with the Np1–O3 bond length of 1.961 Å and by one bridging oxygen with the Np1–O6 bond length of 2.013 Å, while the Np2 is bounded by three-terminal oxygen atoms with the Np2–O3 bond length of 1.797, 1.797, 1.846 Å and by one bridging oxygen with the Np2–O6 bond length of 2.236 Å. Different from the structure of U2O7,25 each Np has four effectively coordinated oxygen atoms, consisting of two Np–O5 single bonds and three Np=O double bonds, which is ascribed to hexavalent U in U2O7 and heptavalent Np in Np2O7. As the investigation on the electronic structure of NpO3 and the NpO3+ cation,14c we have known that Np is hexavalent in NpO3 and heptavalent in NpO3+ cation. Thus, this Np2O7 structure could be understood as two quasi-planar NpO3+ cations connected by an O2− anion, that is oxygen further oxides two Np(v)O3 into Np(vii) with the formation of Np2O7. As noted in Fig. 6, the MO diagram for Np2O7 in correlated to the MOs of one Np1 based NpO3 fragment and one O fragment shows that the upper paired electrons reside in the O 2p-based MOs. For example, the O 2p-based 1a” and 2a’ MOs are completely filled and these two MOs represent strong bonding interactions between Np 5f AOs and O 2p AOs, resulting in Np 5f- and 6d-based antibonding orbitals (4a” and 7a”), destabilized into a virtual band. Meanwhile, the occupied MOs are bonding orbitals with adiabatic polarization of O 2p orbitals toward the Np 5f shell, as shown from the electronic structure of MO 1a” of Np2O7 in Fig. 6. In addition, the bonding between Np and the oxide within the NpO3 fragment has significant f orbitals mixed into the bonding, suggesting that f orbitals participate in chemical bonding in the high Np compounds. Taking the Np1–O bonding orbital HOMO 3a’ as an example, that is mainly composed of 24.8% of the 5f orbitals and 76.7% of the 2p orbitals into the bonding. For Np2O7, the lowest 14 unoccupied MOs are mainly Np 5f character, where seven of them localized on Np1 5f orbitals are shown in Fig. 6. These wavefunction analyses clearly indicate that the Np center has an (s⁰f⁰d⁰) configuration. Thus, Np has been determined as possessing an oxidation state of +VII, and the Np2O7 can be therefore classified as an Np(vii) species, expanding the database for heptavalent Np compounds from a monomer molecular Np(VII) complex, e.g. NpO3(NO3)2− or...
3. Conclusion

We have investigated the geometry and electronic structures of the Np2Ox (x = 1–7) species to explore how the Np oxidation state, as well as chemical bonding between NpO6 and O, directs the structural stability in this series. This work is intended to provide several contributions in charting future directions in the neptunium chemistry with the formation of a specific oxidation state. In general, Np2Ox provides an approach that the chemistry of radioactive Np complexes could be successfully studied via the combination of global-minimum search technology and relativistic quantum chemistry methods. The Np oxidation state traversing from +4 to +7 shows the increased 5f-contribution to the Np O bonding. The significant difference of NpV from lower oxidation states Np implies that the formation of NpV is extremely stable arising from the participation of 5f orbitals in chemical bonding and the ONPO linearity. Thus, the fact that mixed-valent Np2(w/v)O4 occurs between Np(vii)O3 and Np(v)2O3 is not surprising. The presently proposed Np2(vii)O2 complex with the previously reported Np(vii) compounds demonstrates that Np(vii) oxidation state is plausible in both oxides, whose stability comes from the significant interactions between O 2p orbitals and both, the Np 6d and 5f atomic orbitals. Although without spectroscopic studies on these systems, this complete computational study in both aspects of structural conformation and electronic structure corroboration, is able to provide theoretically fundamental understanding in neptunium even to the extent of early actinide elements and provide some guidance for actinide chemistry.

Conflicts of interest

There are no conflicts to declare.

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