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A systematic study of neutral and charged 3d-metal trioxides and tetraoxides

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Using density functional theory with generalized gradient approximation, we have performed a systematic study of the structure and properties of neutral and charged trioxides (MO3) and tetraoxides (MO4) of the 3d-metal atoms. The results of our calculations revealed a number of interesting features when moving along the 3d-metal series. (1) Geometrical configurations of the lowest total energy states of neutral and charged trioxides and tetraoxides are composed of oxo and/or peroxo groups, except for CuO3− and ZnO3− which possess a superoxo group, CuO4+ and ZnO4+ which possess two superoxo groups, and CuO3+, ZnO3+, and ZnO4− which possess an ozonide group. While peroxo groups are found in the early and late transition metals, all oxygen atoms bind chemically to the metal atom in the middle of the series. (2) Attachment or detachment of an electron to/from an oxide often leads to a change in the geometry. In some cases, two dissociatively attached oxygen atoms combine and form a peroxo group or a peroxo group transforms into a superoxo group and vice versa. (3) The adiabatic electron affinity of as many as two trioxides (VO3 and CoO3) and four tetraoxides (TiO4, CrO4, MnO4, and FeO4) are larger than the electron affinity of halogen atoms. All these oxides are hence superhalogens although only VO3 and MnO4 satisfy the general superhalogen formula. © 2011 American Institute of Physics. [doi:10.1063/1.3570578]

I. INTRODUCTION

Different oxidation states of 3d-metals give rise to a variety of metal clusters containing oxygen.1−3 Transition metal oxides are widely used as catalysts4 and are of paramount importance in organometallic, biocatalysis, and surface sciences. From a practical point of view, it is important to identify the reactive sites in heterogeneous catalysis,5 which possesses a superoxo group, CuO4+ and ZnO4+ which possess two superoxo groups, and CuO3+, ZnO3+, and ZnO4− which possess an ozonide group. While peroxo groups are found in the early and late transition metals, all oxygen atoms bind chemically to the metal atom in the middle of the series. (2) Attachment or detachment of an electron to/from an oxide often leads to a change in the geometry. In some cases, two dissociatively attached oxygen atoms combine and form a peroxo group or a peroxo group transforms into a superoxo group and vice versa. (3) The adiabatic electron affinity of as many as two trioxides (VO3 and CoO3) and four tetraoxides (TiO4, CrO4, MnO4, and FeO4) are larger than the electron affinity of halogen atoms. All these oxides are hence superhalogens although only VO3 and MnO4 satisfy the general superhalogen formula. © 2011 American Institute of Physics. [doi:10.1063/1.3570578]

A systematic study of MO and MO2 (M = 3d-metal atoms) and their negative ions has been carried out previously.9, 10 The electron affinities of the monoxides are relatively small and do not exceed 2 eV. The ground-state geometries of MO2 are found to possess the oxo form except for CuO2 and ZnO2. Copper dioxide has the lowest total energy state with a superoxo geometrical configuration; whereas O2 dissociates from Zn atom during geometry optimizations of ZnO2. The ground-state electronic configuration of Cu is 3d104s1 and, correspondingly, the Cu atom has a single valence electron. Consequently, a Cu atom interacts with only one oxygen atom and forms a superoxo configuration. A Zn atom has a 3d104s2 electronic configuration and does not form thermodynamically stable states when interacting with O2. The geometry of ZnO2 reported10 is linear OZnO and the corresponding state is metastable. The ground-state geometry of both CuO3− and ZnO3− has the oxo form similar to that in the rest of the MO2− anions. The electron affinities of the 3d-metal dioxides are larger than those of the monoxides and exceed 3 eV for the late transition metal dioxides.

The shape of the MO2 ground-state geometries shows that all 3d-metal atoms from Sc to Ni are capable of cleaving O2. The ground-state NiO2 neutral is thermodynamically less stable than all other neutral dioxides with the oxo geometries. This is reflected in the high electron affinity of NiO2, which exceeds 3 eV. The formal valence of Ti is 4 and matches the sum of valencies of two oxygen atoms. This can explain why TiO2 is the most thermodynamically stable dioxide in the 3d-metal dioxide series. Correspondingly, the TiO2 electron affinity is smaller than the electron affinity of all other metal dioxides. The adiabatic electron affinities of NiO2, CuO2, and ZnO2 are larger than 3 eV being somewhat smaller than the electron affinity of the Cl atom (3.62 eV).

It has previously been demonstrated that molecules composed of a metal atom (M) surrounded by electronegative ligands (X) can possess electron affinities which are higher than the electron affinity of halogen atoms.11, 12 Such species were named “superhalogens.” A superhalogen has a general formula MX(n+1)/m, where n is the maximal formal valence of the central atom and m is the normal valence of the electronegative atom X.13, 14 LiX2,15 MgX3,16 and ScX4 (Refs. 17 and 18) (X = Cl, F) satisfy the above formula and present examples of superhalogens.

Our previous density functional calculations were performed for the neutral and negatively charged CrO3,19 MnO4−,20, 21 and FeO4− (Ref. 22) for n = 3 and 4. All three

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MO\(_4\) neutrals were found to be superhalogens, whereas only MnO\(_4\) satisfies the above superhalogen formula and possesses the largest electron affinity in the MO\(_4\) series. Among the 3d-metal trioxides, only VO\(_3\) satisfies the superhalogen formula and it was experimentally confirmed to be a superhalogen.\(^{23}\) However, many other oxides may possess electron affinities, which exceed the electron affinity of F or Cl atoms. In our recent study,\(^{24}\) we found FeO\(_{12}\) cluster to be geometrically stable with the adiabatic electron affinity of 3.69 eV, which is close to the adiabatic electron affinity of FeO\(_4\). It is interesting to find out how the electron affinity depends on the number of oxygen atoms and the central atom in other 3d-metal oxides.

This work presents a systematic study of the structure, electron affinities, ionization energies, and thermodynamic stability of the MO\(_2\) clusters (M = Sc to Zn; n = 3, 4) aimed at establishing the trends in the structures and properties when moving along the MO\(_3\) and MO\(_4\) series. In the 3d-metal atoms, the magnetic moment increases from Sc to Mn and then drops to 0 at Zn; therefore, it is interesting to reveal the ability of oxygen to quench these moments when three or four oxygen atoms are added. Another interesting question is how the attachment or detachment of an electron influences the geometry and the total magnetic moment in the MO\(_3\) and MO\(_4\) series. In Sec. II, we outline our theoretical procedure; Sec. III describes the changes in the structures and binding energies when moving along the neutral and singly charged MO\(_3\) series. We discuss the properties of the neutral and charged tetroxides in Sec. IV, and compare our results obtained for the MO\(_3\) and MO\(_4\) series in Sec. V.

II. COMPUTATIONAL DETAILS

Our calculations are performed using density functional theory with generalized gradient approximation (DFT-GGA). The exchange-correlation functional is composed from the Becke’s exchange\(^{25}\) and Perdew–Wangs correlation\(^{26}\), known as the BPW91 functional. The choice of this functional, among many others available nowadays,\(^{27–29}\) is based on our previous assessments of this functional for 3d-metal oxides,\(^{10,24}\) and the BPW91 stability in harmonic frequency calculations of closely spaced states of iron clusters.\(^{30}\) The BPW91 functional is found to produce the results which are quite close to those obtained using the coupled-cluster method with singles and doubles and noniterative inclusion of triples [CCSD(T)] (Ref. 31) for (TiO\(_2\))\(_n\) clusters,\(^{32}\) (CrO\(_3\))\(_n\) clusters,\(^{33,34}\) and FeO\(_2\).\(^{35}\) Good agreement between the BPW91 and experimental data was obtained for Cr\(_3\)O\(_8\).\(^{36}\) The atomic orbitals are represented by the Gaussian basis sets 6–311+G(3df) [metal atoms: (15s11p6d3f1g/10s7p4d3f1g) and O: (12s6p3d1f/5s4p3d1f)].\(^{37,38}\) The geometries were first optimized without any symmetry constraint using the gaussian 03 code.\(^{39}\) Different trial geometries, where oxygen atoms are bound to the metal atom molecularly (peroxo or superoxo), dissociatively (oxo), and as an ozonide, were probed in order to arrive at the ground-state geometries. All possible spin multiplicities were tried in order to determine the total spin of the ground state. The lowest energy states found were reoptimized with symmetry constraints corresponding to the actual nuclear symmetry derived from the results of our symmetry unconstrained optimizations. The convergence threshold for total energy was set to 0.000001 eV and the force threshold was set to 0.001 eV/Å. Harmonic vibrational frequencies of all states are positive, which means that these states correspond to the potential energy surface minima.

The adiabatic electron affinity (EA\(_{ad}\)) is calculated as the difference between total energies, comprised of the total electronic energy and zero point vibrational energy (ZPVE), of a neutral and the corresponding anion at their respective ground-state geometries. Similarly, the adiabatic ionization energy (IE) is computed as the difference between total energies of a cation and the corresponding neutral at their respective ground-state geometries. The vertical detachment energy (VDE) of an extra electron from an anion is computed as the difference in total electronic energies between an anion and its neutral parent at the anion geometry. Similarly, the vertical ionization energy (VIE) is computed as the difference in total electronic energies between a cation and its neutral parent computed at the neutral geometry.

III. TRIOXIDES

A. Neutral MO\(_3\)

The ground-state geometries of MO\(_3\) displayed in Fig. 1 do change when moving from ScO\(_3\) to ZnO\(_3\). In order to understand these changes, we resort to the ground-state geometries of neutral MO\(_2\).\(^{10}\) All dioxide geometries have an oxo form except for CuO\(_2\), which has a superoxo form. Formally, each oxygen atom is divalent since it requires two electrons to fill up its 2p shell. The Sc atom has three valence electrons; nonetheless, its interaction with two oxygen atoms leads to an oxo geometrical configuration of the lowest energy state in ScO\(_2\). The Cu atom in CuO\(_2\) has the electronic configuration close to 3d\(^{10}\)4s\(^1\) with a single valence electron; therefore, it is natural for oxygen in CuO\(_2\) to form a peroxo group. Formally, a Zn atom with a 3d\(^{10}\)4s\(^2\) electronic configuration can be considered as divalent. However, the Zn atom prefers to conserve its closed shell and not to attach to O\(_2\) either in peroxy or superxo form.

In the trioxide series, the formal valence of Sc (3) and Ti (4) is insufficient for the dissociative attachment of three oxygen atoms. Consequently, there are peroxy and oxo groups in the lowest total energy states of ScO\(_3\) and TiO\(_3\). Beginning with V, all MO\(_3\) up to M = Co have a trixo form. Due to a decrease in the valence at the end of the 3d-metal series, the geometries of NiO\(_3\), CuO\(_3\), and ZnO\(_3\) are similar to the ScO\(_3\) geometry and possess one peroxy and one oxo group.

The existence of thermodynamically stable CuO\(_3\) and ZnO\(_3\) is very surprising since CuOO is barely stable while ZnOO is dissociative. Apparently, the addition of an oxygen atom to CuOO or metastable OZnO increases the formal valence of the central atom. This behavior can be related to the strong ionic character of bonding in the 3d-metal trioxides, as follows from the results of the natural bond orbital (NBO) analysis,\(^{40}\) which uses the basis of natural atomic orbitals. The effective electronic configuration of Cu in the quartet ground state of CuO\(_3\) is 3d\(^6\)5s\(^2\)4s\(^0\), which corresponds to a...
The magnetic moment of the central atom is quenched in the ground-state trioxides up to CoO$_3$. The total magnetic moment of trioxides from ScO$_3$ to CoO$_3$ is either 0 or 1 $\mu_B$, depending on the parity of the 4s$^2$ + 3d electron number (see Table I), which corresponds to the spin multiplicities of 1 or 2, respectively. This may be related to the number of valence electrons in Sc, Ti, V, and Cr which is less than or equal to the sum of three oxygen valencies. The number of Mn valence electrons is 7 and the total magnetic moment of MnO$_3$ is 1 $\mu_B$. Ground-state iron and cobalt atoms have the formal valence of 8 and 9 with the magnetic moments of 4 $\mu_B$ and 3 $\mu_B$, respectively. These magnetic moments are quenched in the corresponding trioxides. Surprisingly, the total magnetic moments of trioxides CuO$_3$ (3 $\mu_B$) and ZnO$_3$ (2 $\mu_B$) are larger than the magnetic moments of Cu (1 $\mu_B$) and Zn (0 $\mu_B$) atoms, respectively, i.e., the oxidation increases the total magnetic moment of these trioxides. The excess spin densities, which correspond to the local magnetic moments, at the metal site exceed 0.2e in MnO$_3$ (1.1e), CoO$_3$ (0.4e), NiO$_3$ (0.6e), CuO$_3$ (0.4e), and ZnO$_3$ (0.4e) [see Fig. 1].

Our results obtained for the neutral MO$_3$ species are in good agreement with the results of previous theoretical work performed in order to assign experimental IR frequencies of species trapped in inert matrices. The previous work used mainly the hybrid Hartree–Fock-density-functional-theory (HFDFT) approach B3LYP and smaller basis sets than the basis set we used in the present work. The ground-state structures of ScO$_3$, TiO$_3$, CrO$_3$, MnO$_3$, FeO$_3$, NiO$_3$, and CuO$_3$ (Ref. 49 and 50) along with their computed total magnetic moments are similar to those obtained from our calculations. Our results are, however, different for VO$_3$ and CoO$_3$. The former neutral was previously found to have a trigonal planar geometry of C$_2v$ symmetry while we obtained a slightly distorted D$_3h$ non-planar geometry of C$_3v$ symmetry, in agreement with the results of previous DFT-GGA (Ref. 52) and quantum Monte-Carlo calculations. CoO$_3$ was previously found to possess the 6A$_1$ oxo-peroxo ground state at the HFDFT B1LYP/6-311+G* level, whereas our calculations predict all oxygen to be bound dissociatively in the 2A$_2$ ground state (see Fig. 1). No data were reported for ZnO$_3$ to the best of our knowledge.

Thermodynamic stability of the neutral MO$_3$ clusters is estimated by comparing the O and O$_2$ loss energies, which are computed according to

$$\Delta E_{\text{tot}} = E_{\text{tot}}(\text{MO}_n) - E_{\text{tot}}(\text{MO}_{n-m}) - E_{\text{tot}}(\text{O}_m),$$

$$n = 3, 4; m = 1, 2,$$

TABLE I. The EA$_{\text{ad}}$, VDE, IE, VIE values and the total magnetic moments, M, of the neutral, anionic, and cationic trioxides.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Neutral</th>
<th>Anion</th>
<th>Cation</th>
<th>EA$_{\text{ad}}$</th>
<th>VDE</th>
<th>IE</th>
<th>VIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScO$_3$</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>1.92</td>
<td>2.61</td>
<td>8.67</td>
<td>9.43</td>
</tr>
<tr>
<td>TiO$_3$</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3.38</td>
<td>4.24</td>
<td>4.2 ± 0.1</td>
<td>8.63</td>
</tr>
<tr>
<td>VO$_3$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3.95</td>
<td>4.16</td>
<td>4.36 ± 0.05</td>
<td>10.34</td>
</tr>
<tr>
<td>CrO$_3$</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3.32</td>
<td>3.53</td>
<td>3.66 ± 0.02</td>
<td>11.14</td>
</tr>
<tr>
<td>MnO$_3$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>3.13</td>
<td>3.18</td>
<td>3.21 ± 0.01</td>
<td>11.13</td>
</tr>
<tr>
<td>FeO$_3$</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3.25</td>
<td>3.37</td>
<td>3.26 ± 0.04</td>
<td>11.24</td>
</tr>
<tr>
<td>CoO$_3$</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3.89</td>
<td>4.04</td>
<td>10.32</td>
<td>11.61</td>
</tr>
<tr>
<td>NiO$_3$</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>2.80</td>
<td>3.66</td>
<td>9.83</td>
<td>10.08</td>
</tr>
<tr>
<td>CuO$_3$</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>2.68</td>
<td>3.06</td>
<td>3.19 ± 0.04</td>
<td>9.75</td>
</tr>
<tr>
<td>ZnO$_3$</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2.88</td>
<td>3.11</td>
<td>9.16</td>
<td>9.96</td>
</tr>
</tbody>
</table>

All values are in eV except for the total magnetic moment values, which are in Bohr magnetons $\mu_B$.

$^a$See the experimental references in the text.
ically stable is VO$_4$. This "anomaly" can be related with the

![Image](55x565 to 295x741)

FIG. 2. Fragmentation energies (in eV) of the MO, MO$_2$, MO$_3$, and MO$_4$ series. The filled symbols indicate the atomic oxygen release and open symbols are for the molecular oxygen release. Different colors serve as the indicators of changes in the geometrical shape when moving along the series.

where $E_{\text{tot}}$ includes the ZPVE correction. The smallest dissociation energies in the MO$_3$ and MO$_4$ series computed according to Eq. (1) are plotted in Fig. 2 together with the dissociation energies of the monoxides and dioxides from our previous work.$^9$, $^{10}$ In the monoxide series, ScO, TiO, and VO are significantly more stable compared to the rest of the series, which is related to the formation of triple bonds through a dative mechanism in these monoxides.$^{35}$ The smallest energy decay channel in the MO$_3$ series corresponds to the molecular oxygen release, except for TiO$_3$, VO$_3$, and CrO$_3$ where the yield of atomic oxygen is preferred.

In the MO$_2$ series, the most thermodynamically stable species is TiO$_2$ that correlates with 4 valence electrons of Ti. In the MO$_3$ series, CrO$_3$ is the most stable species that correlates with the maximum formal valence of 6 of the Cr atom. By analogy, FeO$_3$ should be the most stable member of the MO$_4$ series. However, it is not so and the most thermodynamically stable is VO$_4$. This “anomaly” can be related with the geometrical shape of VO$_4$, which is found to be of the dioxygen-peroxo type. If one accepts the formal valence of a peroxo group to be 1, then the sum of oxygen valencies matches the formal valency of V atom.

B. MO$_3^-$ anions

In the MO$_3$ series, VO$_3$ should possess the largest adiabatic electron affinity according to the superhalogen formula, and indeed its computed $E_{\text{Ad}}$ of 3.95 eV is the largest $E_{\text{Ad}}$ in the 3d-metal trioxide series. The computed vertical ionization energy of 4.16 eV of the VO$_3^-$ anion is in good agreement with the experimental value of 4.36 ± 0.05 eV.$^{23}$ The ground state of the VO$_3^-$ anion is a singlet with an equilateral triangle geometrical configuration of $D_3h$ symmetry (see Fig. 1). As it is seen from Fig. 1, the attachment of an extra electron changes the geometrical shape of the trioxide anions of Ti, Cu, Ni, and Zn. In these species, the extra electron breaks either the bond between two oxygen atoms or the bond between the metal atom and an oxygen atom. Similar to the geometries of the neutral parents, the anionic geometries are changing in the beginning and in the end of the series when moving from ScO$_3^-$ to ZnO$_3^-$.

As it is seen from Table I, the $E_{\text{Ad}}$ of VO$_3$ and CoO$_3$ are larger than the EA of the Cl atom. VO$_3$, with a 3d$^3$4s$^2$ valence
electronic configuration of the ground-state metal atom, satisfies the superhalogen formula, while Co possesses a 3d\(^{7}\)4s\(^{2}\) electronic configuration and its superhalogen has to be CoO\(_{3}\). According to the NBO analysis, Co possesses the effective electronic configurations of 3d\(^{7}\)48\(^{3}\)4\(^{0}\)36 and 3d\(^{7}\)49\(^{3}\)4\(^{0}\)37 in CoO\(_{3}\) and CoO\(_{3}\)\(^{−}\), respectively. This means that the extra electron is entirely delocalized over the oxygen atoms, similar to that in VO\(_{3}\)\(^{−}\). Therefore, the CoO\(_{3}\) EA\(_{ad}\) increase with respect to the EA\(_{ad}\) of the neighbor trioxides may be related to a stronger Coulomb attraction exerted by the central atom in the CoO\(_{3}\)\(^{−}\) anion. An extra electron attachment to TiO\(_{3}\) breaks the peroxo bond and the negative ion has D\(_{3h}\) symmetry. This can explain why the EA\(_{ad}\) of TiO\(_{3}\) exceeds the EA\(_{ad}\) of ScO\(_{3}\) by 1.41 eV. Experimental data for TiO\(_{3}\),\(^{56}\) VO\(_{3}\),\(^{23}\) CrO\(_{3}\),\(^{19}\) MnO\(_{3}\),\(^{20}\) FeO\(_{3}\),\(^{57}\) and CuO\(_{3}\) (Ref. 49) are also given in Table I.

The charges on metal atoms in the MO\(_{3}\)\(^{−}\) cations obtained from the NBO analysis are given in Fig. 4(d) relative to the charges on the metal atom in the MO\(_{3}\) neutrals. As it is seen, there is no significant difference in the charges when moving along the cation series. The largest deviation does not exceed 0.4e, which implies that the detached electron originates from the oxygen atoms. The total magnetic moments of the ground-state MO\(_{3}\)\(^{−}\) cations are either 0 or 1 \(\mu_B\), except for ScO\(_{3}\)\(^{−}\), CoO\(_{3}\)\(^{−}\), and CuO\(_{3}\)\(^{−}\), which have the triplet ground states. The local magnetic moments at the metal sites of FeO\(_{3}\)\(^{+}\) (1.7 \(\mu_B\)), CoO\(_{3}\)\(^{+}\) (2.4 \(\mu_B\)), and NiO\(_{3}\)\(^{+}\) (1.4 \(\mu_B\)) are the largest local magnetic moments among all the neutral and charged trioxides.

Experimental vibrational frequencies were obtained\(^{67,68}\) for VO\(_{3}\)\(^{+}\), whose structure was optimized in the accompanying B3LYP/TZVP calculations. The assigned ground state \(^{1}\text{A'}\) (\(\text{C}_s\)) is different from the previous assignment of \(^{1}\text{A'}\) (\(\text{C}_s\)) obtained from the B3LYP/31G* and B3LYP/TZV optimizations.\(^{69,70}\) The experimental vibrational frequencies of 1037 and 1069 cm\(^{−1}\) are in rather poor agreement with the B3LYP frequencies of the both states (1161 and 1228 cm\(^{−1}\) in the \(^3\text{A''}\) state; 1040 and 1178 cm\(^{−1}\) in the \(^1\text{A'}\) state). The VO\(_{3}\)\(^{−}\) ground-state assignment is quite complicated because there are at least three closely spaced states: a singlet state without symmetry shown in Fig. 1, where the excess spin density of 0.9 \(\mu_B\) at V is antiferromagnetically coupled to the excess spin densities of the oxygens; a nonmagnetic \(^1\text{A'}\) (\(\text{C}_s\))
state whose total energy is practically the same as the previous state total energy; and a nonmagnetic $^1\text{A}'$ (C$_1$) state which is above the $^1\text{A}'$ state by 0.03 eV at the BPW91/6-311+G(3df) level. Harmonic vibrational frequencies of 1084 and 1112 cm$^{-1}$ obtained for the nonsymmetric singlet state of VO$_3^+$ are in relatively good agreement with the experiment (note that the spectra were obtained in He$_2$ matrices); however, the intensity ratio of 1:4.6 is far off the experimental ratio of 1:1.6.

IV. TETRAOXIDES

A. Neutral MO$_4$

The optimized ground-state geometries of the neutral 3d-metal tetraoxides are displayed in Fig. 5. The ground-state geometry of the first member of the series, ScO$_4$, contains two peroxo groups. A peroxo group transforms into two oxo atoms in TiO$_4$, VO$_4$, and CrO$_4$, and the second peroxo group transforms into two oxo atoms in MnO$_4$. The structures of FeO$_4$ and MnO$_4$ are similar and correspond to all four oxygen atoms bound dissociatively; however, these states are nearly degenerate in total energy with the states possessing dioxo-peroxo geometries. Beginning with CoO$_4$, all tetraoxides have diperxo geometrical ground-state configurations, where one peroxo-group rotates with respect to another one that results in $D_2$, $D_{2h}$, or $D_{2d}$ symmetry. A geometrically stable isomer of ZnO$_4$ shown in Fig. 5 is thermodynamically metastable because the sum of total energies of Zn and two separated oxygen molecules is lower by ~0.1 eV than the ZnO$_4$ total energy. The total magnetic moments of the neutral tetraoxides MO$_4$ where M = Sc, V, Cr, Mn, Fe, and Cu are either 0 or 1 $\mu_B$. The largest magnetic moment of 3 $\mu_B$ is found for CoO$_4$, and the ground states of the neutral Ti, Ni, and Zn tetraoxides are triplets. Local magnetic moments of the 3d-metal atoms in the neutral tetraoxides do not exceed 0.3 $\mu_B$ except for Ni, whose magnetic moment is 1.5 $\mu_B$.

Figure 2(d) presents the smallest fragmentation energies of the neutral tetraoxides computed according to Eq. (1). The number of valence electrons of Fe is 8 and matches the sum of formal valencies of dissociatively bound oxygen atoms. One could anticipate that FeO$_4$ is the most thermodynamically stable cluster in the neutral tetraoxide series, but it is not so. We found VO$_4$ with five valence electrons of V to be the most thermodynamically stable cluster in the series. FeO$_4$ is also less thermodynamically stable than MnO$_4$, which is consistent with an assignment of a smaller oxidation number to Fe than to Mn (6 and 7, respectively). A sudden decrease in the fragmentation energy of TiO$_4$ as compared to the fragmentation energies of its neighbors ScO$_4$ or VO$_4$ can be attributed to the high thermodynamic stability of the TiO$_2$ dioxide.

The CrO$_4$,$^{19}$ NiO$_4$,$^{48}$ and CuO$_4$ (Ref. 72) ground-state geometrical structures identified on the basis of laser photodetachment data match the corresponding structures obtained in the present work. The lowest total energy $^2\text{A}_2$ state of ScO$_4$ found previously at the B3LYP level has the geometry of $C_{2v}$ symmetry,$^{73}$ where one peroxo group is perpendicular to the second peroxo group. According to our optimizations, the $^2\text{A}''$ ground-state geometry of ScO$_4$ also has two peroxo groups but the geometrical configuration has $C_2$ symmetry with slightly different bond lengths in the peroxo groups (see Fig. 5). The $^2\text{A}_2$ ($C_{2v}$) state is above this $^2\text{A}''$ state by only 0.03 eV in total electronic energy and has an imaginary frequency of $-108i$.

The ground-state structure of VO$_4$ found in our calculations is the same as reported previously.$^{74,75}$ According to the results of B3LYP calculations,$^{76}$ MnO$_4$ has a dioxo-peroxo geometrical structure similar to that of VO$_4$, whereas we found MnO$_4$ to possess a tetragonal geometry of $C_{2v}$ symmetry, which is in accord with the photoelectron spectroscopic
(PES) study.²¹ According to the tentative PES assignment,⁷⁷ FeO₄ has a dioxo-peroxo geometrical structure similar to that of VO₄ while we found that the lowest total energy states of both FeO₄ and FeO₄⁻ possess tetragonal geometrical configurations. The contradiction was attributed²⁸ to the presence of two isomers in the experimental anion flow, which produce two major peaks at ~3.2 and ~3.7 eV. CoO₄ was previously found to have a dioxo-peroxo geometrical configuration of C₂ᵥ symmetry,⁷⁹ while our calculations predict a dioxo-peroxo configuration of D₂ᵥ symmetry. This is very surprising, since both calculations are performed at the same BPW91/6-311+(G(3df)) level. Our optimizations show the 2A₂ state to be above the 4B₁ (D₂) state displayed in Fig. 5 by 0.2 eV. In agreement with the previous studies,⁵⁰,⁸⁰ CuO₄ has a dioxo ground-state structure of D₂h symmetry. No data are found for ZnO₄.

B. MO₄⁻ anions

The ground states of 3d-metal tetraoxide anions are presented in Fig. 5. With respect to the neutral parent geometries, the peroxo groups of ScO₄⁻ and CrO₄⁻ are split into two oxo groups and both peroxo groups of CoO₄⁻ are split into four oxo atoms. The ZnO₄⁻ anion is geometrically stable at the dioxo-peroxo geometry shown in Fig. 5; however, this anion is unstable thermodynamically since its total energy is higher by 0.18 eV than the sum of total energies of ZnO₂⁻ and O₂. Similar to the neutral tetraoxides, the anion geometries do change when moving from ScO₄⁻ to ZnO₄⁻. The ScO₄⁻, TiO₄⁻, and VO₄⁻ anions possess one peroxo group, whereas all oxygen atoms are attached dissociatively in CrO₄⁻, MnO₄⁻, FeO₄⁻, and CoO₄⁻. The NiO₄⁻ and CuO₄⁻ ground-state geometries are similar and have a dioxo-peroxo shape.

The smallest fragmentation energies of MO₄⁻ computed according to Eqs. (2) and (3) are displayed in Fig. 3(b). As expected, MnO₄⁻ is the most thermodynamically stable anion in the series. We found the atomic oxygen yield to be preferred in VO₄⁻, CrO₄⁻, and MnO₄⁻. For ScO₄⁻, TiO₄⁻, and the anions in the end of the series, the smallest energy fragmentation channel corresponds to the dioxoxygen release.

The calculated VDEs of the MO₄⁻ anions and the EA_ads of their neutral parents are collected in Table II. The EA_ads and VDE values are quite close to each other for tetraoxides of Ti, Mn, Fe, Ni, and Cu, which is consistent with the small geometry changes resulting from an extra electron attachment (see Fig. 5). The geometries of neutral ScO₄, CrO₄, and CoO₄ are different from those of the corresponding anions. Consequently, the differences between the corresponding VDE and EA_ads values are larger. An indirect confirmation of a large change in the geometries of the ScO₄ and ScO₄⁻ pair follows from the laser photodetachment spectra⁸¹ of ScO₄⁻, where a wide featureless peak was observed in the area above 3 eV. The VO₄ and VO₄⁻ pair presents an exception since the difference between the EA_ads and VDE is quite large whereas both species have the same topology. However, one can notice rather drastic changes in the bonds of the peroxo group; namely, R(V – O) and R(O – O) are larger in the anion than in the neutral parent by 0.13 and 0.16 Å, respectively. The EA_ads of TiO₄, CrO₄, MnO₄, and FeO₄ are 3.72 4.37, 4.89, and 3.69 eV, respectively, and are larger than the EA of Cl. The experimental values obtained from photoelectron detachment spectra of VO₄,²³ CrO₄,¹⁹ MnO₄,⁵⁷ and CuO₄,⁴⁹ are given in Table II. As it is seen, the experimental values are close to our VDEs.

As mentioned above, the PES spectrum of FeO₄⁻ is likely to originate from two isomers with close total energies. Therefore, one could assume such a possibility for other tetraoxide anions. According to the results of our optimizations, the lowest total energy excited states, the differences Eₜot(first excited state) – Eₜot(ground state) in the tetraoxide anion series are 0.10 eV (Sc), 0.77 eV (Ti), 0.51 eV (V), 0.94 eV (Cr), 1.59 eV (Mn), 0.001 eV (Fe, three degenerate in total energy), 0.08 eV (Co), and 0.23 eV (Ni). The presence of such an anion isomer, which is well separated from the ground state, could be related to the experimental conditions of the anion formation by attaching an extra electron to neutral species. The difference between a tetrahedral ground state of FeO₂⁻ which is above the triply generate doublet states by 0.72 eV. The presence of such an anion isomer, which is well separated from the ground state, could be related to the experimental conditions of the anion formation by attaching an extra electron to neutral species. The difference between a tetrahedral ground state of FeO₂⁻ which is above the triply generate doublet states by 0.72 eV. The presence of such an anion isomer, which is well separated from the ground state, could be related to the experimental conditions of the anion formation by attaching an extra electron to neutral species.
corresponding ground states. The excited state data may be found in the supplementary material.82

According to the NBO analysis, the 3d-metal charge is positive in all MO4 clusters. Figure 6(b) presents the metal charge variation in the anion series with respect to the metal atom charge in the ground-state MO4 neutrals. As it is seen, there is no significant difference in the charge on the metal atoms. This implies that the extra electron is distributed over oxygen atoms in all MO4− anions. A noticeable exception presents CoO4− where the charge on the Co atom increases by ~0.3 e. The local magnetic moments at the metal sites of MO4− are small and do not exceed 0.6 μB (ScO4−).

C. MO4+ cations

The detachment of an electron from the neutral ground-state 3d-metal tetraoxides is accompanied by geometry changes in several cases. Thus, the peroxo groups of TiO4 and VO4 transform into the superoxo groups, while both peroxo groups of CuO4 become the superperoxo groups. Two oxo-atoms of MnO4 and FeO4 combine into the peroxo groups. Our ground state of VO4+ shown in Fig. 5 is similar to the state found previously69 at B3LYP/6–3G* level. The electron detachment from a tetraoxide leads to either rupture of the bond between the metal and an oxygen atom or to a recombination of two oxo-atoms into a peroxo group.

The calculated IE and VIE values of all neutral MO4 are given in Table II and plotted in Fig. 6(c). The values are rather close to each other when M = Sc, Cr, Co, or Ni, which is consistent with the small geometry changes due to the electron detachment (see Fig. 5). The differences between the metal atom charges in the neutral-cation pairs [q(neutral) − q(cation)] obtained from the NBO population analysis are presented in Fig. 6(d). As it is seen, there is no essential dependence of the metal atom charge on the 3d-metal tetraoxide charge. This implies that the detached electron originates from oxygen ligands. The largest differences are observed for the Cu and Zn pairs. This can be attributed to a decreasing interaction between the metal and oxygen atoms as it follows from the smaller fragmentation energies in Fig. 2(d). The total magnetic moments of the MO4+ cations are larger than the total magnetic moments of their neutral parents in a number of cases.

V. COMPARISON OF THE MO3 AND MO4 PROPERTIES

Our calculated fragmentation energies of the neutral and charged MO3 and MO4 species are compared in Fig. 7(a). As it is seen, the neutral trioxides are thermodynamically more stable than the neutral tetraoxides except for the Ni and Cu trioxides. That is, the metal oxide thermodynamic stability decreases when the oxygen content increases. The same conclusion is true for the negative ions as well since the anion fragmentation energies decrease when the oxygen content increases [see Fig. 7(b)].

The computed adiabatic electron affinities of the MO3 and MO4 clusters are compared in Fig. 7(d). The EAad of MnO4 is substantially larger than the EAad of MnO3 despite the MnO4− anion is thermodynamically less stable than the MnO3− anion. MnO4 satisfies the formula for oxygen superhalogens and has the EAad that substantially exceeds the EA of the CI atom. The EAad of TiO4, CrO4, and FeO4 are also larger than the EA of the CI atom and they are superhalogens as well. To qualitatively analyze the superhalogen nature, we calculated the binding energy difference in the neutral–anion pairs plotted in Fig. 7(c). Comparing Figs. 7(c) and 7(d), one can find a strong correlation between the EAad value and the difference between the anion and neutral thermodynamic stability. The only exception presents the MnO3–MnO3− pair. It is worth to mention that the largest difference in the binding energies found for the VO3, MnO3, CoO3, CrO4, MnO4, and FeO4 pairs correlates with the availability of the experimental photoelectron spectra for the corresponding anions.
VI. CONCLUSION

We performed a systematic study of the neutral and singly negatively and positively charged trioxides and tetraoxides of 3d-metal atoms using density functional theory with generalized gradient approximation. The main results obtained can be summarized as follows:

(1) The ground-state geometries of neutral MO$_3^-$ change when moving from Sc to Zn trioxides. The preferred geometry in the beginning and the end of the series has an oxo-peroxo form, while all oxygen atoms are bound dissociatively in the middle of the series from V to Co. In the MO$_4^-$ series, the ground-state geometries have diperoxo (Sc, Co, Ni, Cu, and Zn), dioxo-peroxo (Ti, V, and Cr), and tetraoxo (Mn and Fe) topologies.

(2) The change in geometries due to the attachment or detachment of an electron is characteristic for the early and late 3d-metal atoms. An extra electron attachment transforms a peroxo group into two oxo-atoms or a superoxo group. On the contrary, an electron detachment can lead to a recombination of two oxo-atoms into a peroxo or superoxo group.

(3) The MO$_3^-$ binding energies defined as the smallest energies required for yielding atomic or molecular oxygen are smaller than the MO$_3^-$ binding energies. This can serve as an indicator that molecular oxygen will be less bound to the metal atom when the oxygen content increases.

(4) The adiabatic electron affinities of VO$_3^-$, CoO$_3^-$, TiO$_4^-$, CrO$_4^-$, MnO$_4^-$, and FeO$_2^-$ are larger than the electron affinity of the Cl atom and these species are superhalogens. VO$_3^-$ and MnO$_4^-$ satisfy the superhalogen formula and possess the largest electron affinities in the trioxide and tetraoxide series, respectively.

(5) The difference between binding energies in the MO$_n^-$–MO$_n$$^-$ pairs is the largest for those pairs where the neutral oxide is a superhalogen.

(6) In the ZnO$_3$ series (n = 1–4), only ZnO and ZnO$_3$ are thermodynamically stable, while both ZnO$_2$ and ZnO$_4$ form geometrically stable states, which are unstable with respect to release of molecular oxygen.

(7) The differences between our vertical electron detachment energies of an extra electron from the MO$_3^-$ and MO$_n^-$ anions obtained at the BPW91/6–311+G(3df) level and the corresponding experimental values obtained from the photoelectron spectra do not exceed 0.2 eV within the experimental uncertainty bars.

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92. See supplementary material at http://dx.doi.org/10.1063/1.3570578 for the concise data on all ground and lowest total energy excited states optimized in the present work.