2011

Potential candidates for hyperhalogens: A comparative study of BO_2 , AlO_2 , and VO_3 species

Kalpataru Pradhan

Virginia Commonwealth University, kpradhan@vcu.edu

Purusottam Jena

Virginia Commonwealth University, pjena@vcu.edu

Follow this and additional works at: http://scholarscompass.vcu.edu/phys_pubs

Part of the [Physics Commons](#)

Pradhan, K., and Jena, P. Potential candidates for hyperhalogens: A comparative study of BO_2 , AlO_2 , and VO_3 species. *The Journal of Chemical Physics*, 135, 144305 (2011). Copyright © 2011 American Institute of Physics.

Downloaded from

http://scholarscompass.vcu.edu/phys_pubs/160

This Article is brought to you for free and open access by the Dept. of Physics at VCU Scholars Compass. It has been accepted for inclusion in Physics Publications by an authorized administrator of VCU Scholars Compass. For more information, please contact libcompass@vcu.edu.

Potential candidates for hyperhalogens: A comparative study of BO_2 , AlO_2 , and VO_3 species

Kalpataru Pradhan^{a)} and Purusottam Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284, USA

(Received 28 July 2011; accepted 21 September 2011; published online 12 October 2011)

Recent work has shown that BO_2 which is a superhalogen with an electron affinity of 4.46 eV, can be used as building block of a new class of molecules/clusters whose electron affinities can exceed that of BO_2 . This class of molecules was named hyperhalogens and the concept was illustrated by focusing on $\text{Au}(\text{BO}_2)_2$. Here we explore other superhalogens besides BO_2 to see if they too can be used to form hyperhalogens. We have chosen to focus on AlO_2 which is valence isoelectronic with BO_2 as well as VO_3 which involves a transition metal atom. The results obtained using density functional theory show unexpected behavior: Although AlO_2 and VO_3 are both superhalogens such as BO_2 , only $\text{Na}(\text{BO}_2)_2$ is a hyperhalogen while $\text{Na}(\text{AlO}_2)_2$ and $\text{Na}(\text{VO}_3)_2$ are not. The origin of this anomalous result is traced to the large binding energy of the dimers of AlO_2 and VO_3 . © 2011 American Institute of Physics. [doi:10.1063/1.3650238]

I. INTRODUCTION

Superhalogens are a class of molecules or clusters whose electron affinities are larger than that of the halogen atoms.^{1–4} A typical superhalogen is composed of a central metal atom M surrounded by halogen atoms X. They have the chemical formula MX_{k+1} where k is the maximal formal valence of the central metal atom.² When the number of halogen atoms exceeds the maximal valence of the metal atom, the extra electron in the anion is distributed over all the halogen atoms, further stabilizing the anion. Consequently, the electron affinity exceeds that of the halogen atom. The early works on superhalogens were mainly concentrated on *sp* metals decorated with halogens.^{5–9} These studies have since been extended to systems composed of transition metal atoms^{10–14} at the center surrounded with halogen, oxygen^{15–18} or hydrogen¹⁹ as ligand atoms. The current surge of interest in these systems is due to the fact that negative ions play an important role in chemistry as oxidizing agents, biocatalysts, nucleation centers, and building blocks of new high energetic materials.^{20–23}

Recently, a new class of electronegative species whose electron affinities can even surpass those of superhalogens was discovered. These species called hyperhalogens are composed of a metal atom at the center surrounded by superhalogen moieties.²⁴ In this first ever study, Au atom was decorated with BO_2 moieties and the electron affinity of $\text{Au}(\text{BO}_2)_2$ was found to be 5.70 eV. This electron affinity is 1.24 eV larger than the electron affinity of BO_2 .²⁵ We note that BO_2 , with an electron affinity of 4.46 eV, is a superhalogen. Later studies²⁶ have shown that the electron affinity of $\text{Cu}(\text{BO}_2)_2$ is also higher than that of BO_2 , thus confirming the hyperhalogen concept.

In this paper, we have explored the possibility of using different superhalogens to create new hyperhalogens. We concentrated on AlO_2 and VO_3 as possible candidates for superhalogens. Note that Al is valence isoelectronic with B and

hence like BO_2 , AlO_2 requires one electron for shell closing. This extra electron could be distributed over two O atoms, hence AlO_2 could also be a superhalogen.²⁵ Similarly, with the addition of an electron VO_3 achieves a closed shell configuration as the maximal valence of V ($3d^3 4s^2$) is 5 and the three O atoms require 6 electrons.¹⁷ Our results based on density functional theory (DFT) indeed confirm this expectation. To see if AlO_2 and VO_3 can be used as building blocks of hyperhalogens we have studied neutral and negatively charged NaX_2 ($\text{X} = \text{AlO}_2$, and VO_3) clusters and compared the results with NaF_2 (Ref. 27) and $\text{Na}(\text{BO}_2)_2$. The results are rather unexpected. While $\text{Na}(\text{BO}_2)_2$ is found to be a hyperhalogen, $\text{Na}(\text{AlO}_2)_2$ and $\text{Na}(\text{VO}_3)_2$ are not. On the contrary, the ability of BO_2 as a building block of hyperhalogen is further confirmed by calculating the electron affinities of $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$. The underlying mechanism for the above anomaly in $\text{Na}(\text{AlO}_2)_2$ and $\text{Na}(\text{VO}_3)_2$ is studied by analyzing the relative stability of the dimers of each superhalogen units, namely, $(\text{BO}_2)_2$, $(\text{AlO}_2)_2$, and $(\text{VO}_3)_3$ clusters. Calculations are performed using density functional theory with a hybrid exchange-correlation functional. In Sec. II we provide a brief description of our theoretical procedure. The properties of BO_2 , AlO_2 , VO_3 , and their dimers are described in the Sec. III. The structures and spectroscopic properties of NaX_n and NaX_n^- ($\text{X} = \text{BO}_2$, AlO_2 , and VO_3) are given in Sec. IV and results on $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$ clusters are discussed in Sec. V. In Sec. VI, we provide a brief summary of our work.

II. COMPUTATIONAL DETAILS

Calculations are performed using the combination of Becke's hybrid 3-parameter exchange functional and Lee-Yang-Parr's correlation functional known as B3LYP.²⁸ The atomic orbitals are represented by Gaussian 6-311+G* (Ref. 29) basis sets. The geometries are first optimized without any symmetry constraint using GAUSSIAN 03 code.³⁰

^{a)}Electronic mail: kpradhan@vcu.edu.

Various initial structures with halogen/superhalogen moieties bound to the metal atom were used to determine the ground state geometries. All possible spin multiplicities are probed in order to determine the preferred ground-state spin. The convergence threshold for total energies and forces was set to 0.000001 eV and 0.001 eV/Å, respectively. No imaginary vibrational frequencies were noted, which mean that their geometries belong to the minima on the potential energy surface. The electron affinities (EA) are calculated as the difference between total energies of the anion and its neutral parent computed at the respective ground-state (GS) geometries. The vertical detachment energies (VDE) are computed as the differences in total energies of an anion and its neutral at the anion ground-state geometry. When the ground state geometries of the neutral and its anion are very different, it is likely that in photoelectron spectroscopy experiments, the ground state neutral may not be accessed, since the photoelectron transition is a vertical process. It is then necessary to look for a neutral isomer which is structurally similar to that of the ground state anion. One can also arrive at this structure by optimizing the neutral geometry with the GS geometry of the anionic cluster as a starting point. The energy difference between the GS of the anion and its structurally similar neutral isomer is defined as the adiabatic detachment energy (ADE). Our calculated electron affinity for BO_2 (4.35 eV) matches well with the experimental value (4.46 eV).²⁵ Similarly, the electron affinities of AlO_2 and VO_3 are calculated to be 4.05 eV and 4.47 eV which also agree well their corresponding experimental values of 4.23 eV (Ref. 25) and 4.36 eV,³¹ respectively. To study the sensitiveness of the calculated EA values to the choice of basis set we have repeated the calculations for BO_2 , AlO_2 , and VO_3 using 6-311+G(3df) basis set. The electron affinities of BO_2 , AlO_2 , and VO_3 are 4.32 eV, 4.01 eV, and 4.44 eV, respectively, which are in a good agreement with our results obtained using the 6-311+G* basis set. Our calculated electron affinity of BO_2 using CCSD(T)/6-311+G(3df) is 4.44 eV which also matches well with our B3LYP/6-311+G* calculations. In our earlier study, we had also shown that electron affinity of MnF calculated at the DFT-B3LYP level is very close to the corresponding CCSD(T) values.¹² Henceforth, all results given in this paper are at the B3LYP/6-311+G* level of theory, unless mentioned otherwise.

III. PROPERTIES OF BO_2 , AlO_2 , VO_3 , AND THEIR DIMERS

Previous studies on MF_n ($M = \text{Na}, \text{Mg}$) (Refs. 27 and 7) have shown that two of the F atoms tend to dimerize when number of the F atoms exceeds the maximal valence of the metal atom. In order to understand if such processes can also occur when superhalogens are used to decorate a metal atom, we started by first studying the dimers of BO_2 , AlO_2 , and VO_3 . The ground state geometries of neutral BO_2 , AlO_2 , and VO_3 along with their corresponding anionic geometries are shown in Fig. 1. The neutral and anionic geometries of BO_2 are both linear and have doublet and singlet spin ground states, respectively. Similar is the case with AlO_2 units. However, neutral VO_3 has a C_{3v} symmetry and changes to a more

FIG. 1. The ground state geometries of neutral and anionic BO_2 , AlO_2 , and VO_3 clusters. The bond lengths are in Å.

symmetric structure, D_{3h} in the anionic state. The calculated electron affinities of BO_2 , AlO_2 , and VO_3 are 4.35, 4.05, and 4.47 eV, respectively, and compare well with their respective experimental values 4.46,²⁵ 4.23,²⁵ and 4.36 eV.³¹ We note that these values exceed the electron affinity of halogen atoms and hence AlO_2 and VO_3 , just like BO_2 , are superhalogens.

Next we have studied the dimers of BO_2 , AlO_2 , and VO_3 . From the computed equilibrium geometry, binding energy, and electron affinity and their comparison with F_2 , we can determine to what extent these superhalogens mimic the behavior of halogen molecules. The ground state geometries of neutral and anionic $(\text{BO}_2)_2$, $(\text{AlO}_2)_2$, and $(\text{VO}_3)_2$ are given in Fig. 2. The neutral and anion geometries of $(\text{BO}_2)_2$ are very different; the neutral has an open structure where a linear BO_2 binds to another BO_2 that is bent. The anion geometry, on the other hand, is a closed structure composed of two bent BO_2 molecules. It is composed of two bridged O atoms and two terminal O atoms. The neutral and anion geometries of $(\text{AlO}_2)_2$, on the other hand, are similar and resemble the structure of anionic $(\text{BO}_2)_2$. The neutral and anion dimers of

FIG. 2. The ground state geometries of neutral and anionic $(\text{BO}_2)_2$, $(\text{AlO}_2)_2$, and $(\text{VO}_3)_2$ clusters; the bond lengths are in Å. The spin multiplicities of all the anions are 2.

TABLE I. The electron affinities (EA) of different superhalogen dimers (using 6-311+G* basis set) and their binding energies (BE). The figures in brackets are EA obtained with the 6-311+G(3df) basis set. The electron affinity of F atom is 3.49 (3.46) eV.

Cluster	EA (eV)	Binding energies	
		Channel	BE (eV)
F ₂	3.92 (3.69)	F ₂ → F + F	1.38
(BO ₂) ₂	4.71 (4.64)	(BO ₂) ₂ → BO ₂ + BO ₂	1.70
(AlO ₂) ₂	4.06 (3.97)	(AlO ₂) ₂ → AlO ₂ + AlO ₂	5.49
(VO ₃) ₂	5.52 (5.43)	(VO ₃) ₂ → VO ₃ + VO ₃	4.10

VO₃ also have similar geometries with two O atoms forming a bridge while four O atoms forming terminal bonds. The ground state spin multiplicity of neutral (BO₂)₂ is a singlet while it is a triplet for both (AlO₂)₂ and (VO₃)₂. The GS geometry of (VO₃)₂ is reported³² to be singlet in earlier calculations but we found that it to be 0.24 eV higher in energy than the triplet state. All the anions, on the other hand, have doublet spin states. The calculated electron affinities of (BO₂)₂, (AlO₂)₂, and (VO₃)₂ are 4.71, 4.06, and 5.52 eV, respectively. The electron affinity of (AlO₂)₂ matches well with available experimental value 3.98 eV.³³ We note that both (BO₂)₂ and (VO₃)₂ can be classified as superhalogens even though they do not contain a metal atom at the core.

The binding energies (BE) and electron affinities of the above superhalogen dimers are given in Table I and compared with the corresponding values for F₂. The electron affinity of F₂ molecule is always overestimated using any of the DFT methods.³⁴ The BE of (BO₂)₂, (AlO₂)₂, and (VO₃)₂ are 1.70, 5.49, and 4.10 eV, respectively. In comparison, the binding energy of F₂ is 1.38 eV. We will see in the following that the substantially large binding energies of AlO₂ and VO₃ dimers have important effect on their ability to form building blocks of hyperhalogens.

IV. NaX₂ (X = BO₂, AlO₂, and VO₃)

It has been demonstrated that NaF₂ is a superhalogen.²⁷ Here we want to see if NaX₂ (X = BO₂, AlO₂, and VO₃) can have electron affinities exceeding those of X = BO₂, AlO₂, and VO₃ and hence be termed as hyperhalogens. In order to make this comparison we have calculated the ground state geometries of neutral and anionic NaF₂ as well as the electron affinity at the same level of theory as used for NaX₂. To further validate our theoretical approach, the results on NaF₂ can be compared with previous calculations. In Fig. 3 we have shown the geometries of neutral and anionic NaF₂. The neutral NaF₂ has a bent geometry and transforms to a linear structure in the anionic case. The distance between the quasimolecular F₂ present in the neutral NaF₂ is 2.03 Å where as the calculated bond length of a free F₂ molecule is found to be 1.41 Å at the same level of theory. The calculated electron affinity of NaF₂ (4.69 eV) compares well with 4.86 eV found using a higher level of theory.²⁷ Because of the +1 valence state of Na, the F₂ molecule does not split into two F atoms in neutral NaF₂ but the bond length increases. However, the ex-

FIG. 3. The ground state geometries of neutral and anionic NaF₂, Na(BO₂)₂, Na(AlO₂)₂, and Na(VO₃)₂ clusters.

tra electron in the anionic species is able to split the F atoms. The calculated NBO (Ref. 35) charges on the Na atom are 0.98 e and 0.97 e, respectively in the neutral and anionic NaF₂. This shows clearly that the extra electron in the anion goes to the F atoms and accounts for the larger electron affinity of NaF₂.

In comparing the electron affinity of NaX₂ complexes with NaF₂, we note from Table I that the binding energies of (AlO₂)₂ and (VO₃)₂ dimers are substantially higher than that of F₂ or (BO₂)₂. What role will this play on the structure and electron affinity of Na(AlO₂)₂ and Na(VO₃)₂? In order to answer this question we have calculated the GS geometries and the electron affinities of NaX₂ (X = BO₂, AlO₂, and VO₃) clusters. In Fig. 3 we plot their ground state geometries. Unlike F₂ molecule in NaF₂, the dimers of BO₂, AlO₂ or VO₃ can be attached in many ways to the Na atom. However, we find that in the ground state geometries of neutral NaX₂, the geometries of neutral (BO₂)₂, (AlO₂)₂ or (VO₃)₂ shown in Fig. 2 remain more or less intact. The GS geometry of anionic Na(BO₂)₂ cluster does not retain the geometry of the free optimized neutral or anion of (BO₂)₂ dimers as shown in Fig. 2. Each unit of BO₂ is attached to the Na atom separately and closely resembles the linear structure of anionic NaF₂. But in the other two cases, the GS geometries of anionic Na(AlO₂)₂ or Na(VO₃)₂ clusters resemble the geometries of the corresponding dimers. This is because of the large BE in (AlO₂)₂ and (VO₃)₂ clusters compared to the BE of the (BO₂)₂ case. How does this affect the electron affinities of these two NaX₂ clusters? Interestingly, we find a difference in the electron affinities depending on whether each decorating unit is attached to the Na atom separately or in dimerized form. The electron affinities of Na(BO₂)₂, Na(AlO₂)₂, and Na(VO₃)₂ are 4.78, 3.26, and 4.26 eV, respectively. We have also mentioned the electron affinities using 6-311+G(3df) basis set in Table II. The electron affinities of Na(AlO₂)₂ and Na(VO₃)₂

TABLE II. Theoretical values (using 6-311+G* basis set) of electron affinity (EA), vertical detachment energy (VDE), and adiabatic detachment energy (ADE) (in eV) of NaX_2 ($X = \text{BO}_2$, AlO_2 , and VO_3), and $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$ clusters. NBO charges on Na and Mg atoms in neutral and anionic clusters are also given. The figures in brackets are EA obtained with the 6-311+G(3df) basis set.

Cluster	EA	VDE	ADE	NBO charges on Na/Mg atom	
				Neutral	Anion
$\text{Na}(\text{BO}_2)_2$	4.78 (4.66)	5.54	5.51	0.98 e	0.98 e
$\text{Na}(\text{AlO}_2)_2$	3.26 (3.19)	3.57	3.26	0.98 e	0.97 e
$\text{Na}(\text{VO}_3)_2$	4.26 (4.22)	4.76	4.26	0.96 e	0.94 e
$\text{Mg}(\text{BO}_2)_3$	5.90 (5.81)	6.56	6.54	1.70 e	1.70 e
$\text{Mg}_2(\text{BO}_2)_5$	6.57 (6.44)	6.75	6.62	1.61 e	1.61 e

are smaller than respective AlO_2 and VO_3 moieties. However, the electron affinity of $\text{Na}(\text{BO}_2)_2$ is larger than that of BO_2 , hence it can be classified as a hyperhalogen. Although this increase in the electron affinity is small, namely, 0.43 eV, it is numerically meaningful since the accuracy of the DFT energies is about 0.1 eV. We will show later that there is a larger change in the EAs of $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$ clusters as compared to BO_2 and $(\text{BO}_2)_2$ moieties.

The VDE and ADE values are also given in Table II. It is normally assumed that the ADE values of the anionic cluster measured in the experiments are equal to the EA. But this is not the case if there is a large change in the GS geometries between neutral and anionic clusters. Due to large difference in the GS geometries of neutral and anionic $\text{Na}(\text{BO}_2)_2$ clusters our calculated ADE value is indeed very different from the EA value. However, in $\text{Na}(\text{AlO}_2)_2$ and $\text{Na}(\text{VO}_3)_2$, the ADE values are very close to the EA value as GS geometries of neutral and anion are very similar.

In order to analyze the distribution of the extra charge in the anionic species, we have also given the NBO charges on the Na atom for each of the cluster in Table II. The charges on the Na atom in both neutral and anion clusters are the same. This implies that in all cases the extra charge in the anionic cluster goes to decorating the superhalogen moieties. The sharp contrast between the VDE and EA values of $\text{Na}(\text{AlO}_2)_2$ and $\text{Na}(\text{BO}_2)_2$ then has to originate from the large binding energies of AlO_2 and BO_2 dimers.

Because of the large binding energy of X_2 ($X = \text{AlO}_2$ and VO_3), the geometries of anionic and neutral clusters are similar. Consequently, the $(\text{AlO}_2)_2$ unit attached to Na atom remains almost the same in both neutral and anionic clusters and behaves like NaY [$Y = (\text{AlO}_2)_2$], i.e., $(\text{AlO}_2)_2$ unit behaves as a single ligand. Note that NaF has very small electron affinity²⁷ as compared to F. Thus, one can argue that electron affinity of NaY will be smaller than that of the electron affinity of Y. In fact, the electron affinity of $\text{Na}(\text{AlO}_2)_2$ is found to be much smaller than that of the $(\text{AlO}_2)_2$ cluster and is even smaller than that of AlO_2 . Had AlO_2 been attached to the Na atom as separated units, the electron affinity would have been larger than AlO_2 entity like that found in the case of $\text{Na}(\text{BO}_2)_2$. Similar is the case for $\text{Na}(\text{VO}_3)_2$ cluster.

We have searched for isomers of $\text{Na}(\text{AlO}_2)_2$ and $\text{Na}(\text{VO}_3)_2$ where AlO_2 and VO_3 moieties are differently attached to see if they may have hyperhalogen properties. The geometries and relative energies of the next higher energy iso-

mers for both neutral and anions are given in Fig. 4. In the case of each neutral cluster, the first low lying isomer is composed of Na bound to the dimerized form of BO_2 , AlO_2 , and VO_3 moieties. They are, respectively, 0.04, 0.01, and 0.60 eV above the ground state geometries given in Fig. 3. The inability of Na atom to break the bond between F atoms or superhalogen moieties in the neutral cluster is simply due to its monovalent character. For the anions the situation is different. All the low lying anion isomers are above the ground states with energies ranging from 1.72 eV to 2.17 eV. Their geometries are also very different from the ground state structures in Fig. 3. $\text{Na}(\text{BO}_2)_2$ anion's higher energy isomer is composed of a dimerized BO_2 attached to Na while in the ground state these moieties attach individually. Opposite is the case with anionic $\text{Na}(\text{AlO}_2)_2$. In $\text{Na}(\text{VO}_3)_2$ the low lying isomer shows the V atom sandwiched between two VO_3 units, but this isomer is 2.17 eV higher in energy than that of the ground state configuration in Fig. 3.

V. $\text{Mg}(\text{BO}_2)_3$ AND $\text{Mg}_2(\text{BO}_2)_5$

Since BO_2 superhalogens form hyperhalogens, we have investigated the properties of $\text{Mg}(\text{BO}_2)_3$. In addition, we also studied $\text{Mg}_2(\text{BO}_2)_5$ to see whether this could also be a hyperhalogen. Since Mg is divalent, we expect that $\text{Mg}(\text{BO}_2)_3$ as well as $\text{Mg}_2(\text{BO}_2)_5$ need an extra electron to satisfy their

FIG. 4. Higher energy isomers of neutral and anionic $\text{Na}(\text{BO}_2)_2$, $\text{Na}(\text{AlO}_2)_2$, and $\text{Na}(\text{VO}_3)_2$ clusters and their energy relative to the ground state.

FIG. 5. The ground state geometries of neutral and anionic MgF_3 , $\text{Mg}(\text{BO}_2)_3$ clusters. Bond lengths of Mg borates are not given to avoid cluttering.

electronic shell closure. If this electron is distributed over the BO_2 moieties, the $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$ based clusters should be hyperhalogens. We further compare these with the results in MgF_3 (Ref. 7) and Mg_2F_5 (Ref. 36) to discern the role superhalogens vs halogens play when decorating the Mg atom.

We start with the GS geometries of MgF_3 and Mg_2F_5 clusters in Fig. 5. Because of the divalent nature of Mg atom, two of the F atoms form a quasimolecular species in neutral MgF_3 and but bind individually in the anionic cluster. The neutral Mg_2F_5 is composed of two bridged and three terminal F atoms. Of these three F atoms, two are quasimolecular. The structure changes to a more symmetric form in the anionic cluster with three bridged and two terminal F atoms. The GS geometries of the MgF_3 and Mg_2F_5 clusters matches well with previous calculations. The electron affinities of MgF_3 and Mg_2F_5 are 6.22 and 6.92 eV, respectively. The respective VDE values are 6.61 and 7.56 eV. Previously calculated VDE values using OVGF (Refs. 7 and 36) are even higher than our values and there is no experimental data available for the verification.

The geometries of neutral and anionic $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$ clusters are compared with MgF_3 and Mg_2F_5 in Fig. 5. Analogous to that in MgF_3 , we note that in $\text{Mg}(\text{BO}_2)_3$ cluster two of the BO_2 moieties dimerize while the third one is attached to the Mg atom individually. In the anionic $\text{Mg}(\text{BO}_2)_3$ cluster each BO_2 unit is attached separately to the Mg atom. In the neutral $\text{Mg}_2(\text{BO}_2)_5$ geometry, the two Mg atoms are bridged by two BO_2 units. In addition, one of the Mg atoms is attached to a BO_2 dimer while the other Mg is attached to a single BO_2 unit. This is analogous to what we found in the Mg_2F_5 cluster as well. Once again the anionic GS is very similar to the anionic Mg_2F_5 cluster and can be visualized by replacing each of the F atoms with a BO_2 unit. The electron affinity of $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$ are 5.90 and 6.57 eV. Since these values are larger than electron affinity of BO_2 one can argue that BO_2 is a potential candidate for hyperhalogen.

FIG. 6. Higher energy isomers of neutral and anionic Mg_2F_5 , $\text{Mg}(\text{BO}_2)_3$ clusters and their energy relative to the ground state.

The calculated NBO charge on Mg atom is 1.70 e in both the neutral and anionic $\text{Mg}(\text{BO}_2)_3$ clusters, and 1.61 e in both the neutral and anionic $\text{Mg}_2(\text{BO}_2)_5$ clusters. The VDE values of $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$ are 6.56 and 6.75 eV, respectively. We have also given the ADE for $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$ clusters in Table II which are different from the EA values because of the change in geometry between the neutral and anionic clusters. We look forward to experimental verification of our results.

The geometries and relative energies of the next higher energy isomers for both neutral and anions of $\text{Mg}(\text{BO}_2)_3$ and $\text{Mg}_2(\text{BO}_2)_5$ are given in Fig. 6. The next high energy isomer of neutral $\text{Mg}(\text{BO}_2)_3$ is composed of three of the $(\text{BO}_2)_3$ units³⁷ polymerizing and then binding to Mg. Its energy is 0.11 eV higher than that of the GS geometry. Similarly, in the next higher energy isomer of anionic $\text{Mg}(\text{BO}_2)_3^-$ cluster, two of the BO_2 units form a dimer and attach to the Mg atom as compared to the three separate BO_2 moieties attached to Mg in the GS. The next higher energy isomer of neutral $\text{Mg}_2(\text{BO}_2)_5$ has a similar geometry to that of the anionic GS and the energy is 0.05 eV higher than the neutral GS. In the case of anionic $\text{Mg}_2(\text{BO}_2)_5^-$ the geometry of next isomer is similar to the GS geometry of neutral $\text{Mg}_2(\text{BO}_2)_5$ cluster, but the $(\text{BO}_2)_2$ dimer structure present in the later is separated into two BO_2 units. In the case of anions, the energy difference between the GS and next higher energy isomers are large.

VI. CONCLUSIONS

Using density functional theory, we performed a systematic study of the interaction of various superhalogens (BO_2 , AlO_2 , and VO_3) with Na and Mg atoms and compared these results when the superhalogens are replaced by F. Our study reveals that the binding energy (BE) of $(\text{BO}_2)_2$, $(\text{AlO}_2)_2$, and $(\text{VO}_3)_2$ clusters plays an important role in determining the electron affinity of NaX_2 ($X = \text{BO}_2$, AlO_2 , and VO_3) clusters. The electron affinity of $\text{Na}(\text{BO}_2)_2$ exceeds the electron affinities of BO_2 and hence can be termed as a hyperhalogen. However, in other two cases, the electron affinities are less than their respective superhalogens. This is because the binding energies of AlO_2 and VO_3 dimers are large compared to the energy gain when an extra electron is attached to $\text{Na}(\text{AlO}_2)_2$ and $\text{Na}(\text{VO}_3)_2$ species. Hence, these do not behave as hyperhalogens. We extended our study to Mg atom(s) decorated with BO_2 moieties. Both $\text{Mg}(\text{BO}_2)_2$ and $\text{Mg}_2(\text{BO}_2)_5$

are found to be hyperhalogens. These calculations reveal that BO_2 can serve as a potential candidate for hyperhalogens with other metal atoms at the core. We hope that our theoretical predictions will motivate experimentalists in search of hyperhalogens.

ACKNOWLEDGMENTS

This work was partially supported by grants from the Defense Threat Reduction Agency (Grant No. HDTRA1-09-1-0025) and the Department of Energy (DOE) and used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the (U.S.) DOE (Contract No. DE-AC02-05CH11231).

- ¹N. Bartlett and D. H. Lohmann, *Proc. Chem. Soc., London* **3**, 115 (1962).
- ²G. L. Gutsev and A. I. Boldyrev, *Chem. Phys. Lett.* **108**, 250 (1984).
- ³M. K. Scheller, R. N. Compton, and L. S. Cederbaum, *Science* **270**, 1160 (1995).
- ⁴G. L. Gutsev, B. K. Rao, P. Jena, X.-B. Wang, and L.-S. Wang, *Chem. Phys. Lett.* **312**, 598 (1999).
- ⁵X.-B. Wang, C.-F. Ding, L.-S. Wang, A. I. Boldyrev, and J. Simons, *J. Chem. Phys.* **110**, 4763 (1999).
- ⁶B. M. Elliot, E. Koyle, A. I. Boldyrev, X.-B. Wang, and L.-S. Wang, *J. Phys. Chem. A* **109**, 11560 (2005).
- ⁷I. Anusiewicz, M. Sobczyk, I. Dabkowska, and P. Skurski, *Chem. Phys.* **291**, 171 (2003).
- ⁸G. L. Gutsev, P. Jena, and R. J. Bartlett, *Chem. Phys. Lett.* **292**, 289 (1998).
- ⁹C. Sikorska, S. Smuczynska, P. Skurski, and I. Anusiewicz, *Inorg. Chem.* **47**, 7348 (2008).
- ¹⁰J. Yang, X.-B. Wang, X.-P. Xing, and L.-S. Wang, *J. Chem. Phys.* **128**, 201102 (2008).
- ¹¹K. Pradhan, G. L. Gutsev, and P. Jena, *J. Chem. Phys.* **133**, 144301 (2010).
- ¹²K. Pradhan, G. L. Gutsev, C. A. Weatherford, and P. Jena, *J. Chem. Phys.* **134**, 234311 (2011).
- ¹³X. Yang, X.-B. Wang, and L.-S. Wang, S. Q. Niu, and T. Ichiye, *J. Chem. Phys.* **119**, 8311 (2003).
- ¹⁴P. Koirala, M. Willis, B. Kiran, A. K. Kandalam, and P. Jena, *J. Phys. Chem. C* **114**, 16018 (2010).
- ¹⁵X.-B. Wang, and L.-S. Wang, R. Brown, P. Schwerdtfeger, D. Schroder, and H. Schwarz, *J. Chem. Phys.* **114**, 7388 (2001).
- ¹⁶G. L. Gutsev, P. Jena, H.-J. Zhai, and L.-S. Wang, *J. Chem. Phys.* **115**, 7935 (2001).
- ¹⁷K. Pradhan, G. L. Gutsev, C. A. Weatherford, and P. Jena, *J. Chem. Phys.* **134**, 144305 (2011).
- ¹⁸G. L. Gutsev, C. A. Weatherford, K. Pradhan, and P. Jena, *J. Phys. Chem. A* **114**, 9014 (2010).
- ¹⁹S. Smuczynska and P. Skurski, *Chem. Phys. Lett.* **443**, 190 (2007).
- ²⁰D. F. Hunt, G. C. Stafford, Jr., F. W. Crow, and J. W. Russell, *Anal. Chem.* **48**, 2098 (1976).
- ²¹J. C. Champarnaud-Mesjard and B. Frit, *Eur. J. Solid State Inorg. Chem.* **29**, 161 (1992).
- ²²F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Wiley-Interscience, New York, 1988).
- ²³F. Arnold, *Nature (London)* **284**, 610 (1980).
- ²⁴M. Willis, M. Gotz, A. K. Kandalam, G. F. Gontefor, and P. Jena, *Angew. Chem., Int. Ed.* **49**, 8966 (2010).
- ²⁵H. J. Jhai, L. M. Wang, S. D. Li, and L. S. Wang, *J. Phys. Chem. A* **111**, 1030 (2007).
- ²⁶Y. A. Feng, H. G. Xu, W. J. Zheng, H. M. Jhao, A. K. Kandalam, and P. Jena, *J. Chem. Phys.* **134**, 094309 (2011).
- ²⁷G. L. Gutsev, R. Bartlett, A. I. Boldyrev, and J. Simons, *J. Chem. Phys.* **107**, 3867 (1997).
- ²⁸B. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ²⁹R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).
- ³⁰M. J. Frisch, G. N. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.
- ³¹H. B. Wu and L.-S. Wang, *J. Chem. Phys.* **108**, 5310 (1998).
- ³²Y. Wang, X. Gong, and J. Wang, *Phys. Chem. Chem. Phys.* **12**, 2471 (2010).
- ³³S. R. Desai, H. B. Wu, C. M. Rohlfing, and L. S. Wang, *J. Chem. Phys.* **106**, 1309 (1997).
- ³⁴T. Wroblewski, K. Hubisz, and J. Antonowicz, *Opt. Appl.* **40**, 601 (2010).
- ³⁵A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.* **88**, 899 (1988).
- ³⁶I. Anusiewicz and P. Skurski, *Chem. Phys. Lett.* **440**, 41 (2007).
- ³⁷H. Jin and W. Dingsheng, *Chin. Phys. Lett.* **3**, 157 (1986).