

Theoretical Study of Neutral and Ionic States of Small Clusters of Ga_mO_n ($m, n = 1, 2$)

S. Gowtham,[†] Aurora Costales,^{*,‡} and Ravindra Pandey[†]

Department of Physics, Michigan Technological University, Houghton, Michigan 49931 and Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, 33006-Oviedo, Spain

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The structure, bonding, vibrational, and electronic properties of small clusters of gallium oxide, Ga_mO_n ($m, n = 1, 2$) are studied here with a focus on the changes induced by the addition or removal of an electron from the neutral species. It is found that the addition of an electron introduces relatively larger structural changes than the removal of an electron from the neutral cluster. The values of ionization potential and electron affinity of these clusters are calculated, for the first time, in this study. Analysis of the atomic charges and electronic properties predicts a kind of instability in Ga_2O^- . In Ga_2O_2 , the linear Ga–O–Ga–O isomer forms the ground state of the neutral cluster. The cationic structure also prefers the linear configuration, since the ionized electron comes out of an antibonding molecular orbitals of the neutral Ga_2O_2 . The anionic Ga_2O_2^- , on the other hand, prefers the rhombus structure as a ground state since LUMO of the neutral Ga_2O_2 consists of a Ga–O bonding orbital.

I. Introduction

Nanoscale structures have attracted great research interest due to their unique physical properties and significant applications. Nanotubes and nanowires have novel properties differing from bulk materials, owing to their one-dimensionality. Gallium oxide low dimensional nanostructures have been recently created by physical evaporation¹ and arc-discharge^{2,3} methods, thus opening up a new research area with promising applications.

Monoclinic gallium oxide ($\beta\text{-Ga}_2\text{O}_3$) has the widest band gap (4.8 eV) among semiconducting metal oxides. At high temperatures, gallium oxide thin films have shown significant conductance response to oxygen gas concentrations, and at low temperatures the sensitivity switches to reducing gases such as carbon monoxide, methane, and ammonia. In the form of low dimensional nanostructures such as nanowires, nanosheets, and nanoribbons, it shows a very high surface-to-volume ratio, which provides a larger reaction surface using only very small amounts of the oxide material. This simultaneously increases gas-sensing reaction times while reducing power requirements associated with heating the sensors. These attributes provide great advantages in gas sensing over gallium oxide thin films and can provide a means by which gallium oxide based systems can effectively solve problems associated with conventional tin oxide sensors.

Small clusters of gallium oxide are expected to provide useful prototype models to understand the physics and chemistry of surfaces and nanostructures. The smaller size of the clusters makes it possible to obtain a detailed geometric, electronic, and bonding information that can also be used to benchmark theoretical methods to be used in the larger structural elements. However, there is a dearth of both theoretical and experimental work on gallium oxide at the cluster level. A few scattered studies have been reported on diatomic GaO and triatomic Ga_2O , and on GaO_2 . For example, the vibrational spectrum of the GaO molecule is well known.⁴ Structural and vibrational properties

of neutral GaO_2 have also been reported earlier.^{5,6} In neutral Ga_2O , both experimental studies^{7–15} and ab initio calculations¹⁶ were carried out to settle the controversy of its ground state configuration being either linear or bent.

Our aim is to perform a systematic study of the evolution of the structural, vibrational, bonding, and electronic properties with the cluster size to determine their convergence to the corresponding bulk values. In this paper, as our starting point, we present the results of a theoretical work on neutral and ionized small Ga_mO_n ($m, n = 1, 2$) clusters pursuing analysis of the structural changes induced upon addition or removal of an electron. The organization of the paper is as follows: Section II deals with the computational methodology. Section III discusses the calculated structural and vibrational properties. Section IV presents the atomic and bonding properties. Section V presents a report on the electronic properties. Finally, Section VI gives a summary of the results.

II. Methodology

Electronic structure calculations were performed on neutral and singly ionized small clusters of gallium oxide, Ga_mO_n ($m, n = 1, 2$), solving the Kohn–Sham equations in the framework of Density Functional Theory, using the Gaussian 98 code.¹⁸ The Gradient Corrected Becke's three-parameter hybrid exchange functional¹⁹ and the Lee, Yang, and Parr correlation functional²⁰ were employed in these calculations.

The choice of DFT-B3LYP methodology together with the 6-31+G** basis set is based on our previous experience with small clusters of gallium nitride.²¹ It is also to be noted here that the choice is based on the equilibrium between the criteria of quality and the available computational resources, since we will extend the study to large gallium oxide clusters. Table 1, however, includes the results on the GaO molecule showing the convergence of the bond length and frequency with respect to the basis sets.

All of the isomers analyzed in this study have been fully optimized. The convergence criterion was 10^{-4} hartree/Å for the gradient and 10^{-9} hartree for the energy. The stability of

[†] Michigan Technological University.

[‡] Universidad de Oviedo.

TABLE 1: Electronic State, Bond Length (Å), Dissociation Energy (eV), and Vibrational Frequency (cm⁻¹) of Neutral and Ionized GaO

	$2S+1\Lambda$	$R_e(\text{Å})$	$D_e(\text{eV})$	$\omega_e(\text{cm}^{-1})$
GaO				
experiment ⁴	$^2\Sigma$	1.74		767
this work				
6-31G**	$^2\Sigma$	1.73	4.25	708
6-31+G**	$^2\Sigma$	1.74	4.29	696
6-311G**	$^2\Sigma$	1.72	4.43	739
6-311+G**	$^2\Sigma$	1.72	4.35	726
GaO				
6-31+G**	$^2\Sigma$	1.74	4.29	696
GaO ⁻				
6-31+G**	$^1\Sigma$	1.74	5.22	775
GaO ⁺				
6-31+G**	$^3\Sigma$	1.94	0.43	410

the lowest energy configurations (neutral, anionic, and cationic) was checked by computing the vibrational frequencies under harmonic approximation, with analytical force constants. The atomic and bonding properties have been studied under the Quantum Theory of Atoms in Molecules (QTAM).²² To perform the QTAM analysis, we have used the AIMPAC95 package²³ with the Promega algorithm for integration of the atomic properties in which the error in the total charge is less than 10^{-3} e.

III. Results and Discussion

We will begin our discussion with the diatomic GaO in neutral and singly ionized charged states. The results for the triatomic and dimer clusters will be discussed subsequently.

A. Structural and Vibrational Properties: GaO, GaO⁺, and GaO⁻. The electronic states together with the structural properties for the neutral, anionic, and cationic gallium oxide are collected in Table 1. The dissociation energies are computed with respect to the atoms in their ground states using the same theoretical scheme. However, in the case of GaO⁻ and GaO⁺ dissociation products, the electron added or removed was assigned to oxygen and gallium atoms respectively, in accordance with Pauling's electronegativity values (Ga: 1.6 and O: 3.5). The electronic state for the neutral GaO is predicted to be a $^2\Sigma$ in agreement with the experimental observation.⁴ For GaO⁻ and GaO⁺, calculations find the state to be $^1\Sigma$ and $^3\Sigma$, respectively. Calculations show that the inclusion of a diffuse function in the basis set produces a variation of about 1% in bond length, 2% in dissociation energy, and 2% in frequency. In subsequent calculations, we will therefore include the diffuse function in our small clusters calculations for the optimum quality, but we note that the diffuse function could be ignored for larger clusters without losing too much precision.

The anionic GaO was found to be more stable than the neutral GaO, with nearly the same value for the bond length and a higher stretching frequency (775 cm⁻¹) indicating that the Ga–O bond is stronger than that in neutral GaO. This is consistent with the picture given by the molecular orbitals. The electron added to the neutral GaO occupies the LUMO (i.e., Lowest Occupied Molecular Orbital), which has a σ bonding character. The anionic GaO therefore completes a molecular orbital stabilizing the system. For the cationic case, the ionized electron comes out from a σ bonding orbital of the neutral GaO. It therefore results in the less stable configuration with a larger bond length and a smaller vibrational frequency.

B. Structural and Vibrational Properties: Triatomic Clusters. 1. *GaO₂*. Table 2 collects the results for both linear and bent isomers (see Figure 1), which are found to be in a

TABLE 2: Isomeric Configurations of GaO₂ and Ga₂^a

isomer	I(C _v)	II(D _h)	III(C _{2v})	IV(C _s)	V(C _s)
GaO ₂					
ΔE	0.62	0.12	0.00	stII	stIII
$R_{\text{Ga-O}}$	1.90	1.71	2.08		
\overline{BE}	2.33	2.58	2.54		
GaO ₂ ⁻					
ΔE	2.93	0.00	stII	stII	1.92
$R_{\text{Ga-O}}$	1.78	1.71			1.92
\overline{BE}	2.26	3.24			2.60
GaO ₂ ⁺					
ΔE	0.00	3.27	stII	stII	stI
$R_{\text{Ga-O}}$	2.70	1.74			
\overline{BE}	1.82	0.73			
Ga ₂ O					
ΔE	2.76	0.00	stII	0.56	stII
$R_{\text{Ga-O}}$	1.69	1.83		1.85, 1.95	
\overline{BE}	2.23	3.15		2.96	
Ga ₂ O ⁻					
ΔE	3.51	0.03	0.00	stIII	stII
$R_{\text{Ga-O}}$	1.72	1.84	1.86		
\overline{BE}	1.45	2.61	2.62		
Ga ₂ O ⁺					
ΔE	1.21	0.00	stII	stII	stII
$R_{\text{Ga-O}}$	1.71	1.82			
\overline{BE}	2.00	2.40			

^a ΔE is the energy (eV) relative to the most stable isomer, $R_{\text{Ga-O}}$ is the bond length (Å) and \overline{BE} is the binding energy per atom (eV). The notation stX represents the case where the optimization leads to the configuration X.

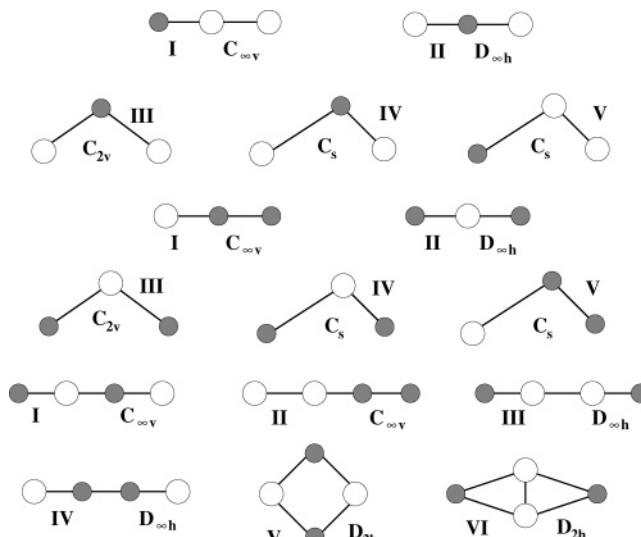


Figure 1. Schematic representation of GaO₂, Ga₂O, and Ga₂O₂ cluster configurations considered here. The filled and empty circles represent Ga and O atoms, respectively.

doublet electronic state. The lowest energy isomer of the neutral GaO₂ is a bent configuration with C_{2v} symmetry in which $R_{\text{Ga-O}}$ is 20% larger than that of GaO. The O–O bond is also 12% larger than the diatomic oxygen molecule, and the O–Ga–O angle is 38°. Analysis of the normal modes of vibration (see Table 3) finds the lowest frequency mode to be the Ga–O asymmetric stretching, the next one to be the Ga–O symmetric stretching, and the highest frequency mode to be stretching of the O–O bond.

In GaO₂⁻ isomers, the singlet electronic state is lower in energy than the triplet. The ground state is a linear D_{∞h} structure

TABLE 3: Frequency Values (ω) in cm^{-1} of the Normal Modes of Vibration for the Neutral, Anionic, and Cationic Clusters

cluster	symmetry	frequency (mode) (cm^{-1})
GaO ₂		
$q = 0$	C_{2v}	319 (b_2), 416 (a_1), 1166 (a_1)
$q = -1$	D_h	213 (π_u), 738 (σ_g), 879 (σ_u)
$q = +1$	C_v	80 (σ), 108 (π), 1645 (σ)
Ga ₂ O		
$q = 0$	D_h	98 (π_u), 285 (σ_g), 812 (σ_u)
$q = -1$	C_{2v}	79 (a_1), 491 (a_1), 536 (b_2)
$q = +1$	D_h	149 (π_u), 275 (σ_g), 625 (σ_u)
Ga ₂ O ₂		
$q = 0$	C_v	75 (π), 201 (π), 282 (σ), 832 (σ), 941 (σ)
$q = -1$	D_{2h}	197 (b_{3u}), 276 (a_g), 450 (b_{1u}), 464 (b_{3g}), 559 (b_{2u}), 629 (a_g)
$q = +1$	C_v	80 (π), 210 (π), 242 (σ), 653 (σ), 896 (σ)

(i.e., O–Ga–O) in which the first vibrational mode corresponds to out-of-plane bending. The next two modes involve symmetric and asymmetric stretching of the Ga–O bonds, respectively. These vibrational frequency values (Table 3) bracket the diatomic anion value (Table 1) in agreement with the coupling of two similar bonds.

Cationic isomers of GaO₂ were found to be lower in energy in the triplet electronic state than in the singlet electronic state, a different behavior compared to the anionic clusters. The ground state is a $C_{\infty v}$ linear configuration (i.e., Ga–O–O) formed by a diatomic oxygen molecule weakly bonded to a gallium cation. The O–O bond length is exactly the same as in the diatomic oxygen molecule, the Ga–O internuclear distance (2.70 Å) is quite a bit larger than the distance (1.74 Å) of GaO. Analyzing the vibrational modes collected in Table 3, we find that the lowest frequency mode corresponds to the stretching movement of the Ga–O bond. The value is small, indicating a weak bond between this pair of atoms. The π mode represents bending out of plane of the molecule. The highest frequency mode involves only the stretching of the O–O bond, and its value is quite close to that of the O₂ molecule (1642 cm^{-1}).

In summary, GaO₂[−] is the most ionic structure, where a Ga ion is bonded to two oxygen ions in a totally symmetric linear configuration having a singlet electronic spin state. Removal of an electron breaks the symmetry in the wave function, resulting in a bent configuration for the neutral GaO₂. Removal of another electron then leads to a new linear asymmetric structure with a triplet spin state for GaO₂⁺.

2. *Ga₂O*. In neutral Ga₂O, the singlet electronic state is found to be lower in energy than the triplet one. The ground state is the $D_{\infty h}$ symmetric linear structure (i.e., Ga–O–Ga). The optimization of the bent configurations (see Figure 1) always leads to the linear configuration. Since the asymmetric linear structure $C_{\infty v}$ is about 3 eV higher in energy, a preference for the metal–oxygen bond over the metal–metal bond can be observed in the neutral Ga₂O. This is consistent with the computed binding energy of 1.47 and 4.27 eV for the Ga–Ga and Ga–O bonds, respectively.

For the neutral Ga₂O, the high temperature electron diffraction results suggest it to be in the C_{2v} configuration with an apex angle of 140° and a bond length of 1.84 Å.⁸ Later, a reassessment of the electron diffraction data suggested that the molecule is linear.⁹ Since then, a few more experimental studies on Ga₂O were not able to provide a unique assignment for its ground state.^{11–14} On the other hand, ab initio calculations at HF, MP2, and CISD levels¹⁶ yielded a linear structure in agreement with the more recent experiments.^{7,15} Our DFT-

TABLE 4: Isomeric Configurations of Ga₂O₂^a

isomer	I(C_v) ^b	II(C_v)	III(D_h)	IV(D_h)	V(D_{2h})	VI(D_{2h})
Ga ₂ O ₂						
ΔE	0.00	5.09	2.50	1.93	0.21	1.30
R_{Ga-O}	1.74	1.77	1.83	1.66	1.86	2.03
\overline{BE}	3.20	1.93	2.58	2.72	3.15	2.88
Ga ₂ O ₂ [−]						
ΔE	1.58	5.55	4.67	2.30	0.00	1.00
R_{Ga-O}	1.92	1.76	1.84	1.73	1.90	1.94
\overline{BE}	2.99	1.99	2.21	2.95	3.38	3.13
Ga ₂ O ₂ ⁺						
ΔE	0.00	2.44	0.97	2.93	0.29	1.14
R_{Ga-O}	1.70	1.80	2.07	1.71	1.85	1.99
\overline{BE}	2.45	1.84	2.21	1.72	2.38	2.17

^a ΔE is energy (eV) relative to the most stable isomer, R_{Ga-O} is the bond length (Å), and \overline{BE} is the binding energy per atom (eV).
^b Other two values of R_{Ga-O} are 1.84, 1.67 (neutral); 1.79, 1.75 (anion); and 1.96, 1.79 (cation).

B3LYP results also predict a symmetric linear structure as a global minimum.

Cationic and anionic Ga₂O have been found to be in the doublet spin electronic state. In both cases, the ground state is governed by the relative strengths of bond energies that favor Ga–O over Ga–Ga bonds. In Ga₂O[−], it is an angular structure (C_{2v}) with angle of 110°, followed by the linear symmetric configuration ($\Delta E = 0.03$ eV). On the other hand, Ga₂O⁺ maintains a linear symmetric structure, as is the case with neutral Ga₂O.

In Ga₂O[−], the lowest frequency vibrational mode corresponds to the flexion movement, and the next two modes correspond to the symmetric and asymmetric stretching of the two Ga–O bonds, respectively. In both neutral and cationic Ga₂O, the degenerate modes represent (out-of-plane) bending movements and the last two σ modes correspond to symmetric and asymmetric stretching of the Ga–O bonds, respectively. For the neutral Ga₂O, our frequency values are in good agreement with the MP2 frequencies obtained by Leszczynski et al.¹⁶ (52, 300, and 854 cm^{-1}).

In neutral Ga₂O, a very good agreement was found with the experimental value of the asymmetric stretching mode (ν_3), 823 cm^{-1} being the most recent value.⁵ The calculated DFT-B3LYP value of ν_3 is 812 cm^{-1} (Table 3). A recent theoretical study by Jones et al.¹⁷ reported the asymmetric and symmetric stretch modes of Ga₂O to be 806 and 300 cm^{-1} , respectively, and our calculations found these to be 812 and 285 cm^{-1} . Hinchcliffe et al.¹³ argue that heavier suboxides should have a bending mode below 100 cm^{-1} , and our calculations found this to be 98 cm^{-1} . Analysis of the vibrational spectrum by Hinchcliffe et al.¹³ also points out a wrong assignment of ν_1 and ν_2 modes at 416 and 596 cm^{-1} , respectively, made by Carlson et al.¹²

C. Structural and Vibrational Properties: Ga₂O₂. Figure 1 shows different isomeric configurations of Ga₂O₂ considered in this study. Total energies of all neutral isomers were computed in singlet and triplet electronic spin states. The results find singlet states to be lower in energy than the triplet ones. The optimal values of the bond lengths and the energies relative to the most stable isomer are collected in Table 4.

The relative stability of the various isomers of Ga₂O₂ can be interpreted in terms of the bond energies, which are calculated to be 4.29, 1.47, and 5.83 eV for the Ga–O, Ga–Ga, and O–O bonds, respectively. The calculated results find the most stable configuration to be the linear structure, I- $C_{\infty v}$. Based on the bond energetics, the isomer III- $D_{\infty h}$ is expected to be the lowest

energy isomer of the neutral Ga_2O_2 . However, it is 2.50 eV higher in energy due to the charge transfer from Ga to O atoms yielding a 12% increase of $R_{\text{O}-\text{O}}$ when compared to the O_2 molecule. On the other hand, the $V-D_{2h}$ rhombic structure consists of a higher number of Ga–O bonds than in the $I-C_{\infty v}$ isomer, but $R_{\text{Ga}-\text{O}}$ is larger than those in the diatomic molecule. This is a consequence of the electrostatic repulsion between equal atoms making the bond angles close to 90° . The competing factors, electrostatic repulsion and a higher number of Ga–O bonds, locate this isomer to be only 0.21 eV above in energy with respect to the lowest $I-C_{\infty v}$ isomer.

In anionic Ga_2O_2 , the presence of an extra electron results in the ground state being the $V-D_{2h}$ structure. This is due to the fact that the LUMO of the ground state ($I-C_{\infty v}$) of the neutral Ga_2O_2 has an antibonding character. This fact results in the increase of interatomic distances, upon accommodation of the extra electron. On the other hand, the LUMO in the neutral rhombus structure of Ga_2O_2 has a bonding character in the Ga–O bonds.

The ground state of the cationic Ga_2O_2 does not show any change in the cluster configuration. The ionized electron comes from an antibonding molecular orbital of neutral Ga_2O_2 . The resulting cationic dimer has a partially filled antibonding molecular orbital.

The relative ordering in terms of energy of the cationic and anionic isomers is similar to that in the neutral case, only with the following difference: the $\text{III}-D_{\infty h}$ is stabilized in the cationic cluster and is destabilized in the anionic cluster. This may be due to the HOMO of the cationic cluster, a bonding orbital mainly localized over the O–O bond resulting in the 7% contraction of O–O interatomic distance relative to that in the neutral Ga_2O_2 . This O–O bond has highest binding energy and determines the stability of the cluster. Also, it is important to notice that the $\text{II}-C_{\infty v}$ is high in energy in both neutral and anionic clusters relative to that in the cationic state. The stabilization in the cationic state may be due to the elongation of the Ga–Ga bond, making it almost a disconnected cluster in which a Ga atom is weakly bonded to the O–O–Ga unit. The $\text{IV}-D_{\infty h}$ anionic isomer is also almost disconnected, because the Ga–Ga interatomic distance is very large and two GaO molecules are weakly bonded by means of the weak Ga–Ga interaction. Due to the lack of experimental and theoretical studies on the gallium oxide dimers, we compare our calculated results with the values reported for the aluminum oxide dimers. Early semiempirical and ab initio calculations performed on Al_2O_2 suggested that there were two stable isomers: one was a square cyclic structure (D_{2h}) and the other was a linear configuration less stable than the square.²⁵ Later SCF and MP2 calculations determined that there were two minima: one almost square and the other a rhombus.^{25–29} The linear and cyclic structures are also found to be the minima for Ga_2O_2 , but two striking differences with Al_2O_2 were noticed: the linear structure is the lowest in energy followed very closely in energy by the square cyclic D_{2h} . To find a rhombus minimum, the optimization procedure should start with a Ga–O–Ga angle close to 160° , otherwise the structure goes to the square one. The rhombus isomer is 1.30 eV above the linear case in energy, and the Ga–O bond length is 2.03 Å.

The values of the normal vibration frequencies are collected in Table 3 for the neutral, cationic, and anionic Ga_2O_2 in their ground states. In the neutral and cationic cases, two low degenerate modes present the bending out-of-plane movements, the first π vibration corresponds to the bending of the Ga–O–Ga angle and the second one is associated with the bending of

both O–Ga–O and Ga–O–Ga angles. The rest of the normal modes correspond to the stretching movements of the cluster. The lower mode is a symmetric stretching of both Ga and the outer O atoms without any participation of the central oxygen in the movement. The next two frequencies are associated with the asymmetric and symmetric stretching of the oxygen atoms, respectively. The oxygen atoms are moving in phase whereas the central gallium is out of phase. In the anionic Ga_2O_2 cluster, the out-of-plane bending of the cluster is associated with the lowest frequency b_{3u} mode. The a_g mode involves the bending of the four angles leading to a rhombic distortion. Next, b_{1u} , and b_{3g} modes show a quasidegeneracy because they correspond to a ring torsion where the movement of two oxygen atoms is in phase and out of phase, respectively. The b_{2u} mode represents O–O symmetric stretching. Lastly, the a_g is a breathing mode of the O–O pair in anionic Ga_2O_2 .

IV. Bonding and Atomic Properties

The QTAM approach is used here for determining the character of the chemical bond in these clusters. The atomic charges were computed to study the effect of addition or removal of an electron in these systems. It is to be noted here that the topological atomic charges are mostly independent of the computation method and are calculated by the integration of the electron density over the atomic basin.²² The topological molecular graphs are constructed by linking atoms that are endpoints of the topological bond paths.²²

The topological structures of neutral and ionized Ga_mO_n ($m, n = 1, 2$) clusters considered in this work are almost the same as those drawn in Figure 1, with the only exception being the neutral GaO_2 , in which two oxygen atoms are bonded, resulting in a closed triangle structure.

The ground state configurations of the clusters considered here contain two different kinds of bonds: Ga–O and O–O. Both ρ and $\nabla^2\rho$ at the bond critical points follow an exponential relationship with the distance for a given pair of atoms.³⁰ In this way, the short bonds have a higher density, indicating a stronger bond. In all cases, Ga–O bond shows a positive $\nabla^2\rho$ value, indicating a non-sharing ionic-like interaction. On the other hand, O–O bonds show a negative $\nabla^2\rho$ value, indicating a sharing covalent-like interaction.

The topological charges for the monomer, triatomic, and dimer clusters in their lowest energy isomers are collected in Table 5. In neutral GaO, there is a considerable charge transfer (about 0.9 e) from gallium to oxygen, in accordance with the chemical intuition and Pauling electronegativities for Ga (1.8) and O (3.5). The Ga–O bond has, therefore, a high ionic character. In other neutral clusters, charge transfer tends to decrease for terminal atoms (O in GaO_2 , Ga in Ga_2O , Ga_1 and O_2 in Ga_2O_2), whereas it tends to increase in higher coordinated atoms (Ga in GaO_2 , O in Ga_2O , Ga_2 and O_2 in Ga_2O_2). The addition or removal of an electron in the monomer is shared more or less equally among the atoms in the cluster.

GaO_2 is a cluster with a partial ionic character, though the anionic cluster is more ionic. The extra electron is localized over oxygen atoms, and, moreover, the formation of linear symmetric structure induces a higher charge transfer from the gallium atom to the oxygen ones. The cationic cluster, GaO_2^+ , presents an important feature. Its structure, as we have previously described, is formed by an oxygen diatomic molecule weakly bonded to the gallium atom. The topological charges indicate that the O_2 unit is almost neutral, but highly polarized by the positive charge of the Ga atom: the outer O possesses a 1.3 e charge, while the inner O has a negative charge, -1.2

TABLE 5: Topological Charges for Oxygen and Gallium Atoms in the Most Stable Neutral and Ionized Isomers of Monomer, Triatomic, and Dimer Clusters

monomer clusters				
	Q_{Ga}	Q_O		
GaO	0.889	-0.888		
GaO ⁻	0.304	-1.303		
GaO ⁺	1.254	-0.254		
triatomic clusters				
	Q_{Ga}	Q_O		
GaO ₂	0.719	-0.359		
(GaO ₂) ^{-a}	1.444	-1.221		
(GaO ₂) ⁺ a	0.992	(-1.226, 1.303)		
Ga ₂ O	0.673	-1.345		
(Ga ₂ O) ^{-a}	0.255	-1.337		
Ga ₂ O ⁺	1.084	-1.167		
dimer clusters				
	Q_{Ga1}	Q_{Ga2}	Q_{O1}	Q_{O2}
Ga ₂ O ₂	0.751	1.594	-1.303	-1.041
Ga ₂ O ₂ ^{-a}	0.772		-1.270	
Ga ₂ O ₂ ⁺	0.904	1.758	-1.185	-0.477

^a Error in total charge is greater than 10^{-3} e.

e. Comparing with the neutral case, the ionized electron comes mainly from the O₂ unit; thus, GaO₂⁺ recovers the triplet character as in a neutral isolated O₂ molecule.

The loss of the electron from the Ga₂O to reach the cationic structure comes mainly from the gallium atoms, and only 10% is provided by the oxygen atom. The topological analysis in the anionic Ga₂O reveals that the total charge for the predicted ground state is -0.8 e, instead of -1.0 e. This discrepancy is not due to any numerical error, but is attributed to a complex shape of the oxygen atomic basin; the electronic charge is going away from the nucleus, which is typical of the excited electronic states.³² We have therefore explored several electronic states other than ²A₁ for Ga₂O⁻, but all of them are at a higher total energy than that of ²A₁. All these considerations lead us to believe that Ga₂O⁻ is an electronically unstable cluster. In a photoelectron spectroscopy study of aluminum oxide clusters, Al₂O⁻ was not observed, despite numerous attempts to produce it at various source conditions.

The neutral Ga₂O₂ consists of two atoms different by symmetry for each type. The inner oxygen atom receives charge from the two gallium atoms while the terminal one receives charge only from the inner gallium. This effect is also present in the cationic Ga₂O₂. All atoms of the cluster contribute to the loss of the electron, but not to the same extent. The larger contribution, about 56%, is from the terminal oxygen atom. The remaining percentage is contributed almost equally by the three atoms. On the other hand, the anionic Ga₂O₂ can be formed by closing the neutral Ga₂O₂. In this way, all atoms in the cluster have the same coordination index. The extra electron is then assigned mostly to the former inner gallium atom in the neutral cluster; thus making both metallic atoms have the same atomic charge. The oxygen atoms in the anionic cluster present an average charge between the terminal and the inner oxygen atoms from the neutral dimer.

V. Electronic Properties

We have computed both adiabatic and vertical electron affinities (EA) and ionization potentials (IP) for the monomer, triatomic, and dimer of gallium oxide clusters. The values are listed in Table 6. The definition of these properties employed in this work is as follows: EA = E(neutral) - E(anion) and IP

TABLE 6: Vertical and Adiabatic Values (eV) of the Electron Affinity and Ionization Potential for the Monomer, Triatomic, and Dimer Clusters

	GaO	GaO ₂	Ga ₂ O	Ga ₂ O ₂
vertical EA	2.56	3.85	0.44	2.59
adiabatic EA	2.56	3.72	0.03	2.33
vertical IP	9.84	9.78	7.89	9.16
adiabatic IP	9.89	8.20	8.27	9.04

TABLE 7: HOMO-LUMO Gap eV for the Most Stable Isomer of Monomer, Triatomic, and Dimer Clusters

	neutral	anion	cation
GaO	2.85	2.72	3.64
GaO ₂	3.70	3.97	5.46
Ga ₂ O	4.83	0.63	2.67
Ga ₂ O ₂	4.99	2.52	1.82

= E(cation) - E(neutral). For all cases, the anionic clusters are more stable than the neutral ones. We want to point out that in Ga₂O, anionic and neutral clusters are almost degenerate in energy, thereby confirming the instability of the anionic Ga₂O cluster.

Due to the lack of experimental studies on GaO clusters, we will compare the calculated values for the electron affinity with the experimental results of the photoelectron spectroscopy on AlO clusters.³³ The values measured by Desai et al.³³ are 2.60, 4.23, and 1.88 for the AlO, AlO₂, and Al₂O₂, respectively. In both cases, aluminum and gallium oxide clusters, we observe a significant increase in the electron affinity when progressing from MO to MO₂. In our calculations, we can also observe an important decrease in the electron affinity values when a gallium atom is added to form Ga₂O. The explanation of this behavior is that clusters that have an excess of oxygen atoms are electron deficient and thus present high electron affinity values.

It is important to note that the adiabatic and vertical values for the electron affinity in the monomer are almost the same, while in rest of the cases, adiabatic values are smaller than the vertical ones. This is because the internuclear distance does not change when an electron is added to the neutral monomer. However, the addition of one electron in triatomic and dimer clusters produces larger changes in the structural parameters, yielding lower values of the adiabatic electron affinity.

The HOMO-LUMO gaps have been computed for the most stable isomers in gallium oxide clusters under study and are listed in Table 7. As a general trend, we can observe an increase in the gap values when the cluster size increases for the neutral clusters. The experimental band gap energy value for the bulk Ga₂O₃ at room temperature is 4.8 eV.³⁴ It appears that the bulk value has been reached for the dimer, but we believe that small oscillations in the HOMO-LUMO gap are expected before converging to the bulk value of the band gap.

VI. Conclusions

In this work, we have found that the DFT-B3LYP theoretical scheme and the 6-31G** give very good results for the small polyatomic gallium oxide clusters. The effect of including the diffuse function in the basis set is negligible even for anionic clusters. All clusters are pseudoionic and present low spin electronic states. The only exception is GaO₂⁺, which was found in a triplet electronic state: it was formed by a Ga⁺ singlet weakly bonded to O₂ triplet. All lowest energy isomers are dominated by the pseudoionic Ga-O bonds over the metal-metal or the oxygen-oxygen bonds, with the exception of GaO₂⁺. Regarding the controversy over the structure of the ground state of Ga₂O, our DFT-B3LYP calculations support

the linear structure. The atomic charges corroborate the high ionicity picture showing that the charge transfer to a given atom increases with its coordination index. Ga_2O^- is revealed as an unstable system due to the excess of electronic charge. This instability is reflected in the topology of the electronic density, the electron affinity, the orbital energy, and the HOMO–LUMO gap. The electron affinity increases in going from the gallium excess clusters to the oxygen excess clusters, as expected.

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