Structural, Energetic, Electronic, Bonding, and Vibrational Properties of Ga_3O, Ga_3O_2, Ga_3O_3, Ga_2O_3, and GaO_3 Clusters

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The results of density functional theory based calculations on Ga_3O, Ga_3O_2, Ga_3O_3, Ga_2O_3, and GaO_3 clusters are reported here. A preference for planar arrangement of the constituent atoms maximizing the ionic interactions is found in the ground state of the clusters considered. The sequential oxidation of the metal-excess clusters increases the binding energy, but the sequential removal of a metal atom from the oxygen-excess clusters decreases the binding energy. The increase in the oxygen to metal ratio in these clusters is accompanied by increase in both electron affinity and ionization potential. The ionization induced structural distortions in the neutral clusters are relatively small, except those for Ga_3O_2. In anionic (cationic) clusters, the added (ionized) electron is shared by the Ga atoms, except in the case of GaO_3. The vibrational frequencies and charge density analysis reveal the importance of the ionic Ga−O bond in stabilizing the gallium oxide clusters considered in this study.

I. Introduction

Thin films of gallium oxide have shown significant conductance response to the oxygen concentrations at high temperatures, while their sensitivity switches to carbon monoxide at low temperatures. In the form of low-dimensional nanostructures,[1−4] gallium oxide shows a very high surface to volume ratio, which increases gas-sensing reaction times while reducing power requirements. These attributes provide advantages to nanostructures over thin films for the gas sensing applications and are expected to solve problems associated with the conventional tin oxide sensors.

Small clusters of gallium oxide can be taken as the prototype model to understand the physics and chemistry of surfaces and nanostructures of this material. However, there is a dearth of both theoretical and experimental work on gallium oxide at the cluster level. A few scattered studies have only been reported on monomer,[5] triatomic,[6−10] and dimer[8,11] clusters. Recently, we have initiated a systematic study of the evolution of the physical and chemical properties of small gallium oxide clusters to determine their convergence to the corresponding bulk values. Our initial study on neutral and ionized small Ga_mO_n (m, n = 1, 2) clusters reported their equilibrium structure, bonding, vibrational, and electronic properties.[12] We now proceed to the next level of calculations on Ga_3O_3, for which we have considered both metal-excess and oxygen-excess fragments to investigate the effect of the oxygen/metal ratio on their structural and electronic properties. Specifically, we would like to investigate the changes induced by the sequential oxidation of Ga_3 to Ga_3O_3, and then the sequential removal of metal atoms up to O_3. To do so, we have performed first principles calculations on Ga_3O, Ga_3O_2, Ga_3O_3, Ga_2O_3, and GaO_3 clusters and report here the results on the equilibrium structure, bonding, electron affinity and ionization potential, and the vibrational frequency spectrum of these clusters.

The organization of the paper is as follows: Section II deals with the computational methodology. Section III discusses the calculated structural, vibrational, bonding, and electronic properties. Finally, we give a summary of the results in section IV.

II. Methodology

Electronic structure calculations were performed on neutral and charged gallium oxide clusters in the framework of density functional theory (DFT), using the Gaussian 98 code.[13] The gradient-corrected B3LYP functional form (i.e., Becke's 3-parameter hybrid exchange functional[14] and Lee, Yang, and Parr correlation functional[15]) was employed here.

The choice of the DFT-B3LYP methodology together with the 6-31G(d,p) basis set is justified by our previous study of monomer and dimer clusters of gallium oxide.[12,16] All isomers analyzed in this study have been fully optimized. The convergence criteria for energy was 10^{-9} hartree while that for the gradient of energy was 10^{-4} hartree/Å. The stability of the lowest energy configurations in the neutral, anionic, and cationic charge state was checked by computing the vibrational frequencies under the harmonic approximation, with analytical force constants.

The atomic and bonding properties have been analyzed under the quantum theory of atoms in molecules (QTAM).[17] To perform the QTAM analysis, we have used the AIMPAC95 package[18] with the Promega algorithm for integration of the atomic properties.

III. Results and Discussion

First principles calculations were performed on several linear, planar, and nonplanar configurations for each of the clusters considered here. Some of the initial configurations were taken from previous studies on small alumina clusters.[19−23]

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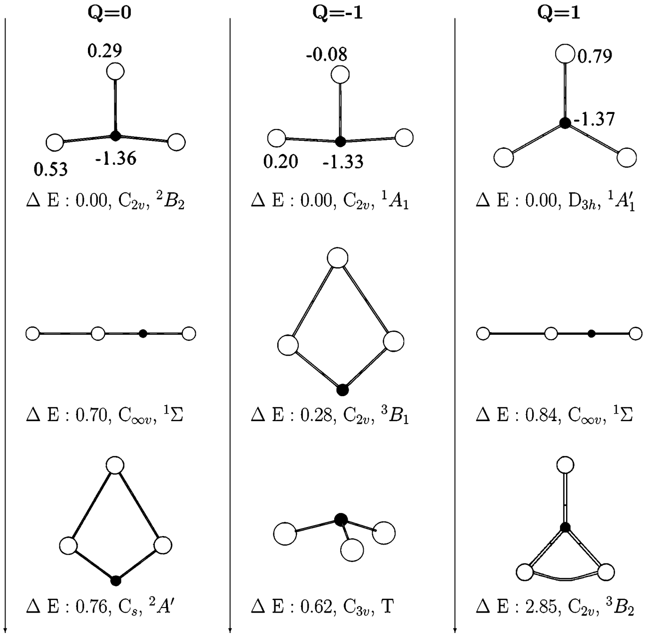
TABLE 1: Total Energy (hartree), Electronic State, Symmetry, and Interatomic Distance (Å) of the Most Stable Configurations of Gallium Oxide Clusters

	E	$^{2S+1}\Lambda$	sym	R_{Ga-Ga}	R_{O-O}	R_{Ga-O}
Ga_3O						
$Q = 0$	−5844.10116	$^2B_2$	C_{2v}	2.96		1.93, 2.05
$Q = -1$	−5844.13361	$^1A_1$	C_{2v}	2.74		1.93, 2.07
$Q = 1$	−5843.90282	$^1A_1'$	D_{3h}	3.46		1.99
Ga_3O_2						
$Q = 0$	−5919.36477	$^2B_2$	C_{2v}	2.83	2.62	1.85, 1.88, 2.00
$Q = -1$	−5919.44125	$^1A'$	C_s	2.96	2.64	1.80, 1.87, 2.11
$Q = 1$	−5919.13182	$^1\Sigma_g$	$D_{\infty h}$	3.64	3.42	1.71, 1.93
Ga_3O_3						
$Q = 0$	−5994.59951	$^2B_2$	C_{2v}	2.69	2.69	1.77, 1.93, 1.96, 1.97
$Q = -1$	−5994.70775	$^1A_1$	C_{2v}	2.72	2.70	1.77, 1.90, 1.99, 2.01
$Q = 1$	−5994.30412	$^3B_2$	C_{2v}	2.68	2.40	1.70, 1.78, 1.87, 1.92
Ga_2O_3						
$Q = 0$	−4071.52564	$^3B_2$	C_{2v}	2.55	2.69	1.81, 1.84, 1.87
$Q = -1$	−4071.64062	$^2A_1$	C_{2v}	2.61	2.70	1.71, 1.84, 1.92
$Q = 1$	−4071.18050	$^2B_2$	C_{2v}	2.49	2.74	1.79, 1.80, 1.91
GaO_3						
$Q = 0$	−2148.43918	$^2A_2$	C_{2v}	-	1.37	1.67, 1.97
$Q = -1$	−2148.54844	$^1A_1$	C_{2v}	-	1.61	1.70, 1.86
$Q = 1$	−2148.08216	$^3B_1$	C_{2v}	-	1.39	1.77, 1.90

Table 1 collects the electronic and structural properties, namely total energy, electronic state, symmetry, and interatomic distances of the lowest energy isomers of neutral, anionic, and cationic gallium oxide clusters. The lowest energy isomers in all cases prefer planar arrangements. They also display the lowest possible spin state, with Ga_2O_3, $Ga_3O_3^+$, and GaO_3^+ being exceptions where the spin state is triplet. The ground-state configuration of a given cluster always prefers to maximize the heteroatomic, Ga−O (ionic-like), interactions as compared to the homodiatomic, Ga−Ga and O−O, interactions. In the following subsections, we will discuss the calculated structural results on Ga_3O, Ga_3O_2, Ga_3O_3, Ga_2O_3, and GaO_3 clusters along with the atomic and bonding properties.

A. Structural, Atomic, and Bonding Properties. *1. Ga_3O.* Figure 1 shows the calculated ground state and some of the low lying structures of the hyper-metallic Ga_3O. On the basis of the fact that the ground state of Ga_3 is predicted to be the C_{2v} isosceles triangle,[24] we have investigated several structural possibilities for Ga_3O including the D_{3h} structure with oxygen at the center of the triangle. The optimization of the D_{3h} configuration leads to lowering of the energy due to Jahn−Teller distortion where competing T or Y type geometries are expected. The T-type $^2B_2$ state is the lowest energy configuration with R_{Ga-Ga} of 2.96 Å, base R_{Ga-O} of 1.93 Å, and an apex R_{Ga-O} of 2.05 Å. The $C_{\infty v}$ linear and distorted C_s rhombus configurations are found to be higher in energy, at about 0.70 and 0.76 eV respectively. We note here that, in the previous study of the Ga_2O cluster, DFT/B3LYP calculations found the linear Ga−O−Ga configuration to be the global minimum. In Ga_3O, gallium atoms prefer a triangular arrangement instead of the linear atomic arrangement, bonding the extra gallium directly to the oxygen atom. This fact makes the number of Ga−O bonds increase, being these bonds preferred over the Ga−Ga bond (compare the two lowest-lying structures).



Δ E : 0.00, C_{2v}, $^2B_2$ Δ E : 0.00, C_{2v}, $^1A_1$ Δ E : 0.00, D_{3h}, $^1A_1'$

Δ E : 0.70, $C_{\infty v}$, $^1\Sigma$ Δ E : 0.28, C_{2v}, $^3B_1$ Δ E : 0.84, $C_{\infty v}$, $^1\Sigma$

Δ E : 0.76, C_s, $^2A'$ Δ E : 0.62, C_{3v}, T Δ E : 2.85, C_{2v}, $^3B_2$

Figure 1. Ga_3O. Oxygen is represented by a smaller circle, while the larger one represents gallium. Numbers alongside the lowest energy isomer denote the Bader charge associated with that atom. The net of bonds depicted in the figure constitutes the real molecular graph.

Addition of an electron is found to stabilize the metallic Ga_3^- configuration with D_{3h} symmetry.[24] When we add oxygen to Ga_3^-, the resulting ground state of Ga_3O^- is the T-type structure in $^1A_1$ state with C_{2v} symmetry where the base R_{Ga-O} remains almost the same as in the neutral case, but R_{Ga-Ga} decreases by 7% because the base atoms are moved toward the apex one closing the angle. This fact finds its explanation in the analysis of the frontier molecular orbitals. The LUMO (lowest unoccupied molecular orbital) in the neutral cluster shows a bonding contribution between the gallium atoms. In this way, the extra electron in the anion cluster is localized on this orbital and this leads to the bent structure. On the other hand, removal of an electron leads to the ground state of the ionized Ga_3O cluster being an equilateral triangle with D_{3h} symmetry and R_{Ga-O} of 1.99 Å and R_{Ga-Ga} of 3.46 Å. As compared to the bond length in the neutral Ga_3O, R_{Ga-O} remained nearly the same while R_{Ga-Ga} is increased by 17%. The molecular orbital picture shows that the HOMO (highest occupied molecular orbital) in the cation cluster exhibits symmetrically bonding contributions along all the three Ga−O bonds.

It is important to notice that the first and third energy isomers in the cationic cluster series are very similar in structure, though there exists a large difference in energy between them, of about 2.85 eV. The explanation of this fact can be found in the topological analysis of the electron density: the third energy isomer shows the same number of Ga−O bonds than the first one, but it also shows a curved Ga−Ga bond. This stressed bond, Ga−Ga bond, introduces an instability in the structure with respect to the first energy isomer, increasing its energy. The formation of the curved Ga−Ga bond is due to the shortening of two Ga−O bond lengths, from 1.99 Å in the first energy isomer to 1.95 Å in the third one, and closening of the Ga−O−Ga angle (from 120 to 82°). In this way, the two gallium atoms reach a particular internuclear distance at which they are linked by a closed-shell interaction as shown by positive value of the Laplacian of the electron density.

The topological QTAM charge analysis for the neutral and ionized lowest energy configurations provides a clue in explaining the predicted changes in the neutral ground state upon addition or removal of an electron. The oxygen charge is maintained almost constant during the ionization process. The added electron goes mainly to the gallium atoms, oxygen receiving only 3% of its charge. The distribution of the electron between gallium atoms is not equivalent, with the apex one accumulating more charge (37%) than the others (33%). In the cationic cluster, the removed electron comes from the gallium atoms, leaving the oxygen atom unchanged. Employing QTAM, we have analyzed the molecular graph of these clusters, finding that there are no Ga−Ga bonds, even in favorable situations like Ga_3O^- with a relatively short distance between the gallium atoms. This shows a strong tendency to form Ga−O bonds. All these bonds have a positive value of the Laplacian of the electron density, indicating their ionic-like character.

The QTAM analysis of high energy isomers finds only the bonds showed in Figure 1. A strong trend to form the highest possible number of Ga−O bonds is observed. The Ga−Ga bonds are only present in those isomers in which the symmetry forces their appearance. We should indicate that a curved Ga−Ga bond exists in the cationic third energy isomer. All Ga−Ga bonds present in these isomers show a closed shell-type interaction in perfect agreement with the interatomic distance criteria.[25]

2. Ga_3O_2. Addition of an oxygen to Ga_3O leads to changes in the structural arrangement, and the lowest energy configuration comes out to be a planar rhombus-like configuration in which the extra oxygen can be seen as attached between two gallium atoms of the Ga_3O cluster. In this configuration, the minimum R_{Ga-O} is 1.85 Å, while R_{Ga-Ga} is 2.83 Å, which is larger than the Ga_2 dimer bond length (2.40 Å). The optimization of a closed-pentagonal ring leads to a planar V shaped (C_{2v}) configuration which is slightly above in energy (0.19 eV). On the other hand, a nonplanar C_{2v} configuration lies 0.96 eV above the ground state. Again, we observe a manifestation of the preference to maximize the number of Ga−O bonds in these clusters. Even though the third isomer in energy has one more Ga−O bond than the lowest one, the average R_{Ga-O} is larger than that in the lowest isomer making it less stable.

$Ga_3O_2^-$ does not show any significant change in the lowest energy configuration relative to that of the neutral structure. The addition of an electron relaxes the structure slightly, breaking the symmetry and with a marginal increase in the average R_{Ga-O} in the ring and a considerable decrease of the terminal Ga−O bond distance. This fact is in agreement with the picture exhibited by the molecular orbitals. The neutral LUMO presents a strong bonding interaction for the terminal Ga−O that makes the anionic cluster show a shorter distance for this bond. The second lowest energy configuration, 0.23 eV above, is similar to the nonplanar structure of the neutral Ga_3O_2, but with C_{3v} symmetry. Notice that in the anionic case there is an inversion of the relative ordering in energy with respect to the neutral clusters, although in $Ga_3O_2^-$ the second and third isomers are almost degenerate in energy.

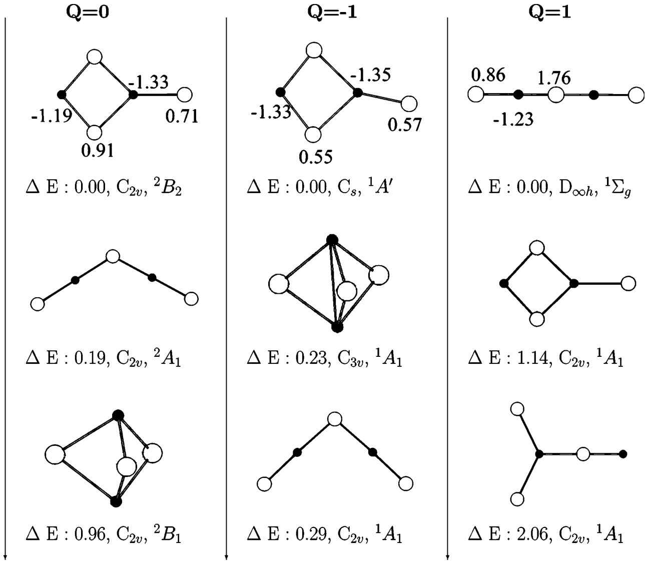


Figure 2. Ga_3O_2. Oxygen is represented by a smaller circle, while the larger one represents gallium. Numbers alongside the lowest energy isomer denote the Bader charge associated with that atom. The net of bonds depicted in the figure constitutes the real molecular graph.

The removal of an electron induces significant changes in the ground state of neutral Ga_3O_2. The ground state of cationic Ga_3O_2 is a linear chain with alternate Ga−O bonds. The formation of this chain can be explained using the frontier molecular orbitals. Since the removed electron comes from the α-HOMO orbital which presents a bonding interaction between the ring Ga−O bonds, the ring bonding interactions decrease, and hence a linear structure is preferred for the cation.

In neutral Ga_3O_2, QTAM charges reflect the expected behavior: greater coordination index leads to greater atomic charge. The oxygen charges are relatively higher indicating an ionic nature in these bonds. In the anionic configuration, the added electron is shared mostly by the gallium atoms, although 14% is localized over the bicoordinated oxygen. The tricoordinated oxygen receives negligible charge. In cationic Ga_3O_2, this leads to the same average electron density charge over the oxygen atoms as that in the neutral species. The total charge over the gallium atoms is one electron less than in the neutral cluster, while the total charge over the oxygens is the same in both clusters. As happened in the case of Ga_3O, a topological analysis of the electron density reveals that these clusters do not have Ga−Ga bonds. All bonds show an ionic character as Laplacian of the electron density values are positive.

The QTAM analysis carried out in the high energy isomers allows us to confirm the absence of Ga−Ga bonds. It is important to notice that a weaker O−O bond exists between the two apical oxygen atoms in the anionic second energy isomer. This bond presents an ionic-like character, with its Laplacian of the electron density showing a positive value.

3. Ga_3O_3. The calculated ground-state geometry of Ga_3O_3 is the planar window-pane C_{2v} structure with a doublet electronic state (Figure 3). Addition of an oxygen to Ga_3O_2 leads to a new structure containing two more Ga−O bonds. Again, we observe a strong tendency to maximize the number of Ga−O bonds in the lowest energy isomer. A rhombus-like structure with a bent terminal Ga−O is found to be almost degenerate with the most stable one, 0.10 eV above. The next isomer is a planar hexagonal cyclic structure with alternating Ga−O sequence at 0.96 eV. The 3-dimensional trigonal bipyramid

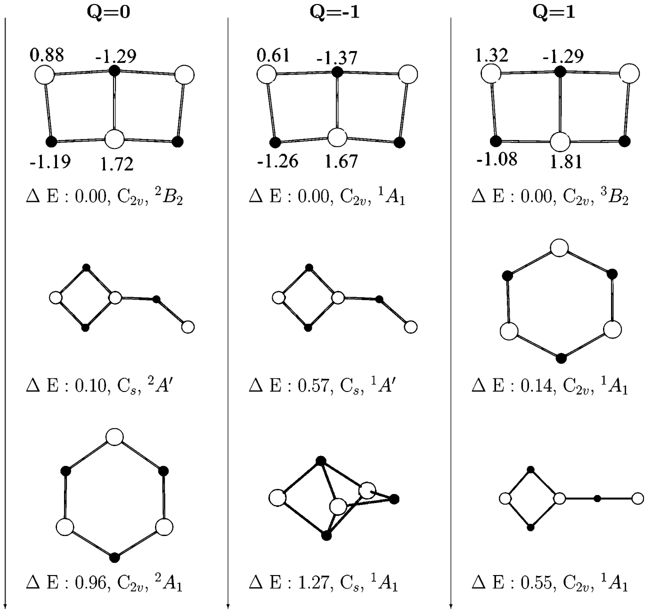


Figure 3. Ga_3O_3. Oxygen is represented by a smaller circle, while the larger one represents gallium. Numbers alongside the lowest energy isomer denote the Bader charge associated with that atom. The net of bonds depicted in the figure constitutes the real molecular graph.

structure with oxygen cap at the base is at 1.28 eV, well above the ground state. In the window-pane structure, the coordination number of the inner Ga and O atoms is 3, while in the hexagonal cyclic structure, the coordination number for all atoms is 2. On the other hand, the coordination numbers of Ga atoms in the competing rhombus-like C_s structure are 3, 2, and 1. This evolutionary trend shows that maximization of the coordination number for Ga atoms appears to play an increasing role in the stability of the gallium oxide clusters.

The calculated ground state of $Ga_3O_3^-$ is similar to the one predicted for neutral Ga_3O_3. Addition of an electron to the neutral cluster relaxes the structure with an increase of 3% in the average R_{Ga-O}. The geometrical features of the ground state are also preserved in going from neutral to cation, although the electronic state becomes triplet. The corresponding configuration in the singlet spin state is 0.26 eV higher in energy. A planar hexagonal ring structure at 0.14 eV is found to be in competition with the triplet window-pane structure. Overall, the energy difference between planar and nonplanar structures is very high in neutral as well as in the charged configurations. The molecular orbitals picture explains the spin multiplicities of the ionized clusters. In the neutral cluster, the HOMO (b_2) is semi-occupied and the HOMO-1 (a_1) is filled and are close in energy. Removing an electron from the HOMO-1 leaves this orbital semi-occupied, leading to the final electronic state of the cluster as $^3B_2$. In the anionic case, the extra electron fills the HOMO (b_2), making the final cation electronic state $^1A_1$.

The QTAM charges for the neutral cluster show a very high value for the tricoordinated gallium, being almost twice that of bicoordinated gallium atoms. However, the difference in the atomic charges between tri- and bicoordinated oxygen atoms is much smaller. In $Ga_3O_3^-$, 75% of the added electron goes to bicoordinated gallium atoms. The extra 25% is shared more or less equally among the oxygen atoms and the tricoordinated gallium atom. In the cationic cluster, the electron comes mainly from the external gallium atoms, giving them 68% of the added charge. We notice that the tricoordinated oxygen atom maintains its charge unaltered with respect to its counterpart in the neutral cluster.

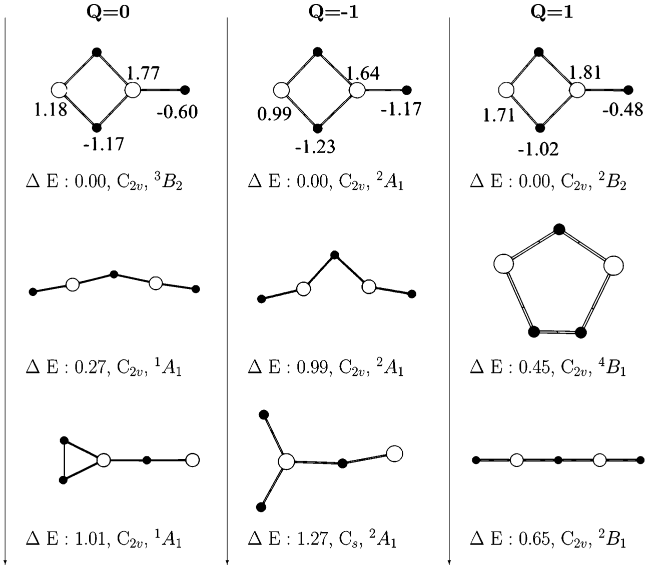


Figure 4. Ga_2O_3. Oxygen is represented by a smaller circle, while the larger one represents gallium. Numbers alongside the lowest energy isomer denote the Bader charge associated with that atom. The net of bonds depicted in the figure constitutes the real molecular graph.

The topological analysis of the electron density in the high energy isomers shows again a strong preference to form Ga−O bonds over Ga−Ga bonds. It is important to point out that in the anionic third isomer all the atoms are linked by Ga−O bonds.

4. Ga_2O_3. Figure 4 shows the low lying configurations of neutral and ionic Ga_2O_3. The ground state of Ga_2O_3 is the rhombus-like C_{2v} configuration in triplet electronic state. The structure is similar to the one in Ga_3O_2 and can be viewed as a rhombus Ga_2O_2 configuration plus an oxygen atom attached to one of the Ga atoms. As compared to Ga_3O_3, the average R_{Ga-O} distance decreases from 1.92 to 1.85 Å. The triplet−singlet energy difference for this configuration is high (1.00 eV) and the singlet configuration is almost degenerate with the Y-shaped configuration. An initial configuration of alternating zigzag arrangement of gallium and oxygen atoms resulted in a V-shaped structure 0.27 eV above the ground state.

Neither addition nor removal of an electron seems to be affecting the geometry of the lowest energy configuration of the neutral Ga_2O_3. The most stable structure of $Ga_2O_3^-$ is the doublet state with a doublet-quartet energy difference of 0.12 eV. The optimization of a zigzag configuration leads to an elongated V shaped structure with C_{2v} symmetry 0.99 eV above the ground state. The structural features in the ground state of cationic Ga_2O_3 are similar to those calculated for the neutral case, but the removal of an electron alters the sequence of other low lying structures. A significant fact is that the ionization process maintains the average Ga−O bond distance. In the anionic case, the extra electron goes into the neutral β-LUMO which exhibits a certain antibonding character over the Ga−O bonds linked to the terminal oxygen. This increases these Ga−O distances, while decreasing all the other Ga−O bond distances. In the cationic cluster, the electron comes from the neutral α-HOMO which presented an antibonding contribution for the bicoordinated Ga−O bond and bonding interactions for the tricoordinated bonds. This fact explains the distance changes when the electron is removed.

QTAM charge analysis shows that the extra electron is localized mainly (60%) over the external oxygen atom. The remaining electron is distributed over the rhombus, with the gallium atoms taking majority of it. In the cationic case, 50%

of the electron comes from the bicoordinated gallium atom, while the other 50% is contributed equally by the three oxygen atoms. The Ga−O bonds are the only ones present in these structures. All of them have a positive value of the Laplacian of the electron density indicating an ionic character.

The QTAM analysis performed in the local minima for all species shows the presence of the Ga−O bond as the only structural feature, with the exception of the neutral third isomer. In this isomer, we found a O−O bond with a positive value in its Laplacian of the electron density indicating a closed-shell interaction in perfect agreement with the interatomic distance criteria.[25]

5. GaO_3. The lowest energy configuration of this oxygen-rich cluster is a Y-type structure which can be considered as a GaO molecule attached to an O_2 molecule. In this configuration, the terminal R_{Ga-O} bond distance is 1.67 Å, shorter than the GaO molecule. The inner R_{Ga-O} bond distances are 1.97 Å, indicating a weak interaction with the O_2 unit. The O−O bond is much longer than the O_2 molecule (1.37 vs 1.21 Å). The quartet is found to be 0.67 eV above the doublet for this configuration. The planar L-type (C_s) structure is almost degenerate with the ground state, with an energy difference of 0.03 eV. A distorted rhombus follows closely at 0.16 eV in which Ga is out of plane with a dihedral angle of 13°.

Similar to Ga_2O_3, addition or removal of an electron does not significantly alter the geometry of the lowest energy neutral isomer. In the anionic case, R_{O-O} is 0.23 Å longer than that in the neutral case, but the inner R_{Ga-O} bond distances decrease significantly, making these interactions stronger than in the neutral cluster. The frontier molecular orbital analysis allows us to interpret this as follows: the extra electron goes to the α-HOMO, partially filled in the neutral cluster, which has an antibonding character between the oxygens and a slightly antibonding character between the terminal Ga−O. The electron density localized over the O−O bond in the neutral cluster is moved in the anionic cluster toward the inner Ga−O bonds. In this way, the latter distance decreases as compared to the neutral case, the O−O distance increases and the terminal Ga−O bond decreases marginally. Also, complete filling the α-HOMO makes the electronic state in this cluster a singlet.

In cationic GaO_3, the most stable isomer is found to be in triplet state with a triplet−singlet energy difference of 2.32 eV. The formation of this triplet can be explained by noting that the α and β-HOMO in the neutral cluster are almost degenerate. The removed electron comes from β-HOMO leaving two molecular orbitals semi-occupied. The O−O bond distance is very similar to that in the neutral case, but the inner Ga−O bond distances decrease due to the bonding character that the neutral β-HOMO had in these interactions. The terminal distance increases due to the antibonding character of these bonds.

In the neutral cluster, the QTAM charge of Ga is 1.62e while that of the terminal oxygen atom is −0.96e. The oxygen atoms forming the O−O bond are associated with a charge of −0.33e each. In GaO_3^-, the atomic charges show us that the extra electron is shared among the three oxygen atoms. In cationic GaO_3, 50% of the removed electron comes from the external oxygen atom, and 25% from the gallium. The topological analysis of the electron density reveals in these systems one important feature exhibited by the neutral, anionic, and cationic lowest energy isomers: the existence of the O−O bond. However, this bond presents a different character in the neutral and ionized clusters. In the neutral and cationic, the Laplacian of the electron density has a negative value, indicating a covalent bond or shared shell interaction. However, in the anionic cluster, with a larger interatomic distance than the others, the Laplacian of the electron density has a positive value, prototypical of the ionic bonds or closed shell interactions. It is seen that the interatomic distance is the parameter controlling the bonding regimes.[25]

The QTAM analysis carried out in the local minima shows the same trend exhibited by the Ga_3O, but exchanging the role of the gallium and oxygen atoms. In these isomers, we find several O−O bonds forced by the symmetry of the particular structure. Depending on the O−O interatomic distance, the bonds present different characters: if the O−O bond length is large, then the interaction is closed-shell type, and if the O−O bond distance is around that of equilibrium diatomic molecule, then it is a shared-shell interaction.

6. General Trends. Since aluminum and gallium are isovalent elements, similarities between structures of small oxide clusters of aluminum and gallium are expected. In the bulk phase, however, Al_2O_3 occurs in the α phase while Ga_2O_3 occurs in the β phase. If we restrict ourselves to a comparison of same size and composition gallium oxide and aluminum oxide clusters, it is found that both prefer planar structures.[19−23] The subtle differences in structural features can be explained by the fact that the Al−O bond is relatively stronger than the Ga−O bond. The binding energy of the AlO molecule is 2.48 eV/atom while that of the GaO molecule is 2.14 eV/atom.

As a relevant structural motif, it is seen that these systems have a clear preference to form the highest number of Ga−O interactions. There is no Ga−Ga bond in these clusters. We found some O−O interactions in the GaO_3 family but no Ga−Ga interactions in the hyper-metallic Ga_3O family. This structural motif is found in all isomer studied in this work. This fact indicates a strong trend to reach the ionic behavior prototypically of the bulk of this material in clusters containing a reduced number of atoms.

A general trend in these clusters is that they prefer low spin electronic state over the higher ones, Ga_2O_3, and the cationic $Ga_3O_3^+$ and GaO_3^+ being exceptions. In the cationic cases, the HOMO is an semi-occupied orbital and the HOMO-1 is filled, but both orbitals are almost degenerate in energy. The removed electron comes from the HOMO-1 instead the HOMO giving rise to a triplet electronic state.

In the metal rich clusters, the extra (removed) electron always is shared by (comes from) the gallium atoms. However, in the oxygen rich clusters, the extra electron is shared by the oxygen atoms.

The average charge over the oxygens follows a decreasing trend when the oxygen/gallium ratio increases (−1.36, −1.26, −1.22, −0.98, and −0.54 for Ga_3O, Ga_3O_2, Ga_3O_3, Ga_2O_3, and GaO_3, respectively), while the opposite is true for the average gallium charge (0.45, 0.84, 1.22, 1.47, and 1.62), as expected. Interestingly, when the total charge transfer is divided by the number of Ga−O bonds present in the cluster (average charge transfer per bond), the values are fairly constant (0.45, 0.50, 0.52, 0.59, and 0.54). The maximum value corresponds to the stoichiometric compound, Ga_2O_3, which exhibits a highest ionicity in the series.

B. Stability. *1. Binding and Fragmentation Energies.* The stability of neutral and charged gallium oxide clusters with respect to their constituent atoms can be characterized by the binding energy. Figure 6 shows the binding energy per atom, which first increases with the oxygen/metal ratio and attains maximum at Ga_3O_3. It then decreases in the oxygen-excess clusters, being lowest for GaO_3. Anionic clusters are relatively more stable with respect to both neutral and cationic clusters.

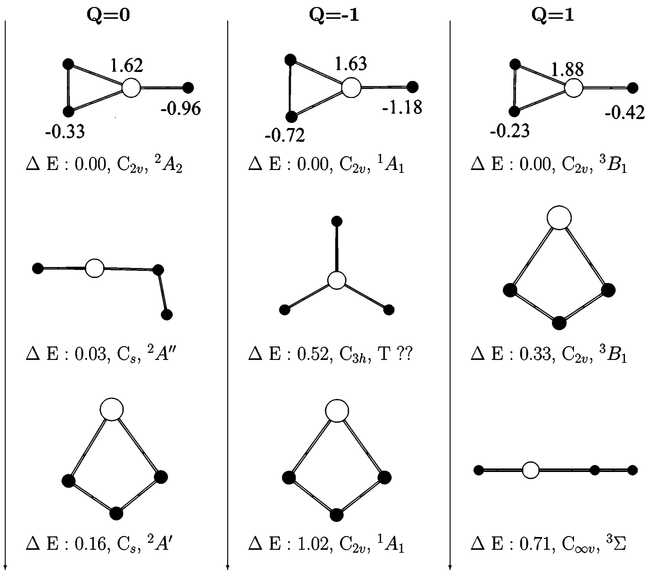


Figure 5. GaO_3. Oxygen is represented by a smaller circle, while the larger one represents gallium. Numbers alongside the lowest energy isomer denote the Bader charge associated with that atom. The net of bonds depicted in the figure constitutes the real molecular graph.

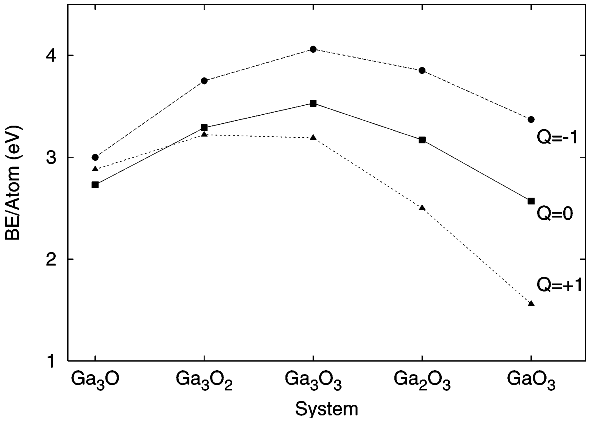


Figure 6. Binding energy per atom (eV) of the most stable isomers

For the neutral cluster, the curve is more or less symmetric with respect to the maximum at Ga_3O_3. We can observe that the metal rich clusters are slightly more stable than their oxygen rich counterparts. This trend is maintained for the cationic cluster with the Ga-excess linear Ga_3O_2 cluster being the most stable, but the oxygen excess anions are more stable than the metal excess anions. This behavior can be explained as follows: when an electron is added to the neutral system, it tends to stabilize over the more electronegative oxygen atoms in the oxygen rich clusters. A part of this electron has to be shared by the Ga atoms in the metal rich clusters, which is a less favorable situation. However, the removed electron comes mainly from the Ga atoms. As a result, the metal rich clusters are more stable in the ionization process. The average coordination indices for these clusters are 0.75, 1, 1.16, 1, and 1 for Ga_3O, Ga_3O_2, Ga_3O_3, Ga_2O_3, and GaO_3, respectively. We can explain the behavior of these curves using this magnitude: Ga_3O_3 is the most stable cluster because it has the highest average coordination index.

We also present the results on the relative stability of the neutral and singly ionized clusters with respect to their fragmentation into atoms or clusters. We only consider the lowest energy configuration for each of the clusters involved, neglecting contributions from the zero point vibration energy. Table 2 collects the energy associated with the fragmentation channels via loss of O, O_2, GaO, Ga, and Ga_2 (the total energies in hartree of O, O_2, GaO, Ga, and Ga_2 are −75.06062, −150.32004, −1998.09669, −1922.87978, and −3845.82017 respectively). The fragmentation energy is defined as: $E_{\text{Fragmentation}} = E_{\text{cluster}} - E_{\text{Fragment1}} - E_{\text{Fragment2}}$ where fragment 2 is either O, O_2, GaO, Ga, or Ga_2. Thus, the cluster is said to be stable with respect to the particular fragments if the fragmentation energy is negative. It is found that all clusters are stable against fragmentation by the channels considered in this study. We find that neutral and anionic clusters tend to favor the GaO channel, while the cationic ones favor the O_2 channel in general. However, Ga_3O_2 cation prefers the Ga_2 fragmentation channel. The preference of the O_2 channel over the O channel for the loss of oxygen is greater in oxygen rich clusters, while the opposite is true for the metal rich clusters. Regarding the Ga and Ga_2 channels, the first one is preferred in most neutral and anion clusters. However in cationic clusters the Ga_2 is the channel preferred except for Ga_3O.

2. Vibrational Frequencies. The configurational stability of the ground state of the neutral, anionic, and cationic clusters considered has further been investigated by computing their vibrational frequencies under the harmonic approximation. Table 3 collects the vibrational frequencies of the lowest energy isomer for the neutral, anionic, and cationic clusters, labeled according to their symmetry.

In the hyper-metallic family, Ga_3O, Ga_3O^-, and Ga_3O^+, the first three modes are related to the bending movement (both in plane and out of plane) of all bonds. In the neutral Ga_3O, the sequence is: bending in plane of the apex Ga−O bond, bending in plane of the other two Ga−O bonds, and bending out of plane of the oxygen atom. In the cationic cluster all the bonds are equivalent by symmetry and the first two degenerate modes involve the bending in plane of all Ga−O bonds, and the next nondegenerate one is related to the out of plane bending of the oxygen atom. For the anionic cluster, there is a different relative ordering, as displayed by the symmetry labels. For neutral and anionic clusters, the three higher frequency modes correspond to the symmetric stretching of the equivalent Ga−O bonds, the asymmetric stretching of the apex Ga−O bond, and the asymmetric stretching of the equivalent Ga−O bonds. For the cationic cluster, the degenerate mode involves the asymmetric movement of all bonds and the a_1' reflects the symmetric displacement. We observe a correlation between the interatomic distance and the vibrational frequency trends.

We discuss the vibrational modes of Ga_3O_2 and $Ga_3O_2^-$ together. Although their symmetry is different they present very similar structures. The first three modes correspond to the in plane bending of the ring, and the asymmetric and symmetric bending out of plane of the oxygen atoms. The remaining vibrational frequencies are stretching modes: the lowest one displays a symmetric stretching of Ga−O bonds in the ring closer to the Ga−O terminal bond, the next one is related to the symmetric stretching of the ring Ga−O bonds, followed by the asymmetric stretching of Ga−O bonds in the ring closer to the Ga−O terminal bond, the next two modes correspond to the symmetric and asymmetric movement of the terminal Ga−O bond, and the last mode presents the symmetric stretching of all Ga−O bonds: ring and terminal. Since the structure for the cationic cluster is linear, it has an extra vibrational mode, and we present a separate description of its normal vibrational modes. Briefly, the two first degenerate modes correspond to the asymmetric out of plane bending of the oxygen and gallium atoms, respectively. The following movement with σ_g symmetry corresponds to the symmetric stretching of terminal Ga−O

TABLE 2: Fragmentation Energies (eV) of Gallium Oxide Clusters via Loss of Oxygen Atom, Oxygen Molecule, and GaO Molecule[a]

	neutral					anion					cation				
	O	O_2	GaO	Ga	Ga_2	O	O_2	GaO	Ga	Ga_2	O	O_2	GaO	Ga	Ga_2
Ga_3O	−7.2		−5.2	−1.1	−4.7	−6.5		−4.8	−1.9	−3.0	−8.2		−6.8	−4.0	−10.2
Ga_3O_2	−5.5	−7.3	−2.8	−8.2	−6.7	−6.7	−7.8	−5.0	−2.8	−5.1	−4.6	−7.4	−4.7	−17.7	−0.6
Ga_3O_3	−4.7	−4.9	−4.2	−5.3	−9.3	−5.6	−6.9	−4.9	−5.1	−9.2	−3.0	−2.2	−5.0	−18.5	−11.3
Ga_2O_3	−3.1	−1.1	−4.1	−5.6	−8.1	−4.0	−4.3	−3.9	−5.8	−9.5	−2.7	−1.1[b]	−4.3	−18.1	−11.2
GaO_3	−2.7	−0.6	−0.6	−4.2		−2.3	−1.3	−2.8	−5.4		−2.6	−0.7	−3.5	−6.6	

[a] The negative value of the energy means the cluster is stable. [b] The geometry of Ga_2O^+ is taken to be the first (linear) in Figure 1 of our previous study.[12]

TABLE 3: Vibrational Frequencies of the Most Stable Neutral, Anionic, and Cationic Clusters[a]

Ga_3O^-		Ga_3O		Ga_3O^+		$Ga_3O_2^-$		Ga_3O_2		$Ga_3O_2^+$		$Ga_3O_3^-$		Ga_3O_3		$Ga_3O_3^+$		$Ga_2O_3^-$		Ga_2O_3		$Ga_2O_3^+$		GaO_3^-		GaO_3		GaO_3^+	
ω_e		ω_e		ω_e		ω_e		ω_e		ω_e		ω_e		ω_e		ω_e		ω_e		ω_e		ω_e		ω_e		ω_e		ω_e	
123	a_1	86	b_2	78	e'	34	a'	33	b_2	36	π_u	102	b_1	107	b_1	110	b_1	137	b_1	131	b_1	133	b_2	175	b_2	59	b_2	86	b_2
137	b_1	93	a_1	78	e'	72	a'	85	b_1	36	π_u	130	a_2	132	a_2	144	a_2	162	b_2	145	b_2	140	b_1	182	b_1	138	b_1	122	b_1
153	b_2	126	b_1	169	a_2''	129	a'	185	b_1	112	π_g	138	a_1	154	a_1	170	a_1	243	b_1	248	b_1	255	b_1	510	b_2	278	b_2	412	b_2
231	a_1	243	a_1	232	a_1'	182	a'	203	a_1	112	π_g	246	b_2	189	b_2	255	b_2	272	a_1	281	a_1	289	a_1	550	a_1	503	a_1	537	a_1
417	a_1	384	a_1	484	e'	238	a'	272	a_1	196	σ_g	252	b_1	258	b_1	257	b_1	459	b_2	516	b_2	467	b_2	790	a_1	888	a_1	712	a_1
597	b_2	577	b_2	484	e'	270	a'	276	b_2	213	π_u	266	a_1	272	a_1	283	a_1	555	a_1	587	a_1	538	a_1	880	a_1	1123	a_1	1070	a_1
						567	a'	522	b_2	213	π_u	380	b_2	451	b_2	507	b_2	611	b_2	625	b_2	674	b_2						
						641	a'	576	a_1	319	σ_u	461	a_1	494	a_1	508	a_1	667	a_1	643	a_1	705	a_1						
						723	a'	705	a_1	819	σ_g	568	b_2	498	b_2	568	a_1	839	a_1	724	a_1	735	a_1						
										924	σ_u	570	a_1	544	a_1	659	a_1												
												686	a_1	672	a_1	701	b_2												
												785	b_2	767	b_2	751	b_2												

[a] The normal modes are labeled by symmetry. The frequency values are given in cm^{-1}.

bonds. The π_u degenerate normal mode shows the symmetric bending out of plane of the oxygen atoms. The last three modes represent stretching movements: the first is the stretching of all bonds in the cluster, the next two are the symmetric and asymmetric stretching of the oxygen atoms. A clear relationship between the interatomic distances and the frequency values is observed.

Ga_3O_3 and the corresponding charged clusters belong to the same symmetry point group, and as we can see in Table 3 they follow the same ordering of the vibrational modes for the neutral, anion and cation. The only exception is $Ga_3O_3^+$, where the 9th and the 11th modes are interchanged. The lower frequency modes correspond to the bending and torsion movements: first one corresponds to the out of plane bending of the central oxygen; the next one displays the asymmetric bending out of plane of the terminal oxygen atoms, followed by the asymmetric in plane bending of the gallium atoms. The fourth mode is the torsion of the ring, generated by the movement of gallium atoms, and the last bending mode corresponds to the symmetric out of plane displacement of all oxygen atoms. The remaining modes are stretching movements. A brief description of them follows: the first one is an asymmetric stretching of the two Ga−O bonds with the tricoordinated oxygen atom; the next mode shows the asymmetric stretching of the two Ga−O bonds perpendicular to the previous mode. The third stretching mode exhibits the movement of inner Ga−O bond. The next one is equivalent to the first stretching mode but the stretching is symmetric. The 10th and 11th modes reflect the symmetric and asymmetric stretching of all Ga−O bonds, and the last one indicates the symmetric displacement of all Ga−O bonds except the inner one.

Neutral, anionic, and cationic Ga_2O_3 again exhibit the same symmetry in their lowest energy isomer and in Table 3 we can notice the same ordering of their normal vibrational modes. As expected, the lower frequency modes are related to the bending vibrations: the first one is the out of plane bending of the terminal Ga−O bond, followed by the bending in plane of this bond, and the last bending mode corresponds to the out of plane displacement of the ring Ga−O bonds. The first stretching mode shows the asymmetric movement of ring gallium atoms. The next two modes represent the symmetric and asymmetric torsion movements of the ring oxygen atoms. The next mode corresponds to the stretching of the ring oxygen atoms. The two highest frequency values are related to the symmetric and asymmetric stretching of all oxygen atoms, respectively.

Finally, all clusters in the GaO_3 family also belong to the same point group and we discuss them together. As is the case with other clusters, the lower vibrational frequencies are related to the bending movements. In this case, the first one corresponds to the asymmetric in plane bending of the oxygen atoms. The second one is the bending out of plane of the terminal oxygen atom. The third mode corresponds to the torsion of the O−O bond. The next one is the asymmetric stretching of the two ring Ga−O bonds. The last two modes represent different movements in the neutral and ionic clusters: the first one is stretching of the terminal Ga−O bond and the last one is stretching of the O−O bond. We want to elaborately discuss these values. Because of the weakness of the bonds between the Ga bridge and the O−O group, the terminal Ga−O group is very similar to the free GaO molecule (R_{Ga-O} 1.74 Å experimental value[5]). In neutral GaO_3, the distance is 1.67 Å and 1.77 Å GaO_3^+. The O−O group is similar to the O_2 molecule (1.21 Å experimental value[5]) but with a larger distance (1.38 and 1.39 Å for GaO_3 and GaO_3^+, respectively). Accordingly, the Ga−O stretching is larger than that of GaO molecule (767 cm^{-1}, experimental value[5]) for the neutral cluster and a little bit smaller for the cationic one, while the O−O stretching is smaller than the O_2 frequency (1581 cm^{-1} experimental value[5]) in both clusters. The two remaining modes in the anionic cluster represent a different behavior with respect to these modes in their in neutral and cationic counterparts. The larger interatomic distance of the O−O group along with the shortening of the bond length between this group and the Ga bridge explains this different behavior. In this way, the vibrational movements are coupled,

TABLE 4: Vertical Attachment Energy (VAE), Vertical Detachment Energy (VDE), Adiabatic Electron Affinity (AEA), Adiabatic Ionization Potential (AIP), and Chemical Hardness, η (eV), of Gallium Oxide Clusters[a]

	O/Ga	VAE	VDE	AEA	VIP	AIP	η
Ga_3O	1/3	0.74	0.98 (1.68)	0.88 (1.57)	5.95	5.40	2.49
Ga_3O_2	2/3	1.91	2.25 (2.29)	2.08 (2.18)	7.67	6.34	2.71
Ga_3O_3	3/3	2.88	3.06 (2.96)	2.95 (2.80)	8.10	8.04	2.52
Ga_2O_3	3/2	2.87	3.40 (3.71)	3.13	9.59	9.39	3.10
GaO_3	3/1	2.13	3.61	2.97	10.22	9.71	3.31

[a] Values given in parentheses for VEA and AEA correspond to aluminum oxide.[19,20] We also give in the second column the O/Ga ratio.

contrary to what was observed in the neutral and cationic clusters. These modes involve the symmetric and asymmetric stretching of all bonds in the cluster.

C. Electronic Properties: Electron Affinity, Ionization Potential, and the HOMO—LUMO Gap. Both adiabatic and vertical values of the electron affinity and ionization potential for the lowest energy isomer of the gallium oxide clusters considered in this study are reported here. The values of electron affinity (EA) and ionization potential (IP) are calculated as follows: $EA = E_{(Q=0)} - E_{(Q=-1)}$, and $IP = E_{(Q=+1)} - E_{(Q=0)}$, where E is the total energy of the cluster and Q is the charge of the cluster.

In this way, the vertical electron affinity (VEA) or vertical detachment energy (VDE)[26] is defined as the energy difference between the anionic and neutral clusters when both are at the optimized geometry of the anionic cluster, while the adiabatic electron affinity (AEA) is defined as the energy difference between the anionic and neutral clusters at their respective optimized geometries. We also calculate the vertical attachment energy (VAE) which is defined as the energy difference between the neutral and anionic clusters with both at the optimized geometry of the neutral cluster. Although this is not attainable through any experiment, it provides a lower bound to the AEA in the same way that the VDE is an upper bound.[26] The vertical ionization potential (VIP) is defined as the energy difference between the cationic and neutral clusters with both at the optimized geometry of the neutral cluster, while the adiabatic ionization potential (AIP) is defined as the energy difference between the cationic and neutral clusters at their respective optimized geometries.

Table 4 collects the calculated values of VAE, VDE, AEA, IP, and chemical hardness (η) for the clusters considered. The electron affinity results show an increasing trend of these values when the number of oxygen atoms in the cluster increases. The explanation of this behavior is that the clusters that have an excess of oxygen atoms are electron deficient and thus present high electron affinity values. In this way, it is important to notice that the addition of oxygen in Ga_3 significantly reduces the EA from 1.68[24] to 0.98. This fact seems to go against of the previously observed trend, but we should point out that there is a noticeable change in the nature of bond when the Ga_3 (metallic) cluster is oxidized to form three Ga−O bonds (ionic).

The IP values increase with a increasing oxygen−gallium ratio. Again, the electron deficient oxygen rich clusters offer a strong resistance to removed an electron.

In the absence of experimental values on gallium oxide clusters, we compare the calculated values to those reported in the photoelectron spectroscopy experiments on small aluminum oxide clusters.[19,20] We observe that EA values increase gradually in going from M_3O to M_2O_3 (where M = Al, Ga). In accordance with the periodic group evolution of this property, we note that values for alumina are higher than those predicted in this study for the gallium clusters.

TABLE 5: HOMO−LUMO Gap (eV) of the Most Stable Isomers

	neutral	anion	cation
Ga_3O	2.31	1.72	4.92
Ga_3O_2	2.34	2.65	4.69
Ga_3O_3	1.55	3.84	3.47
Ga_2O_3	2.71	1.38	2.53
GaO_3	2.55	4.74	3.12

TABLE 6: Dipole Moments, μ_i (in debye), Diagonal Components of Static Polarizability Tensor, α_{ii} and Their Average, α_{avg} (in a.u.) for the Most Stable Neutral Isomers

system	dipole moment μ_z	polarizability tensor α_{xx}	α_{yy}	α_{zz}	α_{avg}
Ga_3O	−0.87	79.40	194.76	133.39	135.85
Ga_3O_2	3.86	79.51	184.97	115.66	126.71
Ga_3O_3	−1.39	67.91	266.26	93.61	142.59
Ga_2O_3	2.12	42.55	46.27	88.20	59.01
GaO_3	−3.50	25.46	30.75	42.48	32.90

We now use a quantification of the concept of chemical hardness[27] for a particular system as $\eta \approx (IP - EA)/2$ where IP and EA are the first vertical ionization energy and electron affinity of the chemical species. Thus, the increase in the oxygen-to-metal ratio is found to increase the chemical hardness of the clusters considered here. This can also be observed in the HOMO−LUMO gap of these clusters (see Table 5), which also relates to another measure of hardness $\eta \approx (HOMO - LUMO)/2$ working under Koopman's approximation.

Table 5 presents the calculated energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for the ground state of the clusters considered. The HOMO−LUMO gap for the neutral configurations varies from 1.55 to 2.71 eV. We note here that the value of the band gap in the bulk monoclinic Ga_2O_3 is 4.80 eV,[28] whereas in the neutral cluster configurations the highest value is 2.71 eV. Because of differences in the structural configuration, a trend in the energy gap is not seen with the increase in the oxygen-to-metal ratio in these clusters.

Since the value of dipole moment, μ_i (in debye), for charged systems depends on the choice of origin as well as orientation of the molecule, we only present them for the most stable neutral isomers (Table 6). Dipole moment is the first derivative of the energy with respect to an applied electric field and is a measure of the asymmetry in the molecular charge distribution. We note that, since all neutral ground states have C_{2v} symmetry, the dipole moment is entirely along the C_2 symmetry z axis. The diagonal components of the static polarizability tensor, α_{ii} and their average, α_{avg} (in au) for the most stable neutral isomers are also given. We note that metal rich clusters exhibit higher α_{avg} values as a result of the higher polarizabilities of the Ga atom whereas sequential removal of Ga atom drastically reduces the average polarizability by an order of magnitude. This should be expected, since Ga_3O_3 are electron-rich, Ga_2O_3 is nominally valence-compensated, and GaO_3 is electron deficient.

IV. Conclusions

We observe that using DFT-B3LYP methodology along with 6-31G(d,p) basis set yields results for neutral and ionic Ga_3O_n and $Ga_{3-m}O_3$ ($m = 1-2$, $n = 1-3$) clusters that show a trend similar to that of aluminum oxide. All cluster configurations preferred planar configurations over three-dimensional structures with the lowest spin state, with the exception of Ga_2O_3, $Ga_3O_3^+$, and GaO_3^+. The analysis of molecular orbitals indicates that Ga−O interactions play a dominant role in deciding the stability of the cluster. Except in Ga_3O, anionic clusters are more stable than neutral, and these are more stable than cationic clusters. Binding energy is seen to increase with oxygen content and is maximum at Ga_3O_3, and then decreases with reduction in metal content. There are no Ga−Ga bonds in these systems and a high preference to maximize the number of Ga−O bonds is observed. The QTAM analysis allows us to classify these kind of clusters as ionic compounds with a high charge transfer from the metal to the oxygen and all the Ga−O bonds are closed shell interactions. Electron affinity and ionization potential values increase from Ga_3O to GaO_3. HOMO−LUMO gap, as predicted in our previous study, continues to exhibit an oscillatory trend in approaching the bulk value of the band gap.

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