Structural and Electronic Properties of Neutral and Ionic Ga_nO_n Clusters with $n = 4-7$

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We report the results of a theoretical study of neutral, anionic, and cationic Ga_nO_n clusters ($n = 4-7$), focusing on their ground-state configurations, stability, and electronic properties. The structural motif of these small gallium oxide clusters appears to be a rhombus or a hexagonal ring with alternate gallium and oxygen atoms. With the increase in the cluster size from Ga_4O_4 to Ga_7O_7, the ground-state configurations show a transition from planar to quasi-planar to three-dimensional structure that maximizes the number of ionic metal−oxygen bonds in the cluster. The ionization-induced distortions in the ground state of the respective neutral clusters are small. However, the nature of the LUMO orbital of the neutral isomers is found to be a key factor in determining the ordering of the low-lying isomers of the corresponding anionic clusters. A sequential addition of a GaO unit to the GaO monomer initially increases the binding energy, though values of the ionization potential and the electron affinity do not show any systematic variation in these clusters.

I. Introduction

Gallium oxide is an important semiconducting oxide with applications in the areas of optics and microelectronics. It is therefore, not surprising that considerable efforts have been made in the past to understand the structural, optical, and electronic properties of gallium oxide. However, the interest in studying the properties of nanostructures and nanoclusters of gallium oxide is relatively recent. In the form of low-dimensional nanostructures such as nanowires, nanosheets, and nanoribbons,[5−8] a very high surface-to-volume ratio is expected, which would facilitate new and novel applications of gallium oxide. Specifically, the use of nanostructures increases gas-sensing reaction time while reducing the power requirements associated with heating the sensors, thereby providing advantages over thin films for the gas-sensing applications.[9]

Small clusters of gallium oxide can be considered a prototype model to understand the physics and chemistry of nanostructures. A few scattered studies have been reported on gallium oxide at the cluster level including monomer,[10,11] triatomic,[12,13] and dimer[14−17] clusters. Recently, we 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, $n = 1, 3$) clusters reported their equilibrium structure, bonding, vibrational, and electronic properties.[17,18] The present study extends the calculations to the stoichiometric Ga_nO_n clusters, with $n = 4-7$. Specifically, we will focus on the equilibrium structure, stability, electron affinity, and ionization potential of Ga_nO_n clusters. The paper is organized as follows: The computational method used in this work will be presented in section II. In section III, we present the results for the ground state of the neutral and ionic clusters. Conclusions will be given in section VI.

II. Computational Details

Electronic structure calculations were performed using first-principles molecular dynamics method based on density functional theory (DFT) within the generalized gradient approximation (GGA) given by Perdew and Wang.[19] For gallium and oxygen atoms, ultrasoft pseudopotentials[20] as implemented in the VASP package[21] were employed here. Several initial planar and nonplanar diverse configurations of neutral, anionic, and cationic clusters were considered for these calculations. The choice of some of the initial geometries was partially dependent upon the previous studies of small clusters of aluminum oxide[22−28] and gallium nitride.[29] It is to be noted here that the linear configurations were not considered here, since our earlier studies find the low-lying isomers of Ga_3O_3 to be planar configurations.[18] The equilibrium geometries of the Ga_nO_n clusters were obtained by quenching a large number of initial configurations using the quasi-Newton method. The clusters were positioned in a cubic supercell with an edge of 20 Å, and periodic boundary conditions were imposed. The cutoff energy for the plane wave was set to 270.2 eV. The calculations were considered to be converged when the force on each ion was less than 0.01 eV/Å with a convergence in the total energy of about 10^{-4} to 10^{-6} eV. The stability of the cluster is further verified by performing the calculations with singlet (doublet) or higher spin states depending on an even (odd) number of valence electrons in the cluster. We note here that the inclusion of the Ga 3d pseudopotential for Ga_3O_3 does not introduce significant changes in its isomeric sequence, energetics, and electronic properties. To reduce the computational cost, the Ga 3d orbitals are, therefore, included in the core part of the Ga pseudopotential in the subsequent calculations.

III. Results and Discussion

A. Structural Properties. To benchmark the modeling elements of the present study, we first compare our results, referred to as DFT-PW91/VASP on GaO, Ga_2O_2, and Ga_3O_3 with the previously reported DFT-B3LYP/*Gaussian 98* calculations[17,18] using 6-31+G** basis set.

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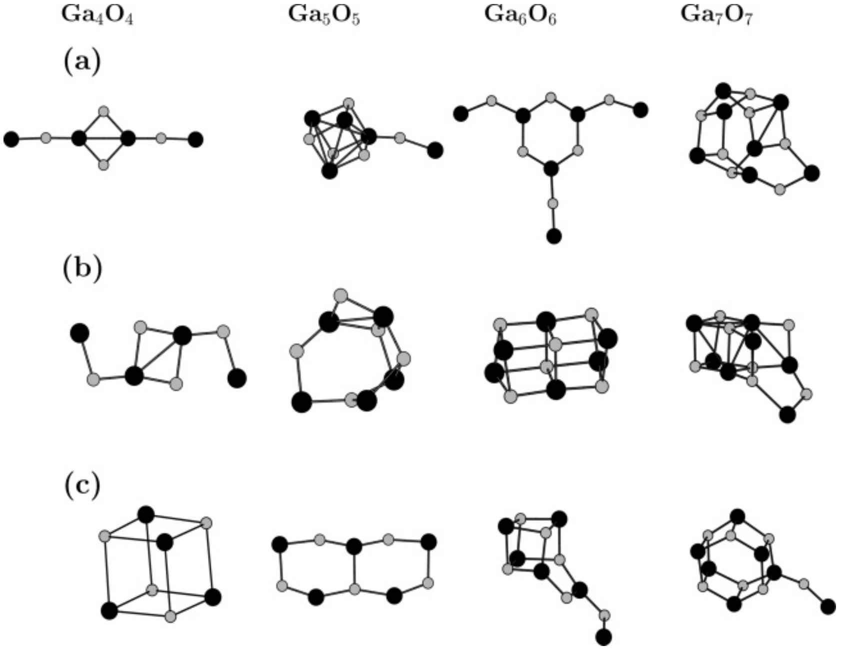

Figure 1. Some of the isomers of Ga_nO_n with $n = 4-7$. The lightly shaded spheres represent the O atoms, and the dark spheres represent the Ga atoms.

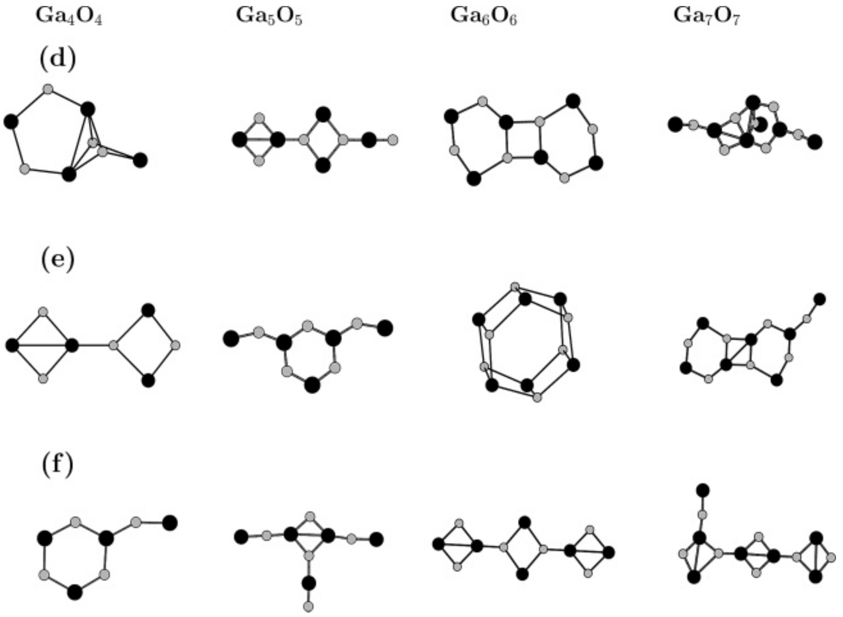

Figure 2. Some of the isomers of Ga_nO_n with $n = 4-7$. The lightly shaded spheres represent the O atoms and the dark spheres represent the Ga atoms.

The calculated electronic state of the GaO monomer is consistent with the experimental observation and with our previous calculations,[17] though the calculated bond length of 1.65 Å is slightly smaller than the experimental[11] value of 1.74 Å. For Ga_2O_2, both DFT-PW91/VASP and DFT-B3LYP/*Gaussian 98* calculations predict the ground state to be the linear Ga−O−Ga−O configuration. Similarly, both DFT-B3LYP/*Gaussian 98* and DFT-PW91/VASP calculations on Ga_3O_3 find the windowpane and kite configurations to be nearly degenerate, except for the fact that the windowpane configuration is lower in energy by 0.1 eV in the former case and the kite configuration is lower in energy by 0.07 eV in the latter case. The calculated values of the ionization potential and electron affinity also compare favorably with the previously reported DFT-B3LYP/*Gaussian 98* values.

Figures 1 and 2 show some of the typical equilibrium structures of neutral and ionic gallium oxide clusters where the lightly shaded spheres represent the O atoms and the dark spheres represent the Ga atoms. Figure 3 presents the lowest-energy configurations of neutral, anionic, and cationic Ga_nO_n clusters ($n = 4-7$). Table 1 collects total energy, spin state, and binding energy for the lowest-energy configuration of these clusters. It is seen that the clusters prefer the lowest spin state in the ground state.

The ground-state configurations show a preference for a quasi-planar arrangement of gallium and oxygen atoms for $n \leq 6$. A transition from the planar to three-dimensional (3D) configuration is predicted for $n = 7$ for neutral configurations, while for anionic clusters, a planar to nonplanar transition is observed at $n = 6$. As we shall see, the nature of bonding and the

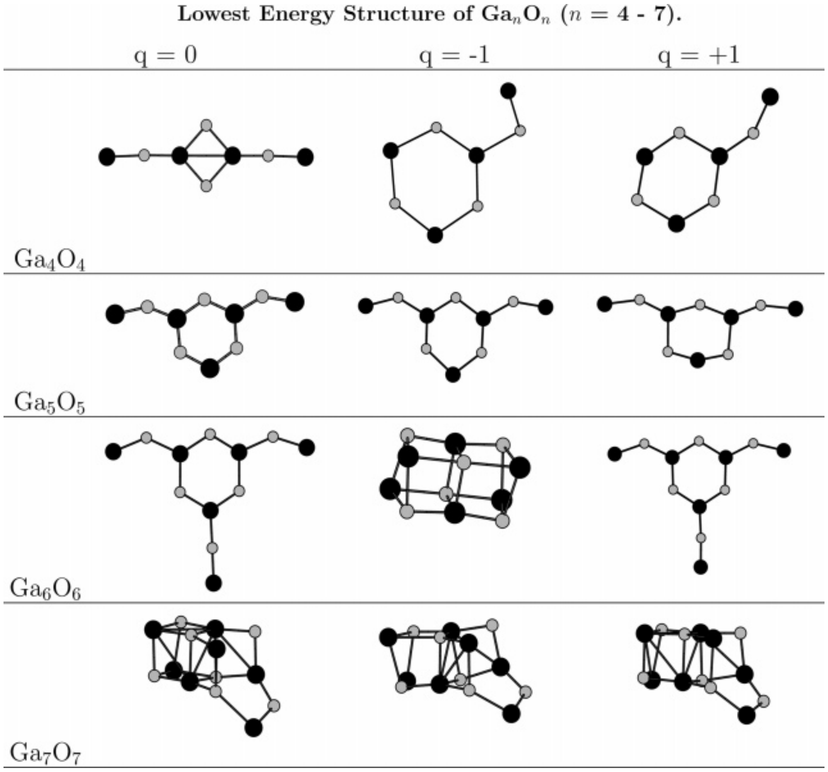

Figure 3. The predicted ground-state geometries of the neutral, anionic, and cationic Ga_nO_n clusters with $n = 4-7$. The lightly shaded spheres represent O atoms, and the dark spheres represent the Ga atoms.

TABLE 1: Total Energy (eV), Spin Multiplicity (2S+1), Binding Energy (eV/atom) for the Ground State of Ga_nO_n (n = 4−7) Clusters

system	charge (q)	E (eV)	2S+1	BE[a] (eV/atom)
Ga_4O_4	0	−2324.8495	1	3.94
	−1	−2327.4505	2	4.21
	+1	−2317.6184	2	3.03
Ga_5O_5	0	−2906.2494	2	3.96
	−1	−2909.7923	1	4.31
	+1	−2900.8692	1	3.42
Ga_6O_6	0	−3488.9164	1	4.08
	−1	−3491.1253	2	4.26
	+1	−3482.0116	2	3.49
Ga_7O_7	0	−4070.7510	2	4.10
	−1	−4073.8344	1	4.32
	+1	−4063.7798	3	3.59

[a] The calculated values for the binding energy of GaO, Ga_2O_2, and Ga_3O_3 are 2.47, 3.49, 3.71 eV/atom, respectively.

coordination index play an important role in stabilizing a given cluster. While interacting with oxygens, the gallium atoms donate their valance electrons, forming a bond which is dominated by the ionic character.

1. Ga_4O_4. A di-bridge rhombus configuration consisting of two Ga−O units attached to Ga atoms is predicted to be the lowest-energy structure. It can also be viewed as a Ga−O unit attached to the ground state of Ga_3O_3 consisting of the kite configuration. The bond distances R_{Ga-O} and R_{Ga-Ga} associated with atoms forming the rhombus are 1.8 and 2.5 Å, respectively. Both R_{Ga-O} and R_{Ga-Ga} remain nearly the same as in Ga_3O_3. The terminal Ga atom is attached to oxygen with R_{Ga-O} of 1.77 Å. The ground-state configuration is followed by the quasi-planar isomer (Figure 1b (Ga_4O_4)), which was obtained by the addition of a GaO unit in the windowpane structure of Ga_3O_3. Alternatively, the quasi-planar configuration can be viewed as a di-bridge rhombus configuration in which two terminal Ga−O units are bent by an angle of 102.17°. The quasi-planar configuration is 0.5 eV higher in energy compared to the ground state. The next isomer is the hexagonal ring configuration with one terminal O−Ga unit (Figure 2f (Ga_4O_4)) which is 0.7 eV above the ground state. Somewhat higher in energy ($\Delta E \approx 1.5$ eV) is a 3D cubic configuration, shown in Figure 1c (Ga_4O_4).

Addition of an electron to the neutral Ga_4O_4 introduces a significant change in the order of the isomeric configurations. The ground state for the anionic Ga_4O_4 is now a quasi-planar hexagonal ring configuration with a terminal Ga−O unit. The terminal Ga atom is slightly bent out of the plane of the ring with the dihedral O−Ga−O−$Ga_{terminal}$ angle of 43.2°. The bending of the Ga−O unit with the Ga−O−$Ga_{terminal}$ angle of 101.60° appears to facilitate the hybridization of molecular orbitals of the terminal Ga and O atoms. The bond distances R_{Ga-O} and R_{Ga-Ga} associated with atoms forming the ring are 1.77 and 3.06 Å, respectively. The terminal Ga atom is attached to oxygen with R_{Ga-O} of 1.78 Å. On the other hand, the di-bridge rhombus configuration, which is the ground state of the neutral Ga_4O_4, is 1.06 eV above the ring isomer. The 3D cubic configuration in the quartet spin state is 0.45 eV above the anionic ground state.

The origin of the change in ordering of the isomers in the anionic Ga_4O_4 can be traced to the nature of the lowest unoccupied molecular orbital (LUMO) of the neutral isomers. In the di-bridge rhombus configuration, the LUMO is associated with the antibonding orbital, while the LUMO of the hexagonal ring configuration is associated with the bonding orbital. It is therefore energetically favorable for an electron to be attached to the bonding orbital yielding the ground state of the anionic Ga_4O_4 to be the ring isomer, instead of the rhombus isomer.

The ground state of the cationic Ga_4O_4 is similar to that of the anionic Ga_4O_4. Here, the dihedral angle of O−Ga−O−$Ga_{terminal}$ is 27.5°, and the Ga−O−$Ga_{terminal}$ angle is 146.5°. The bond distances R_{Ga-O} and R_{Ga-Ga} associated with atoms forming the ring are 1.75 and 2.9 Å, respectively. The terminal Ga atom is attached to oxygen with R_{Ga-O} of 1.82 Å. We note here that the quasi-planar (Figure 1b (Ga_4O_4)) and di-bridge rhombus (Figure 1a (Ga_4O_4)) configurations are at 0.12 and 0.21 eV, respectively, above the cationic ground state.

2. Ga_5O_5. The calculated ground state is the quasi-planar configuration consisting of a hexagonal ring with two terminal Ga−O units, as shown in Figure 3. The structural parameters of the ring essentially remain the same as those in Ga_4O_4. The terminal Ga atoms are slightly out of plane of the ring with a dihedral angle of about 11°. The bond distances R_{Ga-O} and R_{Ga-Ga} associated with atoms forming the ring are 1.75 and 3.09 Å, respectively. The terminal Ga atom is attached to oxygen with R_{Ga-O} of 1.78 Å, and the $Ga-O-Ga_{terminal}$ angle is 147.21°. In going from Ga_3O_3 to Ga_5O_5, R_{Ga-O} associated with atoms in the ring decreases by 2%. The ground state is closely followed by the singlet cubic configuration with a terminal GaO molecule (Figure 1a (Ga_5O_5)) at 0.37 eV. All the other planar configurations such as extended windowpane, tri-bridge rhombus, and pair−rhombus configurations are about 2.0 eV higher in energy relative to the ground state.

Addition of an electron to Ga_5O_5 does not affect the isomeric sequence except in some of the cases where the isomer prefers the triplet spin state instead of the singlet spin state. The predicted ground state consists of the quasi-planar hexagonal ring with two Ga−O units. The dihedral $O-Ga-O-Ga_{terminal}$ angle is about 11°. The bond distances R_{Ga-O} and R_{Ga-Ga} associated with atoms forming the ring are 1.8 and 3.2 Å, respectively. The terminal Ga atoms are attached to oxygens with R_{Ga-O} of 1.74 Å, and the $Ga-O-Ga_{terminal}$ angles are 135.3° and 141.8°, respectively. We note here that LUMOs of both ring and cubic isomers in the neutral charge state are associated with the bonding orbitals. Similarly, removal of an electron from the neutral Ga_5O_5 does not introduce noticeable distortions in the cluster. In the ground state, the dihedral $O-Ga-O-Ga_{terminal}$ angle is 17.3°, and the $Ga-O-Ga_{terminal}$ angles are 147.1° and 152.9°.

3. Ga_6O_6. The ground state of Ga_6O_6 retains the features of the lowest-energy configuration of Ga_5O_5, and the structural parameters of the ring essentially remain the same. It consists of a quasi-planar hexagonal ring in which each Ga atom of the ring is terminated by a O−Ga unit, resulting in a coordination index of 3 for the ring Ga atoms. The dihedral $O-Ga-O-Ga_{terminal}$ angles are 29.1°, 29.1°, and 67.2° in the cluster. The bond distances R_{Ga-O} and R_{Ga-Ga} associated with atoms forming the ring are about 1.77 and 3.1 Å, respectively. The terminal Ga atom is attached to oxygen with R_{Ga-O} of 1.73 Å. The distorted cubic configuration, shown in Figure 1b (Ga_6O_6) is 1.7 eV above the ground state.

As in the case with Ga_4O_4, ordering of the isomeric sequence of the anionic Ga_6O_6 is different from that of the neutral Ga_6O_6. The distorted cubic configuration (Figure 1b (Ga_6O_6)) is predicted to be the ground state of the anionic Ga_6O_6, which is 0.39 eV lower in energy than the ring isomer. The LUMOs of the ring and cubic isomers in the neutral charge state are given in Figure 4, showing clearly their association with antibonding and bonding orbitals, respectively. The anionic ground state is therefore expected to prefer the cubic configuration, as predicted by the present calculations. In the cationic Ga_6O_6, removal of an electron does not make significant changes in the ring configuration, as was the case with the other gallium oxide clusters. The 3D isomer is found to be 0.75 eV above the ground state.

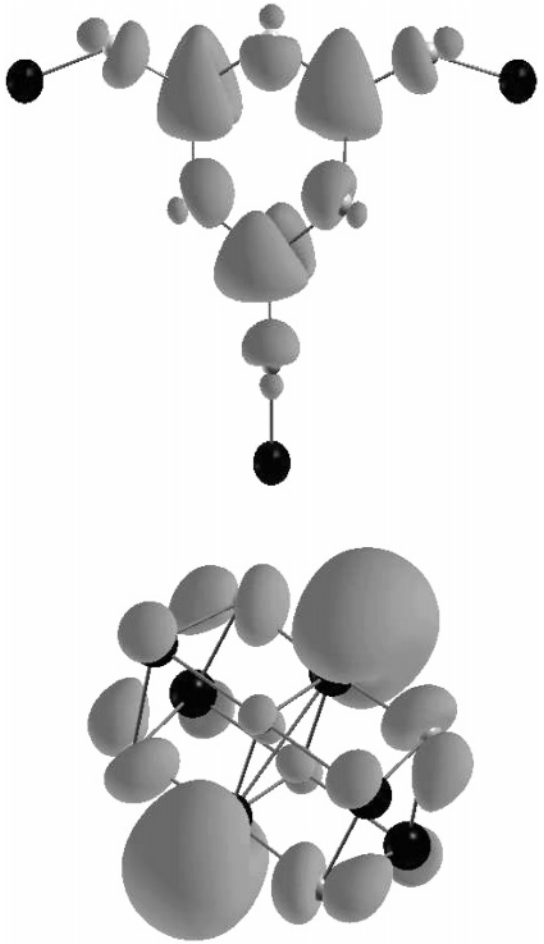

Figure 4. The isodensity surface corresponding to LUMO for the ring- and cubic-type isomers of Ga_6O_6. The lightly shaded spheres represent O atoms, and the dark spheres represent the Ga atoms.

4. Ga_7O_7. A transition to the 3D configuration is seen for Ga_7O_7. Addition of GaO to Ga_6O_6 yields the ground state consisting of a distorted cubic configuration, shown in Figure 3, in which a GaO terminal unit is attached to one of the edges of the cube. In this configuration, two gallium atoms appear to have a coordination number of 4 with R_{Ga-O} of (1.75, 1.80, 1.91, 2.02) and (1.76, 1.81, 1.94, 2.05) Å, respectively. R_{Ga-O} of the attached GaO unit is 1.90 Å. It is to be noted here that R_{Ga-O} of the tetrahedrally coordinated Ga atom in the crystalline β-Ga_2O_3 is 1.83 Å.[30] The planar low-lying isomer, two hexagonal rings with a terminal O−Ga unit (Figure 2e (Ga_7O_7)), is 0.7 eV above the 3D configuration. The predicted ground state of both cationic and anionic Ga_7O_7 clusters is similar to the neutral Ga_7O_7 and shows very small changes in the structural parameters.

The valence electron configurations of the Ga and O atoms are $4s^24p^1$ and $2s^22p^4$, respectively. While interacting with the oxygen atoms, gallium donates its valance electrons to oxygen to form a bond which is ionic in nature. This is in accordance with expectations from differences in the electronegativity of Ga and O atoms, which are are 1.8 and 3.44, respectively.

To show the nature of bonding in these clusters, we have shown the isosurface charge density of Ga_6O_6 in Figure 5. The localized charge density is evidently seen around O atoms. It is also seen that the charge density associated with oxygens is polarized toward gallium atoms. In a cluster, each oxygen prefers to be coordinated by two gallium atoms with a large apex angle. A large apex angle tends to facilitate a stronger coupling between Ga s and O p orbitals, and therefore makes the ring

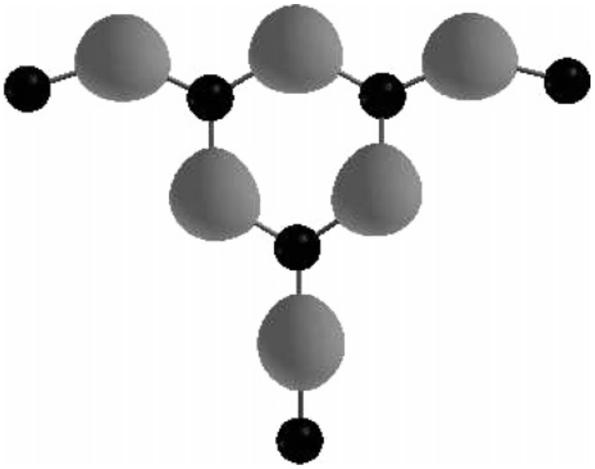

Figure 5. Total (isosurface) charge density at the value of $^1/_7$ of the maximum total charge density in the ground state of Ga_6O_6. The lightly shaded spheres represent O atoms, and the dark spheres represent the Ga atoms.

isomers energetically favorable over the cubic isomers. With the increase in the cluster size, the electrostatic interaction between Ga and O atoms begins to dominate, making the cubic isomers energetically favorable over the ring isomers. In making the transition to the 3D configuration, Ga_7O_7 maximizes the ionic metal−oxygen bonds in the cluster.

For Ga_6O_6, in the ring structure, all the Ga atoms are threefold coordinated, but the 3D structure is intermediate between the three-coordinated states in small clusters and the four-coordinated situation in β-Ga_2O_3. The structures reported here do not reflect the configuration of β-Ga_2O_3. Thus, there are two main factors determining whether a ring or three-dimensional structure will be the lowest-energy configuration for small gallium oxide clusters: the stability of very obtuse O−Ga−O bond angles and the stability gained from higher coordination. For Ga_nO_n, $n = 1-6$, the first term outweighs the second, and the ring structure is predicted to be the lowest-energy configuration. For $n = 7$, however, the size of the cluster allows both obtuse O−Ga−O bond angles and higher coordination in three-dimensional configurations, making the 3D structure the most stable.

From our previous studies,[17,18] it is observed that the geometries of gallium oxide clusters are nearly similar to those of aluminum oxide clusters. We have also compared the reported studies of stoichiometric Al_nO_n clusters with Ga_nO_n clusters which are limited to $n < 4$. For the neutral Al_4O_4, the DFT-B3P86 calculations[28] reported the singlet di-bridge rhombus and triplet cubic isomers to be nearly degenerate. The present DFT-PW91/VASP calculations find the triplet cubic isomer to be 1.5 eV higher in energy than the di-bridge rhombus configuration.

IV. Stability

The clusters considered are bound and stable against the fragmentation via a loss of the GaO molecule. Table 1 collects values of the binding energy. It can be seen that, after $n = 4$, the increase in binding energy is very marginal, on the order of 0.03 eV/atom. This is an indication that the clusters in the size range above 7 or 8 are unstable. This is consistent with the fact that the extended solid has the stoichiometry of Ga_2O_3. Indeed, we find that adding two more oxygen to Ga_7O_7 (i.e., Ga_7O_9 cluster) enhances the binding energy by 0.1 eV/atom, indicating that more oxygens are required to stabilizing the clusters. We have also carried out a limited search for Ga_8O_8 (about ten structures) and found that the binding energy of the lowest-energy configuration is nearly same as that of Ga_7O_7. The Ga_nO_n ($n = 4-7$) clusters are also stable against a loss of the GaO molecule. The fragmentation energy comes out to be 4.3, 3.1, 4.4, and 3.5 eV for Ga_4O_4, Ga_5O_5, Ga_6O_6, and Ga_7O_7, respectively.

TABLE 2: Vertical and Adiabatic Values (eV) of the Electron Affinity[a] and Ionization potential for Ga_4O_4, Ga_5O_5, Ga_6O_6, and Ga_7O_7

	Ga_4O_4	Ga_5O_5	Ga_6O_6	Ga_7O_7
vertical EA	3.8	4.1	4.0	4.5
adiabatic EA	2.6	3.5	2.2	3.1
vertical IP	7.5	6.7	7.0	6.3
adiabatic IP	7.2	5.3	6.9	6.9

[a] The vertical electron affinity is also referred to as the vertical detachment energy.

V. Electronic Properties

The computed values of the vertical and adiabatic electron affinity (EA) and ionization potential (IP) are presented in Table 2. The vertical electron affinity (VEA) or vertical detachment energy (VDE)[31] is defined as the energy difference between the anionic and neutral clusters with both at the optimized geometry of the anionic cluster. Adiabatic electron affinity (AEA) is defined as the energy difference between the anionic and neutral clusters at their own respective optimized geometries. Similarly, the vertical ionization potential 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 is defined as the energy difference between the cationic and neutral clusters at their own respective optimized geometries. According to Table 2, the computed EA and IP values do not show any systematic variation in going from Ga_4O_4 to Ga_7O_7, though a large difference in the vertical and adiabatic EA values for Ga_4O_4 and Ga_6O_6 is due to topologically different ground-state configurations in their neutral and negatively charged clusters.

The energy differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are calculated to be 3.9, 3.4, 3.7, and 2.6 eV for the neutral Ga_4O_4, Ga_5O_5, Ga_6O_6, and Ga_7O_7, respectively. The experimental band gap energy for the bulk Ga_2O_3 is 4.8 eV.

VI. Conclusions

The equilibrium structures, energetics, chemical bonding, and electronic properties of the neutral and ionic Ga_nO_n clusters with $n = 4-7$ are reported here. Calculations based on density functional theory find the structural motifs, namely, rhombus and hexagonal ring associated with the ground state of these clusters. The ionization induced changes in the structural parameters to be small. However, ordering of the isomeric configuration significantly changes upon addition of an electron for Ga_4O_4 and Ga_6O_6. The clusters considered prefer planar or quasi-planar configurations for $n \leq 6$. A transition to the 3D configuration is predicted for $n = 7$. Our analysis of binding energies indicate that larger clusters of Ga_nO_n may not be thermodynamically stable. The values for the electron affinity and ionization potential are consistent with the fact that the clusters considered are mainly ionic clusters dominated by the metal−oxygen bond.

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