Aluminum and Gallium Oxide Clusters

In this chapter, we have presented the results for the study of alumina and gallium oxide clusters using DFT. We present here ground state geometries, binding energies, relative stabilities, and HOMO-LUMO gap. A detailed comparison have been made between Al$_2$O$_3$ and Ga$_2$O$_3$ clusters along with their bulk phases and with available experimental results.

### 3.1 Introduction

The structural diversity is not as great for the heavier Group 13A elements, although a number of different structures are adopted by their oxides. Oxides of these materials span wide range of physical and chemical properties and has wide technological applications ranging from electronics, optics, biomedical, and mechanical engineering to catalyst support [93, 197]. Among all, solid Al$_2$O$_3$ is well studied material with numerous applications. There are seven different phases of Al$_2$O$_3$, although $\alpha$, $\gamma$, $\delta$, and $\theta$, are typically involved in most of the industrial processes [128]. Under normal pressure and temperature bulk alumina crystallizes as $\alpha$-Al$_2$O$_3$ better known as corundum, its unit cell has a hexagonal cell structure, with a rhombohedral primitive cell [198]. In the $\gamma$-phase of Al$_2$O$_3$, Al ions have tetrahedral and octahedral neighbourhoods and it is widely used as support in catalysis [199]. There are several allotropic forms of boron. Boron compounds can be classified into two groups, amorphous boron oxide and crystalline boron oxide. The amorphous boron oxide ($g$-B$_2$O$_3$) has glassy structure. The crystalline form ($\alpha$-B$_2$O$_3$) is exclusively

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1Structural and electronic properties of (Al$_2$O$_3$)$_n$ clusters with $n = 1 - 10$ from first principles calculations, Amol Rahane, Mrinalini Deshpande and Vijay Kumar, J. Phys. Chem. C, 115, 18111 (2011).

Structural and electronic properties of neutral and ionic (Ga$_2$O$_3$)$_n$ clusters with $n = 1 - 10$, Amol Rahane and Mrinalini Deshpande, J. Phys. Chem. C, 116, 2691 (2012)
composed of $\text{BO}_3$ triangles. This trigonal, quartz-like network undergoes a transformation to monoclinic $\beta$-$\text{B}_2\text{O}_3$ at 9.5 GigaPascals (GPa) [200, 201, 202]. Gallium oxide can exist in several forms, including $\alpha$, $\beta$, $\gamma$, $\delta$, and $\eta$ [136]. $\alpha$-$\text{Ga}_2\text{O}_3$ and high pressure phase of $\text{In}_2\text{O}_3$ crystallizes with corundum structure [136]. The thermodynamically stable phase $\beta$-$\text{Ga}_2\text{O}_3$ has monoclinic structure similar to that of $\delta$-$\text{Al}_2\text{O}_3$, with both tetrahedral and octahedral sites equally occupied by Ga ions within a distorted cubic close-packed oxide lattice [137]. The primary form of $\text{In}_2\text{O}_3$ adopts the cubic bixbyite structure which is common amongst the transition metal and rare earth sesquioxides [203]. The same structure is adopted by $\text{Tl}_2\text{O}_3$ [204]. A second phase with perovskite structure. Due to preference for lower oxidation states thallium is known to form other binary oxides like $\text{TlO}_2$.

With this diversity in their physical and chemical properties the nanostructures of group 13A metal oxides are also fascinating because of the small size, special shapes, and presence of under-co-ordinated atoms. The size and composition dependent properties are seen which are different from their bulk form. The vibrational spectroscopy of thin film of alumina has been studied by several groups [90, 129, 130]. The distinct feature is observed at the nanoscale that the structure get stabilize in $\gamma$-$\text{Al}_2\text{O}_3$ structure instead of the stable phase $\alpha$-$\text{Al}_2\text{O}_3$. Hale et al. [205] have studied experimentally as well as theoretically the surface structures formed upon deposition of $\text{In}_2\text{O}_3$ and $\text{Ga}_2\text{O}_3$ by molecular epitaxy onto arsenic rich GaAs(001)-c(2×8)/(2×4) surface. It is found that bond angle flexibility, bond stiffness, and atomic size are the main factors for determining the chemisorption sites. As technology evolves, having an exact understanding of the variation in electronic properties with size and composition, interface bonding structure, are imperative for optimal device performance. Experiments on mass selected clusters are useful to provide insight into the physics and chemistry.

Clusters of aluminum oxide have, consequently, been studied both theoretically [125, 131, 132, 154, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221] and experimentally [132, 213, 215, 222, 223, 224, 225] to better understand the relationship
between atomic structures, bonding nature, and other properties. Research has suggested that the gas-phase alumina clusters shows substantially different properties from the bulk alumina. Natural aluminum oxide clusters have been studied by low-temperature matrix isolation spectroscopy. However, these experiments have led to conflicting and contradictory assignments due to lack of direct information on the stoichiometry of the absorbing molecular species. Desai et al. [213] studied photoelectron spectra (PES) Al$_x$O$_y^-$, ($x = 1, 2$, $y = 1 - 5$) however, these clusters are too small to exhibit structural features of bulk. Meloni et al. [224] measured the photoelectron spectra of the Al$_2$O$_3^-$, Al$_3$O$_5^-$, Al$_4$O$_x^-$, Al$_5$O$_x^-$, and Al$_7$O$_x^-$ clusters. They assigned structures to the Al$_3$O$_2^-$ and Al$_4$O$_3^-$ clusters and their neutral counterparts on the basis of DFT. In 2003, Heijenbergen et al. [125], discovered the large abundance of AlO.(Al$_2$O$_3$)$_{15}$ cluster cation in the mass spectrum of gas phase aluminum oxide clusters. However, the structure has not been determined so far because of searching a structure with large size for AlO.(Al$_2$O$_3$)$_{15}$ clusters being beyond the current computing ability. In 2004, Demyk et al. [126] performed IR-REMPI spectra of gas phase AlO.(Al$_2$O$_3$)$_n$ clusters with, $n = 5 - 70$, they have provided preliminary evidence of $\gamma$-alumina structures however they have not provided information of the individual clusters.

Theoretical studies small alumina clusters of (Al$_2$O$_3$)$_n$ with $n$ up to about five that have been more extensively studied [131, 132, 154, 207, 211, 214, 215]. For larger clusters, the structures and properties have not been well established. Some of the earlier studies on clusters assumed that small aluminum oxide clusters have bulk-like structure. However, it is known that the gas phase clusters in general, and metal oxide clusters, in particular exhibit structures which may differ radically from the bulk system. Some researchers [208, 212, 219, 221] have studied cage structures while in some other studies [206, 209], amorphous structures have been suggested to be favored. There are large number of works devoted to the study of (Al$_2$O$_3$)$_4$ cluster. For (Al$_2$O$_3$)$_4$, the bulk corundum derived configuration (D$_{3d}$) was presumed to be the global minimum by most of the studies [206,
3. Aluminum and Gallium Oxide Clusters

For example, a recent first principles study [206] a water adsorption on alumina clusters assumed corundum (α-Al₂O₃) derived configuration for Al₈O₁₂. Sun et al. [208] constructed the structures of (Al₂O₃)ₙ with n = 1 − 10, suggested cubic structure for Al₈O₁₂. Their study revealing that cage structures are the global minimum at n = 1 − 5, and cage-dimer structures at n = 6 − 10.

A combined experimental (IR-MPD) and DFT study for neutral and cationic (Al₂O₃)₄⁺ clusters was performed by Sierka et al. [215]. They have shown that neither the bulk-like nor the caged structure is the global minimum. In the experimental IR-MPD spectrum the most intense absorption band is at 997 cm⁻¹ with a clear shoulder at 1024 cm⁻¹. However, no such band observed for corundum derived (Al₂O₃)₄⁺ configuration using the theoretical computation. i.e. no signs of α-(Al₂O₃)₄⁺ was seen in the observed clusters. However, they suggested arrow-head configuration with one terminal O, of (Al₂O₃)₄⁺, shows experimentally observed feature.

With this background of the previous studies on alumina clusters, we have started evolving the structural and electronic properties of alumina clusters with n = 1 − 10 using DFT. Similar to aluminum oxide, gallium oxide is an important semiconducting oxide with applications in the areas of optics and microelectronics. Gallium oxide low dimensional nanostructures have been recently created by physical evaporation and arc-discharge methods, thus opening up a new research area with promising applications.

Gallium oxide nanostructures such as rods, wires, belts, tubes, and spheres have been fabricated through a number of advanced nanolithography techniques, thermal evaporation, vapor deposition, or solution-based methods etc. [140, 141, 142, 143, 144, 145, 146, 147, 148]. In an recent experimental study [230] on composites of Ga₂O₃ clusters and zeolite ZSM-5 were evaluated for the transformation of methanol to hydrocarbons. Comparison of the activity with ZSM-5 showed that the Ga₂O₃ clusters are responsible for the enhanced selectivity to aromatics via contact synergy, thus opening applications of Ga₂O₃ clusters in catalysis.
At the cluster level, a few scattered experimental and theoretical studies have been reported on gallium oxide. Most of these studies focus on the structural, electronic, and bonding properties of gallium oxide dimers (GaO) [231, 232, 233, 234], suboxides (Ga$_2$O) [232, 234, 235, 236, 237] and superoxides (GaO$_2$) [232, 238, 239]. A DFT study by Archibong et al. [240] predicted the linear configuration for Ga$_2$O$_2$ and rhombus structure for Al$_2$O$_2$. Recently, Gowtham et al. performed systematic studies [155, 156] on the evolution of structural and electronic properties of small size gallium oxide clusters. In their initial study on gallium oxide clusters reported the structural, vibrational, and electronic properties of Ga$_m$O$_n$ ($m, n = 1, 3$). The authors have also considered both metal-excess and oxygen-excess fragments to investigate the effect of the oxygen/metal ratio on the structural and electronic properties of the clusters. The results of a experimental study by Meloni et al. [151] find a very good agreement with calculated adiabatic electron affinity value by Gowtham et al. [155] for GaO monomer and the Ga-O bond distances in neutral and anionic GaO$_2$. DFT investigations by Deshpande et al. [157] for stoichiometric Ga$_n$O$_n$ ($n = 1−7$) reported [157] that the structural motif of these small clusters appears to be rhombus or a hexagonal rings with alternate gallium and oxygen atoms. However, the stability analysis of these clusters indicates that the larger clusters of Ga$_n$O$_n$ may not be thermodynamically stable, due to the difference in the composition of these clusters from bulk stoichiometry (Ga$_2$O$_3$).

For Ga$_2$O$_3$, the results of earlier studies by Gowtham et al. [156] using DFT-B3LYP indicate that kite-shaped ($C_{2v}$) structure is a lowest energy configuration. On the other hand, the results at the DFT-B3LYP/MP2/CCSD(T) levels using flexible one particle basis sets showed that the ground state geometry of Ga$_2$O$_3^{-}$ is the kite-shaped while the neutral Ga$_2$O$_3$ prefers the V-shaped geometry [152, 153]. Recently, S. Woodley [154] carried out study on structural and electronic properties of (M$_2$O$_3$)$_n$, where $n = 1−5$, M = B, Al, Ga, In, and Tl using DFT. In their study Ga$_2$O$_3$ prefers the kite-shaped configuration, while $\alpha$-Ga$_2$O$_3$ derived configuration is preferred for (Ga$_2$O$_3$)$_4$. The structural
and electronic properties of large size clusters are still lacking.

We have studied the \( (\text{Ga}_2\text{O}_3)_n \) clusters, with \( n = 1 - 10 \) using density functional theory with plane wave pseudopotential approach. Our aim was to understand the evolution of structural and electronic properties of clusters with the stoichiometry of the bulk \( \text{Ga}_2\text{O}_3 \) and to determine their convergence to the corresponding bulk values. We have performed the study on the equilibrium structure, stability, bonding, electron affinity, and ionization potential of \( (\text{Ga}_2\text{O}_3)_n \) clusters.

A proper knowledge of the atomic structures would not only be important for understanding the nanostructures of alumina and gallium oxide, but such a study is likely to have wider implications for nanoparticles of other oxides such as \( \text{In}_2\text{O}_3 \) etc., and related materials as well as in the development of optoelectronic devices.

### 3.2 Computational Details

The calculations have been performed using projector augmented wave (PAW) pseudopotential method \cite{179, 241} as implemented in Vienna \textit{Ab initio} Simulation Package (VASP) \cite{158} within the framework of the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof \cite{242}. The clusters were placed in a cubic supercell with an edge length of 24 Å and periodic boundary conditions were imposed. The cut-off energy for the plane wave expansion was set to be 282.8 eV. The calculations were considered to be converged when the force on each ion was less than 0.001 eV/Å with the convergence in the total energy of about \( 10^{-5} \) eV.

Several initial choices of the atomic structures for the geometry optimization of \( \text{Al}_2\text{O}_3 \) clusters were considered including structures obtained in previous studies. Several new structures were constructed by successively adding an \( \text{Al}_2\text{O}_3 \) unit on small converged clusters. Furthermore, simulated annealing (SA) calculations have been carried out on \( (\text{Al}_2\text{O}_3)_n \) clusters with \( n = 5 - 10 \). In these calculations the initial cluster configuration was heated up to 2500 K followed by slow cooling. The equilibrium geometries of the
lowest and the low-lying isomers were obtained by quenching a number of configurations obtained during the simulated annealing runs using the quasi-Newton method [243].

Spin-polarized calculations were also performed for small size neutral and for charged clusters. The structural symmetry is calculated using visual molecular dynamics (VMD) package [244]. The configurational stability is further studied by calculating the IR and Raman spectra for some of the clusters using Gaussian 03 code [245]. We have used Stuttgart Dresden basis set (SDD) [246] with B3PW91 exchange correlation hybrid functional [247]. To benchmark the accuracy of these calculations, we first considered a Al$_2$O$_3$ molecule for which we obtain triplet state to be 1.19 eV lower in energy as compared to the singlet state. The calculated IR harmonic frequency with the highest intensity for the triplet state is 880.5 cm$^{-1}$ in agreement with the experimental results [213] of 850 cm$^{-1}$. We have also calculated the IR spectrum using 6-311+G basis set and the IR harmonic frequency is 875.2 cm$^{-1}$. Changing the exchange-correlation functional to B3LYP leads to improved IR frequency of 869.9 cm$^{-1}$, but the difference is small. Therefore SDD basis set with B3PW91 exchange-correlation combination predicts quite good quality results and the true frequencies can be expected to be slightly lower. We also calculated the electron affinity of Al$_2$O$_3$ molecule using SDD/B3PW91 and 6-311+6/B3LYP and the values are 4.21 eV and 3.52 eV, respectively, as compared to the experimental value of 3.71 eV [213]. For comparison we have also performed calculations on bulk $\alpha$- and $\gamma$-Al$_2$O$_3$ phases using VASP by keeping the same exchange-correlation functional and energy cut-off as for nanoclusters. For $\alpha$-Al$_2$O$_3$ the supercell consists of six Al$_2$O$_3$ units and for $\gamma$-Al$_2$O$_3$ the supercell consists of eight Al$_2$O$_3$ units. We use a 6 × 6 × 2 Monkhorst-Pack (MP) [248] k-point sampling for Brilluion Zone integrations. The calculated lattice parameters for $\alpha$-Al$_2$O$_3$, $a = b = 4.81$ Å, $c = 13.21$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ agree well with the experimental values [198] of $a = b = 4.76$ Å, $c = 12.99$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. For $\gamma$-Al$_2$O$_3$ the calculated lattice parameters, $a = 5.63$ Å, $b = 5.59$ Å, $c = 13.68$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$ agree well with the previously calculated values [249] of $a =$
5.61 Å, \( b = 5.57 \) Å, \( c = 13.48 \) Å, \( \alpha = \beta = 90^\circ \), and \( \gamma = 120^\circ \). From our calculations the \( \alpha-\text{Al}_2\text{O}_3 \) is more stable than the \( \gamma-\text{Al}_2\text{O}_3 \).

For \((\text{Ga}_2\text{O}_3)_n\) clusters, several initial diverse configurations were considered for these calculations. The choice of the initial geometries was partially dependent upon the previous studies of clusters of aluminum oxide [154, 208, 210, 215, 250], indium oxide [33], and gallium oxide [154, 157, 251]. 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 neutral (ionic) cluster. Based on our earlier experience, Ga-3\(d\) orbitals are included in the core part of the Ga pseudopotential in the subsequent calculations.

For comparison, we have also performed the calculations on bulk \( \beta- \) and \( \alpha-\text{Ga}_2\text{O}_3 \) phases using VASP by keeping the same exchange-correlation functional and energy cut-off as for cluster calculations. For \( \beta-\text{Ga}_2\text{O}_3 \) the supercell consist of two \( \text{Ga}_2\text{O}_3 \) units and for \( \alpha-\text{Ga}_2\text{O}_3 \) the supercell consist of six \( \text{Ga}_2\text{O}_3 \) units. We use a \( 6 \times 6 \times 6 \) MP [248] \( \mathbf{k} \)-point sampling for BZ integrations. The calculated lattice parameters within GGA-PBE for \( \beta-\text{Ga}_2\text{O}_3 \), \( a = 12.35 \) Å, \( b = 3.07 \) Å, \( c = 5.87 \) Å, and \( \beta = 103.7^\circ \) are consistent with the experimental values [137] \( a = 12.27 \) Å, \( b = 3.03 \) Å, \( c = 5.80 \) Å, and \( \beta = 103.7^\circ \). For \( \alpha-\text{Ga}_2\text{O}_3 \), the calculated lattice parameters, \( a = 5.07 \) Å and \( c = 13.66 \) Å agree well with the experimental values [138] of \( a = 4.98 \) Å, and \( c = 13.43 \) Å. Our results are also in agreement with previous theoretical calculations by He et al. [252]. For \( \beta-\text{Ga}_2\text{O}_3 \), the Ga atoms have tetrahedral- and octahedral-coordination in the lattice while for \( \alpha-\text{Ga}_2\text{O}_3 \), gallium ions occupy the octahedral sites. The calculated cohesive energy for \( \beta-\text{Ga}_2\text{O}_3 \) and \( \alpha-\text{Ga}_2\text{O}_3 \) per atom is 5.02 and 4.99 eV, respectively.
### 3. Aluminum and Gallium Oxide Clusters

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Figure 3.1: The lowest energy and some of the low-lying isomers of \((\text{Al}_2\text{O}_3)_n\), \(n = 1 - 4\) clusters with their point group symmetry. The energy of an isomer is given with respect to the energy (taken to be zero) of the lowest energy isomer for a given size. White (larger) spheres represent Al atoms and red (smaller) spheres represent O atoms.
3. Results and Discussion

3.3 Atomic Structures of $(\text{Al}_2\text{O}_3)_n$ Clusters with $n = 1 - 4$

The lowest energy atomic structures as well as a few other isomers for each size of $(\text{Al}_2\text{O}_3)_n$ clusters, with $n = 1 - 4$, are shown in Figure 3.1. An analysis of the atomic structures shows that the lowest energy structures evolve with 4-membered $\text{Al}_2\text{O}_2$, 6-membered $\text{Al}_3\text{O}_3$, and 8-membered $\text{Al}_4\text{O}_4$ rings having alternate Al and O atoms. Among these, there is preference for 4-membered and 6-membered rings. It is to be noted that such 4- and 6-membered rings are also found in nanoparticles of ZnO, GaN, and other compounds in which case also there is very significant ionic bonding, though the stoichiometry is different. The stability of different isomers of a nanoparticle with a given size often depends on the number of such rings and how they are distributed. In the following we discuss the calculated atomic structures of alumina clusters in detail.

Earlier theoretical studies [125, 132, 154, 206, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 222, 223, 224, 225] have explored the structural and electronic properties of small $(\text{Al}_2\text{O}_3)_n$ clusters with $n$ up to about 5. Our results of the lowest energy isomers are consistent with those obtained in reference [154] for $n$ up to 5 and for $n = 4$, our result of the lowest energy isomer agrees with the results of Sierka et al. [215]. Here, we describe these results for completeness. For $\text{Al}_2\text{O}_3$ molecule, the lowest energy configuration (1(a) in Figure 3.1) is a rhombus with an oxygen atom attached to one of the Al atoms. It has a triplet state. A linear structure shown as 1(b) in Figure 3.1 lies 0.29 eV higher in energy while another symmetric isomer (1(c) in Figure 3.1) lies 1.24 eV higher in energy. Note that the atomic distribution in isomer 1(c) is found in bulk $\alpha$-alumina. Isomer 1(d) which differs slightly from 1(a) in the way one Al atom is placed with an $\text{AlO}_3$ fragment, becomes 1.86 eV higher in energy than the lowest energy isomer. This result shows that small changes in these structures could make a large difference in energy.
In the lowest energy configuration of \((\text{Al}_2\text{O}_3)_2\), four Al atoms form a tetrahedron and O atoms cap the edges of the tetrahedron. This configuration with \(T_d\) symmetry consists of four 6-membered rings. The global optimization using DFT with B3LYP functional has shown the cage-like \(T_d\) symmetric structure is the lowest energy configuration for neutral \((\text{Al}_2\text{O}_3)_2\) cluster [132]. A similar structure has been obtained for \(\text{Mo}_4\text{S}_6\) and it is highly stable [253]. Another isomer that has both 6-membered and 4-membered rings lies 0.49 eV higher in energy while a few other isomers shown in Figure 3.1 lie more than 1 eV higher in energy. For \(n = 3\), we find three isomers which are nearly degenerate. In this case isomer 3(b) has two 6-membered and three 8-membered rings (no 4-membered ring) while isomer 3(c) has 4-, 6-, and 8-membered rings. The lowest energy isomer has a capped pentagon of Al atoms and oxygen atoms cap its edges. All but one oxygen atoms have two coordination of Al atoms. For \(n = 4\), the lowest energy isomer (4(a) in Figure 3.1) consists of three 4-membered, four 6-membered, and three 8-membered rings. The 4-membered rings are interconnected and are capped by an \(\text{AlO}_3\) unit from above and below. The minimum Al-O bond length is 1.73 Å (average bond length 1.76 Å) which is shorter than the calculated value of 1.87 Å and 1.99 Å in bulk \(\alpha\)-alumina and 1.75 Å to 1.98 Å in \(\gamma\)-alumina from our bulk calculations. Shortening of the bond distances is normally expected with a reduction in the coordination such as in clusters. The bulk corundum \(\alpha\)-\(\text{Al}_2\text{O}_3\) fragment structure 4(b) which has been obtained as the lowest energy isomer for this size by some groups [206, 228, 229, 254], is of 0.21 eV higher energy in our calculations. The mean nearest neighbour bond length is 1.80 Å and this isomer is more compact compared to 4(a). It consists of six 4-membered and six 6-membered rings and it has 3-fold rotational symmetry (\(D_{3d}\)). In general in other isomers, most Al atoms are 3-fold coordinated with oxygen and only a few are with four oxygen neighbours. But in the corundum fragment isomer, two Al atoms are 3-fold coordinated and six Al atoms are 4-fold coordinated. The local environments of 4-fold coordinated Al atoms are in between those of octahedral and tetrahedral arrangements. Therefore fragments of
corundum (\(\alpha\)-alumina) tend to transform to environments in \(\gamma\)-alumina.

If we consider O-Al-O bond angles in the AlO\(_4\) tetrahedral units in 4(a) isomer, we find six O-Al-O angles in the range of 87.17\(^\circ\)-132.09\(^\circ\), while in the corundum fragment isomer 4(b), the values are in the range of 84.40\(^\circ\)-163.87\(^\circ\) compared with the bond angle of 109.47\(^\circ\) in an ideal tetrahedron. Therefore the O-Al-O bond angles in the AlO\(_4\) units in the lowest energy configuration are closer to the ideal tetrahedral bond angle and thus to \(\gamma\)-alumina. There is an isomer 4(c) with cubic symmetry which is 0.32 eV higher in energy than 4(a). An arrow headed isomer 4(e) that was suggested in an earlier study [215], lies very high in energy. However, if the terminal oxygen in this isomer is changed, we obtained another isomer shown in 4(d) which is only 0.34 eV higher in energy than 4(a). Therefore isomers 4(a) to 4(d) are competitive. But in cation form isomer 4(e) becomes important as it will be discussed later along with the IR and Raman spectra.

3.3.2 IR and Raman Spectra of (Al\(_2\)O\(_3\))\(_n\) Clusters with \(n = 1 - 4\)

Earlier studies [206, 228, 229, 254] have shown the corundum fragment structure 4(b) to be of the lowest energy while in some studies [208, 212] the cubic isomer 4(c) of Al\(_8\)O\(_{12}\) has been predicted to be of the lowest energy. In our Gaussian calculations also we get the neutral corundum isomer 4(b) to be of the lowest energy and the cubic isomer to be the second best with 0.51 eV higher energy. Isomers 4(a) and 4(d) are nearly degenerate with the cubic isomer while the arrowhead isomer 4(e) lies 1.97 eV higher in energy than 4(b). Considering thermal contribution to the free energy at room temperature reduces the difference in isomers 4(b) and 4(c) to 0.35 eV. Thus the energy ordering of the isomers with Gaussian method is different from the one we have obtained from VASP and it is likely to be due to different exchange-correlation functional we have used in Gaussian calculations. A recent theoretical work in combination with IR-multiple photon dissociation (MPD) experiments [215] has shown that the corundum fragment is neither the global minimum for the neutral (Al\(_2\)O\(_3\))\(_4\) cluster nor for the cationic (Al\(_2\)O\(_3\))\(_4^+\) cluster.
Figure 3.2: The calculated IR and Raman spectra of the lowest energy neutral isomers (1a, 2a, and 3a) of $n = 1 - 3$ as in Figure 3.1 and obtained from the Gaussian program. The calculated spectra have been convoluted with Gaussian functions (full width at half maximum (FWHM) $\approx 23 \text{ cm}^{-1}$).
Figure 3.3: The experimental IR-multiple photon dissociation spectrum of a [(Al₂O₃)₄]⁺ cation cluster taken from reference [215], along with the calculated IR spectra of cation and neutral isomers (4a), (4b), (4c), (4d), and (4e) in Figure 3.1 for \( n = 4 \). For a comparison, the calculated spectra in (4a-4e) have been convoluted with Gaussian functions (FWHM \( \approx 23 \) cm\(^{-1} \)). Note that, the x-scale on the experimental and calculated spectra is different.
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Figure 3.4: The calculated Raman spectra of \((\text{Al}_2\text{O}_3)_4\) cation and neutral isomers \((4a), (4b), (4c), (4d), \) and \((4e)\) in Figure 3.1. The calculated spectra have been convoluted with Gaussian functions (FWHM \(\approx 23\) cm\(^{-1}\)).
in gas phase and they suggested the arrowhead isomer 4(e). We have calculated the IR spectra of neutral and cationic isomers for \( n = 4 \) as well as for the lowest energy isomers of neutral clusters with \( n = 1 - 3 \) using Gaussian program. As mentioned earlier, our results of the highest intensity IR frequency for neutral \( \text{Al}_2\text{O}_3 \) molecule agree well with the available experimental results of IR spectrum [213] with a slight overestimation. Our calculated IR and Raman spectra for \( n = 1 - 3 \) are shown in Figure 3.2. One can see that the highest frequency mode in these clusters is at 880.5, 844.7, and 963.5 cm\(^{-1}\), respectively for \( n = 1, 2, \) and 3 as compared to the bulk IR mode at 822 cm\(^{-1}\) for \( \alpha \)-alumina [225] and 738.6 cm\(^{-1}\) (medium strong peak) and 846.9 cm\(^{-1}\) (relatively weak intensity) for \( \gamma \)-alumina [255]. In general the mean Al-O bond length in clusters is shorter than in bulk and it slowly increases towards the bulk value. Therefore, we can expect the highest vibrational frequency to be larger in clusters as compared to bulk. This is the case for \( n = 1, 2, \) and 3 neutral clusters for which the shortest and mean Al-O bond lengths are, respectively, 1.70, 1.74, 1.76, and 1.75, 1.74, 1.77 Å. In the triplet state of \( \text{Al}_2\text{O}_3 \) the Al-O bonds are slightly elongated as compared to singlet state. For \( n = 3 \), a shorter bond length leads to higher frequency mode in this cluster.

The spin-polarized calculations on cations of \( n = 4 \) cluster give a doublet electronic configuration and the arrowhead isomer 4(e) has the lowest energy as also obtained earlier [215] while the cubic isomer 4(c) is the second best with 0.77 eV higher energy. Cations of 4(b) and 4(d) isomers lie 0.98 and 0.93 eV higher in energy than cation of 4(e) and are nearly degenerate with the cation of isomer 4(c) while the cation of neutral isomer 4(a) is 1.39 eV higher in energy. Therefore, the energy ordering for neutral and cation isomers changes significantly. Figure 3.3 shows the experimental IR-MPD spectrum [215] along with the calculated IR spectra for all the neutral and cationic isomers. The experimental spectrum for \( (\text{Al}_2\text{O}_3)_4^+ \) shows a characteristic IR frequency at 1030 cm\(^{-1}\). The calculated IR spectrum for the cation of isomer 4(a) has a peak at 1019.6 cm\(^{-1}\) and shows similarity with the experimental spectrum. The positions of the other peaks also have similar values.
as in the experimental spectrum. The cation of the cubic isomer as well as the cation of the corundum isomer have no similarity with the experimental spectrum. For the corundum configuration the calculated spectrum does not have a strong high frequency peak and so it is not in agreement with the experimental results. Also in the case of the cation of the cubic isomer 4(c) there is no sharp peak at around 1000 cm\(^{-1}\) as the IR intensities for all high frequency modes are zero. For the neutral cubic cluster there is indeed a high frequency peak. The cation of the arrowhead isomer 4(e) has a high frequency IR mode at 1049.3 cm\(^{-1}\) and the IR spectrum has similarity with the experimental spectrum, though we do not get a shoulder at the high frequency as observed, but there is another peak of slightly lower intensity at a slightly lower frequency. The IR spectra of the neutral isomers 4(a) and 4(e) have also much similarity with the experimental data on cation of Al\(_8\)O\(_{12}\) and in this respect the charge on these isomers has weak effect on the IR spectra. The effect of removal of electron is evidently seen in the dipole moments of these isomers. The large dipole moments indicate the asymmetry in the molecular charge distribution. Removal of electron from the lowest energy configuration 4(a) enhances the dipole moments (in debye) from the value of 1.57 D for the neutral isomer to 4.90 D for the cationic configuration. In the case of the isomer 4(e), due to the terminal oxygen, a large dipole moment (10.24 D) is seen in the neutral configuration while for the cationic cluster, it reduces to 1.45 D. The highly symmetric isomers 4(b) and 4(c) have lower dipole moments (\(\approx\) 0 D). The dipole moments for 4(d) neutral and cationic isomers are 6.06 D and 3.51 D, respectively. However, interestingly the IR spectra of other isomers such as 4(b) - 4(d) show significant difference between neutral and cation clusters. It should be noted that for bulk, the highest vibrational bands were observed at 846.9 cm\(^{-1}\) for \(\gamma\)-Al\(_2\)O\(_3\) phase and 822 cm\(^{-1}\) for \(\alpha\)-Al\(_2\)O\(_3\) phase in experiments [125, 225]. These results (both experimental and the calculated ones) suggest IR spectra of cluster isomers to be closer to that of \(\gamma\)-phase and that the high frequency mode is due to shorter Al-O bonds as compared to bulk. Our results of the IR spectra on cations of \(n = 4\) clusters show the possibility of both 4(a) and
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4(e) isomers in experiments.

The Raman spectra of the neutral and cation isomers of \( n = 4 \) cluster are also shown in Figure 3.4. The highest peak in the spectra of the different isomers is at quite different positions. Also for the cations of isomers 4(a) and 4(e), the highest Raman peaks are at quite different positions from the IR spectra. For the cation of isomer 4(a), there are Raman modes at 830.5, 938.3, and 951.6 cm\(^{-1}\) with high intensities and this is reflected as a sharp peak in the Raman spectra around 900-1000 cm\(^{-1}\) while for the cation of isomer 4(e), the highest Raman intensity is at 409.5 cm\(^{-1}\). A similar behavior has also been seen for the Raman spectra of \( n = 1, 2, \) and 3 clusters where also the highest intensity peaks appear at different positions from those in the IR spectra. We are not aware of any experimental results on Raman spectra on these clusters and our data could serve as an additional check to determine the lowest energy isomers of \((\text{Al}_8\text{O}_{12})^+\) produced in experiments.

3.3.3 Atomic Structures of \((\text{Al}_2\text{O}_3)_n\) Clusters with \( n = 5 - 10 \)

For larger clusters \((n = 5 - 10)\), several initial structures, both ordered and distorted ones were chosen for each \(n\). In this size range, with the addition of \(\text{Al}_2\text{O}_3\) units, the clusters evolve around the corundum fragment 4(b) and are more symmetric with a layered structure. The lowest energy and some of the low-lying configurations of \((\text{Al}_2\text{O}_3)_n\), \((n = 5 - 10)\) clusters are shown in Figure 3.5.

For \(n = 5\), a \(\text{Al}_2\text{O}_3\) unit is added to the corundum fragment 4(b) (in Figure 3.5) and it gets attached to the central 3-fold coordinated Al atom in this isomer. This leads to the formation of a T-shaped AlO\(_3\) unit above the plane of the outer perimeter ring and a trigonal AlO\(_3\) unit in the plane of the perimeter ring (as shown in Fig. 3.1-5(a)). The O-Al-O bond angles in the T-shaped AlO\(_3\) unit are 168.81\(^\circ\), 93.05\(^\circ\), and 99.55\(^\circ\) while in the trigonal AlO\(_3\) unit these are 121.66\(^\circ\), 121.46\(^\circ\), and 116.40\(^\circ\). The T-shaped AlO\(_3\) unit is more favourable and is present in large size clusters. Another isomer derived from 4(b)
Figure 3.5: The lowest energy and some of the low-lying isomers of \((\text{Al}_2\text{O}_3)_n\), \((n = 5 - 10)\) clusters with their point group symmetry. Other details are same as in Figure 3.1.
is distorted and is shown in 5(b). It has $C_s$ symmetry. It is 0.86 eV higher in energy than isomer 5(a). An isomer 5(c) derived from 4(d) lies 0.89 eV higher in energy while an open cage isomer 5(d) with D$_{5h}$ symmetry (two 10-membered and five 8-membered rings) lies 1.03 eV higher in energy than the ground state we have obtained. Another cage like isomer with $C_{3v}$ symmetry lies 1.62 eV higher in energy than 5(a). Therefore, open cage isomers are unlikely.

Further addition of an Al$_2$O$_3$ unit to Al$_{10}$O$_{15}$ distorts the cluster significantly. As noted in the case of 5(a), for $n = 6$ also, the added Al$_2$O$_3$ unit prefers to attach to the same 3-fold coordinated Al atom of 4(b) and it forms a second layer of Al$_2$O$_2$ units over the perimetric ring of the cluster. The lowest energy configuration has C$_1$ symmetry. The maximum coordination of Al atoms is four while for O atoms it is three. The Al-O bond distances are in the range of 1.69-1.84 Å. Another isomer 6(b) with C$_i$ symmetry was obtained by adding two Al$_2$O$_3$ units near the 3-fold coordinated Al atoms of 4(b) on the opposite sides of the perimeter. The converged isomer has trigonal AlO$_3$ units on the two opposite sides of the perimeter ring of 4(b) and it is 1.04 eV higher in energy. The cage dimer configuration 6(e), which is a combination of two Al$_6$O$_9$ cages 3(b), is 1.85 eV higher in energy than the lowest energy configuration.

The lowest energy isomer of (Al$_2$O$_3$)$_7$ is bi-layered with $C_s$ symmetry (Fig. 3.5-7(a)). This configuration consists of fifteen 4-membered and nine 6-membered rings. The stacking of Al$_2$O$_2$ rings facilitates an increase in the coordination number of Al and O atoms with three Al atoms 5-fold coordinated, ten Al atoms 4-fold coordinated and one Al atom 3-fold coordinated. The O atoms are 2-, 3-, and 4-fold coordinated. Note, that the maximum coordination of Al atoms in bulk $\alpha$-Al$_2$O$_3$ is six while that of oxygen it is four. The Al-O bond distances within a layer are 1.77-1.82 Å and between the two layers, 1.82-1.87 Å. If we consider the ring statistics for the lowest energy and the second lowest energy (7(b), $\Delta E = 1.03$ eV) isomers, it is observed that isomer 7(a) has fifteen 4-membered and nine 6-membered rings while in isomer 7(b) there are eight 4-membered,
six 6-membered, and five 8-membered rings. The presence of 8-membered rings decreases the overall coordination of the low symmetrical $C_1$ configuration.

The lowest energy isomer for $(\text{Al}_2\text{O}_3)_8$ is a three layered pyramidal cage structure with $D_{2d}$ symmetry (Fig. 3.5-8(a)). Two oxygen atoms are inside the pyramidal cage structure. It consists of twenty two 4-membered and eight 6-membered rings. There are four Al atoms with 5-fold coordination and twelve Al atoms with 4-fold coordination. The maximum coordination of oxygen is four as in bulk corundum structure. The minimum Al-O bond distance is 1.74 Å but there are a few Al-O bonds of length about 2.1 Å. Isomer 8(b) was obtained from a local minimum via simulated annealing run. It lies 0.59 eV higher in energy than the lowest energy isomer 8(a). Isomers 8(c) and 8(d) were derived from isomers of Al$_{14}$O$_{21}$ and they lie significantly higher in energy. We have also studied a cage dimer configuration of $(\text{Al}_8\text{O}_{12})_2$ as shown in 8(e) and it is 2.79 eV higher in energy than the lowest energy configuration.

For $(\text{Al}_2\text{O}_3)_9$ the lowest energy isomer (Fig. 3.5-9(a)) has $D_{2d}$ symmetry with two T-shaped units attached (one above and one below) to the pyramidal structure of $(\text{Al}_2\text{O}_3)_8$. There are twenty six 4-membered and eight 6-membered rings. There are four 5-fold coordinated, eleven 4-fold coordinated and three 3-fold coordinated Al atoms. There is a 4-fold coordinated interior oxygen atom with tetrahedral arrangement of neighbouring Al atoms. The Al-O bond distances are in the range of 1.71-1.90 Å. Isomers 9(b) and 9(c) have been obtained from local minima via simulated annealing runs while isomer 9(d) is derived from isomer 8(c). Isomer 9(e) is based on $n = 4$ and $n = 5$ cage structures fused together. All these isomers lie more than 1 eV higher in energy than the lowest energy isomer 9(a).

For $n = 10$, a four layered pyramidal cage configuration with $C_1$ symmetry has the lowest energy (Fig. 3.5-10(a)). There are one 5-fold coordinated Al and five 3-fold coordinated O atoms inside the cage which is formed by nineteen Al atoms and twenty five oxygen atoms. In all there are three 3-fold coordinated, sixteen 4-fold coordinated and one
3. Aluminum and Gallium Oxide Clusters

5-fold coordinated Al atoms. The Al-O bond distances are in the range of 1.68 to 1.97 Å. Isomer 10(b) is obtained by optimizing a local minimum configuration via simulated annealing run. It has $C_i$ symmetry and lies 0.82 eV higher in energy than 10(a). An isomer derived from 9(a) is shown in 10(c). It lies 1.26 eV higher in energy. It has four outward T-shaped units. We have also considered open cage and cage dimer configurations studied by Sun et al. [208]. All these configurations are quite high in energy compared with the compact lowest energy configurations obtained in our study. The energy difference between the lowest energy configuration and open cage configurations increases with the cluster size. For $n = 10$, the open cage configuration has $I_h$ symmetry 10(e) with twelve 10-membered rings and it lies 7.81 eV higher in energy as compared to the lowest energy configuration 10(a). All the Al atoms in the open cage configuration are 3-fold coordinated and O atoms are 2-fold coordinated. The cage dimer configuration ($D_2$) shown in 10(d) is at relatively lower energy than the open cage configuration as shown in 10(e) in Figure 3.5. All the Al-O bond distances in the open cage configuration are 1.69 Å and all the O-Al-O bond angles are $119.9^\circ$. These results clearly show that empty cage structures are not favourable for these clusters with $n > 4$.

The overall trend shows that the lowest energy isomers of $(\text{Al}_2\text{O}_3)_n$ clusters with $n \geq 5$, prefer structures that evolve from the corundum fragment configuration 4(b) of $n = 4$. We have shown the growth behavior in Figure 3.5 and the formation of layered configuration can be noted. With the addition of Al₂O₃ units there is an increase in the overall coordination of the atoms. Clusters with $n \geq 5$ consist of 4-membered and 6-membered rings in the lowest energy configuration. Isomers with larger rings are at relatively higher energy. In some of the low-lying isomers, the presence of 8- and/or 10-membered rings decreases the coordination of Al and O atoms which makes the clusters relatively less stable. The layered configurations are observed from $n \geq 7$. The maximum coordination of Al atoms in the lowest energy configuration increases to five with the increase in cluster size. But the cluster size is still small so that most of the atoms are on
3. Aluminum and Gallium Oxide Clusters

the surface. The maximum coordination is still lower than the bulk coordination (six) for Al atoms in α-alumina. Tetrahedral environments of some O and Al atoms are evident in large size clusters. The corundum structure of Al₂O₃ has octahedral environment of Al atoms while the γ-phase has both tetrahedral and octahedral environments. In this respect alumina clusters have similarity to the atomic structure of γ-phase [125]. An increase in the number of AlO₄ units results in the formation of Al₂O₂ rings which are found to be quite abundant in the lowest energy isomers. The Al-O bond-distances are in the range of 1.68-1.97 Å that are similar to those found in amorphous phase [256] of alumina. For 4-membered rings the Al-O-Al angle is in the range of 86.0°-99.0° while for 6-membered rings it is in the range of 102.9°-135.7°. It further increases in the case of 8- and 10-membered rings. Thus as the ring size increases, the Al-O-Al arrangement becomes more linear and the average coordination of atoms decreases.

From the earlier studies, it is observed that the geometries of gallium oxide clusters are nearly similar to those of alumina clusters [155, 156, 157]. A present DFT calculations find that the structures of (Ga₂O₃)ₙ in the size range of n = 1 – 10 shows small variations as compared to that of (Al₂O₃)ₙ clusters.

3.3.4 Atomic Structures of (Ga₂O₃)ₙ Clusters with n = 1 – 10

We have calculated the lowest energy and low-lying configurations of of (Ga₂O₃)ₙ (n = 1 – 10) clusters. As noted earlier, the lowest energy configurations for (Ga₂O₃)ₙ clusters are nearly similar to that of (Al₂O₃)ₙ clusters except for n = 1, 2, 4 and 10. We are using the same Figures 3.1 and 3.5 to discuss various configurations of Ga₂O₃ clusters. Similar to that of (Al₂O₃)ₙ clusters the lowest energy configurations of (Ga₂O₃)ₙ show preference for 4-membered Ga₂O₂ and 6-membered Ga₃O₃ rings. For the Al₂O₃ molecule, the lowest energy configuration is kite-shaped while Ga₂O₃ shows the preference for V-shaped geometry (C₂ᵥ) (not shown). For n = 2, (Al₂O₃)₂ is with T₄d symmetry consists of four 6-membered rings while Ga₂O₃ dimer prefers a capped windowpane configuration.
(2(b) in Figure 3.1) with $C_{2v}$ symmetry. The structure consists of five interconnected 4-membered ($\text{Ga}_2\text{O}_2$) rings. In alumina clusters, the lowest energy isomers show preference for 4- and 6-membered rings, though in some cases 8-membered rings are also obtained, while in gallia clusters the preference for 4-membered and chiral shaped 6-membered rings are observed. The major change in the lowest energy configuration is obtained for $n = 4$. The ($\text{Ga}_2\text{O}_3$)$_4$ cluster prefers the compact corundum configuration (4(b) in Figure 3.1) while for alumina cluster, the corundum configuration is one of the low-lying configuration. The lowest energy configuration (4(b)) of ($\text{Ga}_2\text{O}_3$)$_4$ consists of three 4-membered, four 6-membered, and three 8-membered rings. In alumina cluster, each oxygen prefers to bind with maximum number of Al atoms with a large apex angle. The large Al-O-Al angle makes the ring $\text{Al}_3\text{O}_3$ energetically favourable over the $\text{Al}_2\text{O}_2$ unit in small sized clusters. The preference of ring configuration may help to reduce the strain caused by a large sized Al atom. With the increase in size, the electrostatic interaction between Al and O begins to dominate, making the $\text{Al}_2\text{O}_2$ unit more favourable over a $\text{Al}_3\text{O}_3$ ring. From $n \geq 5$, the $\text{Ga}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ structures are nearly similar, except for $n = 10$. The Al-O bond lengths are in the range of 1.68 - 1.97 Å which are similar to those found in the amorphous alumina [256]. The Ga-O bond lengths are in the range of 1.67 - 2.06 Å, smaller than that of in $\alpha$- and $\beta$-$\text{Ga}_2\text{O}_3$ phases.

Gautham et al. [156, 157], have observed that in small gallium oxide clusters the ionization induced changes in the structural parameters to be small. However, ordering of the isomeric configuration significantly changes upon addition of electron. To study ionization induced changes in structural and electronic properties, we have also considered the lowest and some of the low-lying configurations of ($\text{Ga}_2\text{O}_3$)$_n$ clusters. It is found that in ionic clusters, the addition or the removal of an electron to the neutral cluster do not induce significant changes in most of the isomers analysed in this work. The configurational symmetry of the anionic as well as cationic lowest energy structure remain similar to that of neutral cluster except for $n = 1$ and 2. For $n = 1$, the kite-shaped
configuration (1(a) in Figure 3.1) is appear as the lowest energy for both the cationic and anionic Ga$_2$O$_3$. This configuration is well separated at 1.1 eV from the V-shape configuration in the anionic configuration, while for the cationic case it is nearly degenerate ($\Delta E = 0.08$ eV) to the kite-shaped configuration. The results for the anionic cluster are in agreement with the previous study at the DFT-B3LYP and MP2 level of the theory [152]. Addition of the electron increases the Ga-O bond distances in the Ga$_2$O$_2$ ring by around 1 - 2 %, and decreases the bond distance of the terminal Ga-O by 2 %. For the cationic case the Ga-O bond distance for the terminal oxygen and Ga-O bond distances associated with the 2-fold coordinated Ga atoms decrease by 1 - 2 %. For (Ga$_2$O$_3$)$_2$ cation the D$_{4h}$ configuration (2(d) in Figure 3.1) appears as the lowest energy. The lowest energy configuration for the neutral case (2(b) in Figure 3.1) having C$_{2h}$ symmetry is 0.3 eV higher in energy. The lowest energy configuration of the anion is similar to the neutral lowest energy configuration (2(b)). The Ga-O bond distances for the neutral clusters are in the range of 1.67 - 2.06 Å, while that of anionic and cationic clusters are in the range of 1.72 - 2.09 Å and 1.70 - 2.05 Å, respectively. It is also found that, for the anionic clusters, the Ga-O bond lengths increase by about 2 - 3 % with respect to the neutral cluster while the removal of electron decreases the Ga-O bond lengths by about 1 %. The addition or removal of an electron in these clusters is shared more or less equally among the atoms in the cluster. The anionic and cationic configurations prefer the doublet spin state.

Table 3.1: Adiabatic and vertical values (eV) of the ionization potential and electron affinity for (Ga$_2$O$_3$)$_n$, ($n = 1 - 10$) clusters.

<table>
<thead>
<tr>
<th>System</th>
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<td>7.43</td>
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<tr>
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<td>4.54</td>
<td>3.91</td>
<td>3.88</td>
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In this study, we have calculated the EA and the IP for (Ga$_2$O$_3$)$_n$, ($n = 1 - 10$) clusters which are presented in Table 3.1. Both the EAs and IPs have considerable importance
in the chemisorption. Hydrogen chemisorption on the various gallium oxide polymorphs is being actively performed for various catalytic and surface chemistry applications [257, 258]. For electronegative adsorbates (e.g. H, OH, CH$_3$) the charge transfer is away from the cluster and hence it is the IP of the cluster that is relevant in determining bond energy. On the other hand, for electropositive adsorbates (e.g. Li, Na, K) the charge transfer should be towards the cluster and hence EA is more relevant in determining the bond energy [259]. We have therefore calculated the vertical and adiabatic values of EA and IP. The adiabatic electron affinity (AEA) is defined as the energy difference between the anionic and neutral clusters at their own respective optimized geometries. On the other hand vertical electron affinity (VEA) or vertical detachment energy (VDE) is defined as the energy difference between the anionic and neutral clusters with both at the optimized geometry of the anionic cluster. The adiabatic ionization potential (AIP) is defined as the energy difference between the cationic and neutral clusters at their own respective optimized geometries. 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. The vertical and adiabatic EAs and IPs are nearly same which indicate that there is not much topological differences between neutral and ionic configurations of (Ga$_2$O$_3$)$_n$ clusters. It is observed that VIP decreases and VEA increases with the addition of Ga$_2$O$_3$ unit in the cluster. After $n \geq 6$, the decrease in IP is very small and the EA also starts decreasing slowly. This is consistent with trend observed in the binding energy of these clusters. The calculated IP for $n = 1$ agrees well with the value predicted by Gowtham et al. [156]. The calculated VEA and AEA values of 4.70 and 4.29 eV, for $n = 1$ are in agreement with the values 4.47 and 4.34 eV, respectively given by Archibong et al. [152] with the DFT-B3LYP level of the theory. Woodley et al. [154] computed the IP’s and EA’s for (Ga$_2$O$_3$)$_n$, $n = 1 – 5$ clusters by DFT method with local numerical orbital basis set [154]. Our calculated values of IPs and EAs are higher than their reported values.
3.3.5 Stability and Electronic Properties of (Al₂O₃)ₙ and (Ga₂O₃)ₙ Clusters with \( n = 1 - 10 \).

![Graph showing binding energy and mean coordination number for Al₂O₃ and Ga₂O₃ clusters.](image)

Figure 3.6: The BE (eV/atom) for (a) the lowest energy isomers of (Al₂O₃)ₙ clusters with \( n = 1 - 10 \), along with the average coordination number (CN) for aluminum and oxygen atoms (inset). The BE and the average CN for Al and O atoms in \( \alpha \)- and \( \gamma \)-Al₂O₃ phases are also shown. The BE for (b) the lowest energy neutral and ionic (Ga₂O₃)ₙ clusters with \( n = 1 - 10 \), along with the average CN for gallium and oxygen atoms (inset). The BE and the average CN for Ga and O atoms in \( \alpha \)- and \( \beta \)-Ga₂O₃ phases are also shown.

Figure 3.6 (a) and (b) shows the binding energy (BE) (eV/atom) in the lowest energy configurations of (Al₂O₃)ₙ and (Ga₂O₃)ₙ clusters, respectively, obtained from the VASP calculations. The BE denoted by \( E_b \) is calculated as

\[
E_b[(M₂O₃)_n] = (-E[(M₂O₃)_n] + 2nE[M] + 3nE[O])/(5n)
\]  

(3.1)

where \( E \) is the total energy of the system, and \( M \) is for Al/Ga.

For (Al₂O₃)ₙ clusters the variation of the mean number of the nearest neighbours of Al and O atoms for Al₂O₃ clusters shown in the inset of Figure 3.6 (a). With the successive addition of an Al₂O₃ unit, there is an increase in the BE and the average coordination of Al and O atoms. The mean coordination increases with \( n \) up to 4 and it decreases slightly for \( n = 6 \). The mean coordination number again increases up to a local maximum.
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at \( n = 8 \). The maxima at \( n = 4 \) and 8 correspond to the completion of the layered ring structures for these two sizes and this shows the importance of the atomic structure in the stability of these clusters. While the presence of the T-shaped AlO\(_3\) units decreases the coordination on both sides of these sizes. The average coordination of Al and O atoms is found (Figure 3.6 (a), inset) to be about 4.0 and 2.5, respectively. The average coordination number for amorphous alumina is about 4.33 [256] as compared to 6 of Al atoms in bulk \( \alpha\)-Al\(_2\)O\(_3\). Sun et al. [208] studied an open cage (Bucky ball) configuration for \( n = 10 \). The BE for Al\(_2\)O\(_3\), Bucky ball is 3.65 eV/atom which is significantly lower than the value of 5.95 eV/atom for our lowest energy isomer of \( n = 10 \). We have also calculated the BE per Al\(_2\)O\(_3\) for all the clusters. For \( n = 10 \), the BE per Al\(_2\)O\(_3\) is 29.75 eV, which is lower than the calculated bulk value of the cohesive energy (32.27 eV) in \( \alpha\)-alumina. The latter compares well with the experimental value [260, 261] of 31.8 eV. The reduced coordination number in clusters leads to a lower value of the BE than that of the cohesive energy of bulk alumina [260, 261, 262].

The BE (eV/atom) for (Ga\(_2\)O\(_3\))\(_n\) neutral and ionic clusters against the number of atoms is shown in Figure 3.6 (b). The variation of the average number of the nearest neighbours of Ga and O atoms in the lowest energy isomers is also shown in the inset. Overall the BE and average CN for Ga\(_2\)O\(_3\) clusters shows similar nature as that of Al\(_2\)O\(_3\) clusters. With successive addition of Ga\(_2\)O\(_3\) unit, there is an increase in the BE and the average coordination of Ga and O atoms. The structures are stabilized with the coordination of four for Ga atoms and three for O atoms. As noted earlier, with the increase in size, some of the Ga atoms prefer the coordination with five oxygen atoms and oxygen atoms are tetrahedrally coordinated. The average coordination for \( \alpha\)-Ga\(_2\)O\(_3\) is 6 for Ga atoms. We have also calculated the BE per Ga\(_2\)O\(_3\) for all the clusters. For \( n=10 \), the BE per Ga\(_2\)O\(_3\) is 22.74 eV, which is lower than the calculated bulk values of the cohesive energy (25.10 eV) in \( \beta\)-Ga\(_2\)O\(_3\) and (24.95 eV) \( \alpha\)-Ga\(_2\)O\(_3\).

It is observed that the Al\(_2\)O\(_3\) clusters are more stable than Ga\(_2\)O\(_3\) clusters. The
binding energy for \((\text{Ga}_2\text{O}_3)_n\), for \(n=10\) is 4.55 eV/atom, which is slightly smaller than the bulk cohesive energy 5.02 eV/atom for \(\beta\)-Ga\(_2\)O\(_3\) in our calculations with the same pseudopotentials. While for \((\text{Al}_2\text{O}_3)_{10}\), the binding energy is 5.93 eV/atom compared to the bulk cohesive energy of 6.45 eV/atom for \(\alpha\)-Al\(_2\)O\(_3\). This suggests that in this size range \((\text{Ga}_2\text{O}_3)_n\) clusters approaching towards the bulk value earlier than the \((\text{Al}_2\text{O}_3)_n\) clusters.

We have also calculated the HOMO-LUMO gap for Ga\(_2\)O\(_3\) and Al\(_2\)O\(_3\) clusters. The HOMO-LUMO gap for the lowest energy isomers of \((\text{Al}_2\text{O}_3)_n\) clusters are in the range of Al\(_2\)O\(_3\) 3-4 eV, whereas that of \((\text{Ga}_2\text{O}_3)_n\) are in the range of 1.98 - 2.55 eV. Note that, the experimental band gap for the bulk \(\alpha\)-Al\(_2\)O\(_3\) is 8.7 eV and \(\beta\)-Ga\(_2\)O\(_3\) is 4.8 eV. The underestimation of the calculated values of the cluster HOMO-LUMO gap and the bulk band gap is due to the use of GGA.

In bulk Al\(_2\)O\(_3\) and Ga\(_2\)O\(_3\), the nature of bonding is mainly ionic [213, 86]. In order to understand the nature of bonding in clusters, we have calculated the total density of states (DOS), and the projected density of states (PDOS). The calculated DOS further provides explanation for the structural evolution with an increase in cluster size \(n\). In Figure 3.7, we have shown the Gaussian broadened electronic spectra of the lowest energy isomers of \((\text{Al}_2\text{O}_3)_n\) clusters with \(n = 1 - 10\). For the small size clusters the spectra show sharp peaks but with the increase in the cluster size, the spectra become broader. The lower energy part of the spectra is dominated by 2s orbitals of oxygen atoms. The middle part of the spectra consists of hybridized \(sp\) orbitals of the Al atoms with the 2\(p\) states of the oxygen. The states from the 4-fold and 5-fold coordinated Al atoms are more delocalized (wider extent) compared to states from the 3-fold coordinated Al atoms. With the increase in the coordination of Al atoms, there is an increase in the degree of hybridization between \(sp\) orbitals of metal and O-\(p\) orbitals, which results in shifting the states to higher binding energy. The states near HOMO arise from the nonbonding 2\(p\) orbitals of 2-fold coordinated oxygen atoms. Below these states, there are nonbonding 2\(p\)
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states from 3-fold coordinated oxygen atoms. We have also shown the density of states for the bulk phases for both alumina. The bulk spectra shows more or less a band like structure and the various energy bands can be easily noticed. The states near the Fermi level (Valence Band Maximum, (VBM)) consists of the O-$p$ orbitals. The $s$ and $p$ orbitals of the metal (Al) atoms shows their appearance respectively in the lower and middle part of the valence band along with the O-$p$ states. The O-$s$ states shows their presence in the lower energy part of the spectra. The states in the Conduction Band Minimum (CBM) consists mainly of the unoccupied 4$s$ levels of the tetrahedrally coordinated metal (Al) atoms. The $\alpha$-$\text{Al}_2\text{O}_3$ spectra is more localized compared to that of $\gamma$-$\text{Al}_2\text{O}_3$.

In order to understand the differences in the electronic spectra for Al$_2$O$_3$ and Ga$_2$O$_3$ clusters we have also considered PDOS for these clusters. Figure 3.8 shows the DOS and PDOS for the lowest energy configurations of (Al$_2$O$_3$)$_n$ and (Ga$_2$O$_3$)$_n$ clusters for $n = 2, 4$ and 10 along with the bulk spectra. The DOS for the (Ga$_2$O$_3$)$_n$ clusters shows similar nature as that of (Al$_2$O$_3$)$_n$ clusters. It is seen that the electronic spectra for Al$_2$O$_3$ clusters is shifted to the lower energy (away from the Fermi level) compared to that of Ga$_2$O$_3$. For, $n = 4$, the localized nature of the Ga-$s$ states (narrow distribution of states) decreases the degree of mixing between Ga-$sp$ and O-$p$ orbitals compared to that of Al-$sp$ and O-$p$. The DOS and PDOS for the lowest energy configuration of (Al$_2$O$_3$)$_{10}$ shows delocalized nature with a wider distribution of states as compared to that of the (Ga$_2$O$_3$)$_{10}$. It is seen that the electronic structure of the clusters is similar to that of the bulk spectra.

To understand the nature of bonding in detail in these systems, we have also examined the total charge density, electron localization function (ELF) [263], and molecular orbitals. The localized charge density is evidently seen around O atoms. It is also seen that the charge density associated with oxygen is polarized towards metal atoms. The small deviation from spherical symmetry around the oxygen suggest the presence of some covalency in the cluster. These remarks are further explained by studying the ELF in these clusters. In Figure 3.9, we have shown the typical charge density and ELF surfaces.
Figure 3.7: The total DOS for the lowest energy configurations for (Al$_2$O$_3$)$_n$, ($n = 1 - 10$) clusters. The total DOS for the bulk $\alpha$- and $\gamma$-Al$_2$O$_3$ phases are also shown. The Fermi level has been shifted to zero.
Figure 3.8: The total DOS and PDOS for the lowest energy configurations of (a) $\text{(Al}_2\text{O}_3)_n$ and (b) $\text{(Ga}_2\text{O}_3)_n$, with $n = 4$ and 10 clusters. The Fermi level has been shifted to zero.
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Figure 3.9: The (a) total charge density and (b) ELF for the lowest energy configurations of (Al$_2$O$_3$)$_4$ and (Ga$_2$O$_3$)$_4$ clusters at 75% of the maximum value. The Bader charges on three- and four-fold coordinated Al and Ga atoms and two- and three-fold coordinated O atoms are also shown.
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for (Al₂O₃)₄ and (Ga₂O₃)₄ clusters along with the Bader charges on Al, Ga and O atoms. For (Ga₂O₃)ₙ clusters with n = 4, the high degree of covalency is seen to be associated with Ga-O bonds. At higher values of ELF (around 90%), we find that the electrons are localized in basins around O atoms. As the ELF value is decreased to 75% of maximum value, these basins merge into each other suggesting the presence of small amount of covalency in the cluster. This is expected due to lower coordination in this cluster. As the coordination number increases, for n = 10, electrons are localized in basins around O atoms. For (Al₂O₃)ₙ clusters with n = 4, the electrons localized in the basins around O atoms. There is no bond localization region along Al-O bonds suggesting a mainly ionic bonding in this cluster compared to that of (Ga₂O₃)₄. It is also observed that an increase in the coordination increases the polarization of the electron cloud around the oxygen ions due to the positive charge of cations in contact with it. In the lowest energy configurations of (Ga₂O₃)ₙ and (Al₂O₃)ₙ clusters the delocalize s and p orbitals significantly alter charge density around oxygen (delocalization of Oₚ states). This may facilitate the formation of additional chemical bonds (polar covalent character) and further orbital hybridization to form stable configuration. Previous theoretical studies [264, 265] reported some degree of covalency is associated with Ga-O bonds in β-Ga₂O₃. There is also some covalent character of bonding in Al-O bond as it was also shown earlier [208].

Further, we have calculated Bader [266] charges for some of the lowest energy and low-lying configurations of these clusters. In these configurations, the Bader charges reflect the expected behavior: a greater coordination index leads to greater atomic charge. The oxygen charges are relatively higher indicating ionic nature of the bonds. In these clusters the charge transfer increases with higher coordination. We have compared the Bader charge transfer from metal ion to oxygen in the lowest energy configurations of Ga₂O₃ (V-shape) and Al₂O₃ (kite-shaped) molecular clusters. The charge transfer analysis shows each one of the two bi-coordinated Ga atoms in Ga₂O₃ gives 1.32e charge to the surrounding O atoms. While in Al₂O₃ the bi-coordinated Al gives 1.76e, while the tri-
coordinated Al atom gives nearly 2.27e to the surrounding oxygen atoms. For the larger size clusters, e.g. \( n = 4 \), the average charge transfer from the Ga atom is around 1.5e to the surrounding oxygen atoms, while the average charge transfer from Al atom to the surrounding oxygen atoms is around 2.3e. Also, the average extra charge on the oxygen atoms in \((\text{Al}_2\text{O}_3)_4\) is around 35 - 40 % more than that of in \((\text{Ga}_2\text{O}_3)_4\). The more charge transfer from Al atom to oxygen suggests that the Al-O bond is more ionic compared to the Ga-O bond. This is in accordance with expectation from the differences in the electronegativities of Ga (1.8), Al (1.5), and O (2.44). This also reflects in the stability (BE) of the clusters.

For \((\text{Ga}_2\text{O}_3)_n\) clusters with \( n = 10 \), the charge transfer increases to 1.60e for 4-fold coordinated Ga and 1.66e for 5-fold coordinated Ga and charge gain by oxygen increases to 1.11e for 3-fold coordinated oxygen and 1.18e for 4-fold coordinated oxygen. For comparison we have calculated the Bader charges for the bulk phases. In bulk \(\alpha\)-\(\text{Ga}_2\text{O}_3\), the Bader charges on all the Ga atoms are +1.70e and on all the O atoms are -1.13e. In bulk \(\beta\)-\(\text{Ga}_2\text{O}_3\) the Bader charges on the 4-fold and 6-fold coordinated Ga atoms are respectively +1.67e and +1.73e and on oxygen atoms around -1.14e. It is seen that the amount of charge transfer from Ga to O is increases with the coordination number. The amount of charge transfer from Ga to O is in the range of 1.60e - 1.66e for \( n = 10 \), which is comparable to that of \(\beta\)-\(\text{Ga}_2\text{O}_3\), but it is still lower than that of \(\alpha\)-\(\text{Ga}_2\text{O}_3\). For \((\text{Al}_2\text{O}_3)_n\) clusters with the increase in cluster size, for \( n = 10 \), the charge transfer from Al atom increases to +2.46e which is in the range of the value in bulk \(\alpha\)-\(\text{Al}_2\text{O}_3\) (+2.45e). For \(\gamma\)-\(\text{Al}_2\text{O}_3\), there is +2.41e charge transfer from the tetrahedrally coordinated Al atom to oxygens and for the octahedrally coordinated Al it is 2.44e - 2.46e. Overall, with the increase in the cluster size and coordination number, the charge transfer from Al to O is approaching towards the bulk value.

In bulk phases of alumina and gallia, two kinds of atomic arrangements are observed: 1) in which the elementary units mainly consist of \(\text{MO}_6\) octahedra (M being Al, Ga) and
2) another phase where most of the units consist of MO$_4$ tetrahedra. In the range of cluster sizes we have studied, we observe the presence of MO$_5$ partial octahedral, MO$_4$ tetrahedral and MO$_3$ trigonal units. In this size range with the increase in the cluster size the MO$_4$ units are more prevalent. With the increase in size the presence of MO$_5$ units are also observed. The atomic structures of alumina clusters have more similarity to $\gamma$-alumina phase, whereas the gallium oxide clusters have more similarity to $\alpha$-Ga$_2$O$_3$.

### 3.4 Conclusions

In conclusion, we have studied the structural stability and electronic properties of (Al$_2$O$_3$)$_n$ and (Ga$_2$O$_3$)$_n$ clusters with $n = 1−10$ using density functional pseudopotential theory. In general, it is found that the lowest energy configurations for (Al$_2$O$_3$)$_n$ and (Ga$_2$O$_3$)$_n$ are nearly similar except for $n = 1, 2, 4,$ and 10. The lowest energy isomers show preference for 4- and 6-membered rings, larger rings lead to open structures and in general such isomers are higher in energy than the lowest energy configurations. Our results show that cage structures are not favored for both Al$_2$O$_3$ and Ga$_2$O$_3$ clusters. In fact the cage structures for $n \geq 4$ lie much higher in energy than the lowest energy isomer and are unlikely to be found in experiments. The BE of these clusters increases with the cluster size ($n$). The Al$_2$O$_3$ clusters have higher binding energy than that of Ga$_2$O$_3$ clusters. The stability of the clusters is dominated by the ionic Al-O and Ga-O interactions with weak covalent bonding. The higher energy bulk phases appear at the lowest energy for these clusters. For (Al$_2$O$_3$)$_n$ clusters a comparison of the BE, HOMO-LUMO gap, and mean coordination of Al and O atoms with those of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ phases shows similarity of atomic structures of clusters with $\gamma$-Al$_2$O$_3$ while the mean coordinations of Al and O atoms also have similarity with amorphous alumina. For (Ga$_2$O$_3$)$_n$ clusters a comparison of the BE and average coordination of Ga and O atoms with those of $\beta$-Ga$_2$O$_3$ and $\alpha$-Ga$_2$O$_3$ phases shows similarity of atomic structures of clusters with $\alpha$-Ga$_2$O$_3$. The average coordination of Ga and O atoms still lower than the average coordination of Ga.
and O atoms in bulk $\beta$-Ga$_2$O$_3$ and $\alpha$-Ga$_2$O$_3$ phases.

As alumina and gallia derived compounds have tremendous applications in catalysis, ceramics, mechanical engineering, lasers, gas sensing and optoelectronic devices, we hope that these clusters considered here would serve as reasonable models to study binding modes and reactions and for gaining qualitative insights into the behavior of dopants on non-ideal surfaces. The clusters studied here are also useful to understand the doping effects as well as magnetic and optical properties of these metal oxide systems.