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Theoretical study of sequential oxidation of clusters of gallium oxide: Ga_3O_n (n: 4–8)

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Abstract

We report the results of a theoretical study of sequential oxidation of gallium oxide clusters from Ga_3O_4 to Ga_3O_8. These results, based on density functional theory calculations, find the ground state of the neutral clusters to be in the lowest spin state with nearly the same binding energy of 3.5 eV per atom. Electron affinity, ionization potential and HOMO–LUMO gap values of these oxygen-rich clusters show an oscillatory trend which may be due to the fact that sequential oxidation as well as addition (and removal) of an electron leads to significant changes in the geometry of the respective neutral clusters.

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1. Introduction

Ga_2O_3 has attracted a lot of attention due to its remarkable physical and chemical properties. It is a ceramic material with high melting point of about 1900 °C. Owing to its wide band gap (4.80 eV), [1] it behaves like an insulator at room temperature and as a semi-conductor above 800 °C. These characteristics have made Ga_2O_3 a very good candidate for fabricating electronic devices that operate at high temperatures. Low dimensional structures such as nanowires, nanoribbons and nanosheets display interesting properties which can be exploited in fabricating the next generation of optoelectronic and sensing devices.

Small clusters of gallium oxide can be taken as a model to understand the physics and chemistry of nanostructures of this material. Such a study was initiated by our group where we reported structural, vibrational and electronic properties of neutral and ionized small Ga_mO_n (m,n = 1,2) clusters [2]. Addition of an electron introduced relatively larger structural changes than the removal of an electron from the neutral gallium oxide clusters. The results of a recent experimental study by Meloni et al. [3] find a very good agreement with the calculated adiabatic electron affinity value [2] for GaO, and the Ga–O bond distances in the neutral and anionic GaO_2. In a follow-up study by our group, we considered sequential oxidation of Ga_3O up to Ga_3O_3 and then sequential removal of gallium down to GaO_3 [4]. Unlike in our initial study on monomer, triatomic and dimer gallium oxide clusters, we found that the structural changes induced by addition and removal of an electron are relatively small, Ga_3O_2 being an exception. Most stable structures showed a preference for planar arrangement of atoms, maximizing the Ga–O interactions in the cluster.

In this Letter, we now present the results of calculations, based on density functional theory, on the oxygen-rich gallium oxide clusters. Our aim is to study the changes in structural and electronic properties of gallium oxide clusters as a result of their sequential oxidation starting from Ga_3O_4 to Ga_3O_8, as well as to compare the results with aluminum oxide clusters of the same size. Specifically, we would like to know if the stability of the oxygen-rich gallium oxide clusters is governed by the formation of the O–O bonds. It is to be noted that sequential oxidation of Al_3O_5 considered in a previous theoretical study [5] revealed a tendency to form O–O bonds in the oxygen-rich alumina cluster.

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Rest of the letter is organized as follows: Section 2 describes the computational methodology. Section 3 is devoted to discussion of calculated results. Section 4 summarizes the results and concludes the work.

2. Methodology

We have performed first-principles calculations on neutral and charged gallium oxide clusters using the GAUSSIAN 98 code [6]. The gradient-corrected B3LYP functional form (i.e., Becke's 3-parameter hybrid exchange functional [8] and, Lee, Yang and Parr correlation functional [8]) was employed for these density functional theory (DFT) calculations.

The choice of DFT-B3LYP methodology along with 6-31G(d,p) basis set is based on our previous studies on small clusters of gallium oxide [2,4]. All isomers of Ga_3O_n clusters considered were fully optimized with 10^{-9} hartree as the energy convergence criteria and 10^{-4} hartree/Å as that for the energy gradient. An extensive search for the ground state of Ga_3O_n clusters was performed which included several two- and three-dimensional configurations. For example, some of the initial structures for Ga_3O_4 are schematically represented in Fig. 1 which are based on an addition of GaO_2 to Ga_2O_2, an addition of O_2 to Ga_3O_2, and an addition of O to Ga_3O_3. Linear structures considered in this study were found to have higher energies compared to ground state structures. Other structures, not shown in Fig. 1, can be obtained by appropriately interchanging gallium and oxygen atoms. Since the neutral Ga_3O_n clusters have an odd number of electrons, calculations were carried out in doublet and quartet spin states for neutral, and singlet and triplet spin states in singly charged clusters, all of them within the unrestricted spin scheme. In order to verify the stability of the lowest energy configurations, we computed vibrational frequencies under the harmonic approximation, with analytical force constants.

3. Results and discussion

In Table 1, we present the total energy, electronic state, symmetry, Ga–O (R_{Ga-O}) and O–O (R_{O-O}) bond distances corresponding to the most stable isomers of neutral and ionic oxide clusters. Lowest energy isomers in the case of neutral clusters were found in doublet electronic state whereas charged clusters displayed triplet spin states, except for $Ga_3O_4^-$, $Ga_3O_4^+$, and $Ga_3O_5^-$, which were singlets. Results pertaining to structural properties, stability and electronic properties of these cluster systems are discussed in the following subsections.

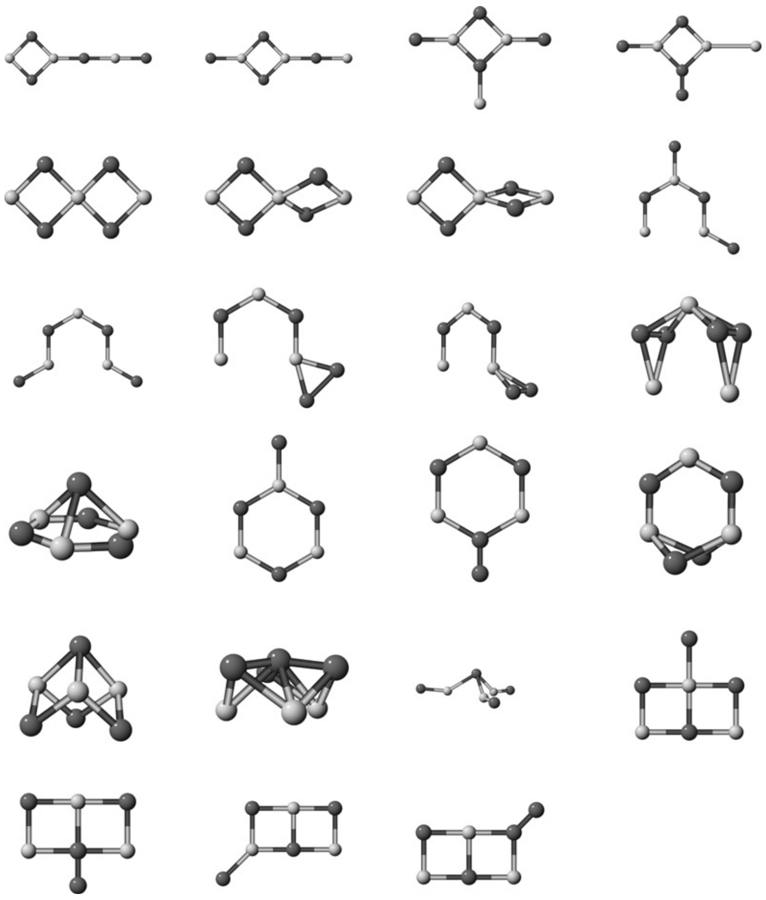

Fig. 1. Schematic representation of initial structures considered for Ga_3O_4. Smaller (lighter shade) spheres represent gallium atoms while while larger (darker shade) ones represent oxygen atoms.

Table 1
Total energy (hartree), electronic state, symmetry, and inter-atomic distance (Å) of the most stable configurations of gallium oxide clusters

	E	$^{2S+1}\Lambda$	Symmetry	$R_{Ga–O}$	$R_{O–O}$
Ga_3O_4					
$Q = 0$	−6069.80494	$^2B_2$	C_{3v}	1.86, 1.95	–
$Q = -1$	−6069.92380	$^1A'$	C_s	1.70, 1.77, 1.78, 1.90, 1.93, 1.99, 2.03	–
$Q = 1$	−6069.50239	$^1A_1$	C_{3v}	1.85, 1.93	–
Ga_3O_5					
$Q = 0$	−6144.99150	$^2A''$	C_s	1.79, 1.82, 1.86, 1.92, 1.93, 2.00	–
$Q = -1$	−6145.12939	$^1A_1$	C_{2v}	1.69, 1.77, 1.90, 1.93	–
$Q = 1$	−6144.67329	$^3B_2$	C_{2v}	1.78, 1.79, 1.84, 1.87, 1.99	–
Ga_3O_6					
$Q = 0$	−6220.15670	$^2A_1$	D_{3h}	1.80, 1.82	–
$Q = -1$	−6220.31820	$^3A''$	C_s	1.79, 1.84, 1.86, 1.92, 1.95, 1.98	–
$Q = 1$	−6219.85077	$^3A''$	C_s	1.78, 1.79, 1.84, 1.85, 1.87, 1.92	1.39
Ga_3O_7					
$Q = 0$	−6295.34003	$^2B_1$	C_{2v}	1.80, 1.82, 1.96	1.37
$Q = -1$	−6295.48407	$^3B_1$	C_{2v}	1.80, 1.81, 1.82, 1.90, 1.91, 1.99	1.37
$Q = 1$	−6295.02820	$^3B_2$	C_{2v}	1.78, 1.85, 1.86, 2.00	1.39
Ga_3O_8					
$Q = 0$	−6370.52323	$^2A_1$	C_{2v}	1.80, 1.81, 1.82, 1.96	1.37
$Q = -1$	−6370.67418	^3A	C_1	1.80, 1.85, 1.90, 1.93, 1.94, 2.00, 2.14	1.37
$Q = 1$	−6370.17319	$^3B_2$	C_{2v}	1.77, 1.80, 1.83, 1.96	1.27

3.1. Structural properties

In neutral Ga_3O_4 (Fig. 2), the lowest energy isomer is found to consist of two equilateral triangles, one of oxygen atoms and another one of gallium atoms on its top, with the fourth oxygen above the gallium triangle. Alternatively, this C_{3v} structure can be visualized as an oxygen tetrahedron intercepted by a gallium triangle. The bond distance between any gallium atom to an oxygen atom at the base of the tetrahedron is 1.86 Å while that to the apical oxygen is 1.95 Å.

Upon addition of an electron, window-pane structure becomes the lowest energy isomer in anionic Ga_3O_4. We note here that the window-pane structure is about 0.44 eV higher in energy relative to the corresponding lowest energy configuration in neutral Ga_3O_4. In the anionic window-pane cluster, $R_{Ga–O}$ varies between 1.70 and 2.03 Å. Based on Mulliken population analysis, the three gallium atoms account for most of the added electron (63%) to the neutral cluster. Removal of an electron, however, has almost no effect on the structural parameters. In the lowest energy cationic isomer, the electron mainly comes out of gallium atoms.

In the case of Ga_3O_5 (Fig. 2), the most stable structure is an extension of the corresponding structure in Ga_3O_4, with an additional oxygen attached to one of the gallium atoms leading to C_{2v} symmetry for the isomer. Similar to Ga_3O_4, the anionic cluster has a window-pane C_{2v} geometry as the lowest energy isomer, and the added electron is shared by the gallium and the terminal oxygen atoms. Unlike neutral Ga_3O_4, removal of an electron leads to a significant change in the geometry of the lowest energy isomer of cationic Ga_3O_5. The structure appears very much similar to the corresponding anionic isomer but in triplet spin state. Gallium atoms and the terminal oxygen atoms contribute almost equally to the removed electron.

The lowest energy isomer of neutral Ga_3O_6 (Fig. 2) has a planar hexagonal arrangement of gallium–oxygen atoms, with three oxygens attached to gallium atoms forming a D_{3h} structure. $R_{Ga–O}$ is 1.80 Å in the ring and 1.82 Å for terminal bonds. The lowest energy isomer in the anionic case is a distorted three-dimensional window-pane C_s structure, with an oxygen cap in the triplet spin state. Removal of an electron also changes the geometrical appearance of the lowest energy isomer – a pyramidical structure in triplet state, with an O_2 bond attached to one of the window-corner gallium atoms. $R_{Ga–O}$ ranges between 1.78 and 1.92 Å and $R_{O–O}$ is about 1.39 Å.

The most stable isomer of neutral Ga_3O_7 (Fig. 2) shows a preference for O–O bonds and the structure can be visualized as an extension of Ga_3O_6 – with an extra oxygen atom attached to one of the apical oxygen atoms (C_{2v}). The average $R_{Ga–O}$ remains almost the same as in the previous system (1.84 Å) and $R_{O–O}$ is about 1.37 Å. The lowest energy isomer in the case of $Ga_3O_7^-$ is a twisted rhombic pair in triplet state with C_{2v} symmetry and two tetrahedrally-coordinated Ga atoms. This isomer exhibits strong Ga–O interactions with $R_{Ga–O}$ ranging between 1.80 and 1.99 Å and the O_2 bond distance is about 1.37 Å. The added electron is shared almost equally by the gallium and terminal oxygen atoms compared to the corresponding neutral isomer. The lowest energy cationic isomer is a window-pane with O_2 units attached to each of the window-corner gallium atoms.

The lowest energy isomer of neutral Ga_3O_8 (Fig. 2) can be visualized as an extension of Ga_3O_7 with the extra oxygen attached to another of the terminal oxygens, thus forming a pair of handles (C_{2v}). The lowest energy isomer in anionic case is also a three-dimensional structure analogous to neutral Ga_3O_4 with two extra O–O bonds (attached to the gallium atoms at the corner) and an oxygen cap over the gallium triangle. Nearly half of the added electron is

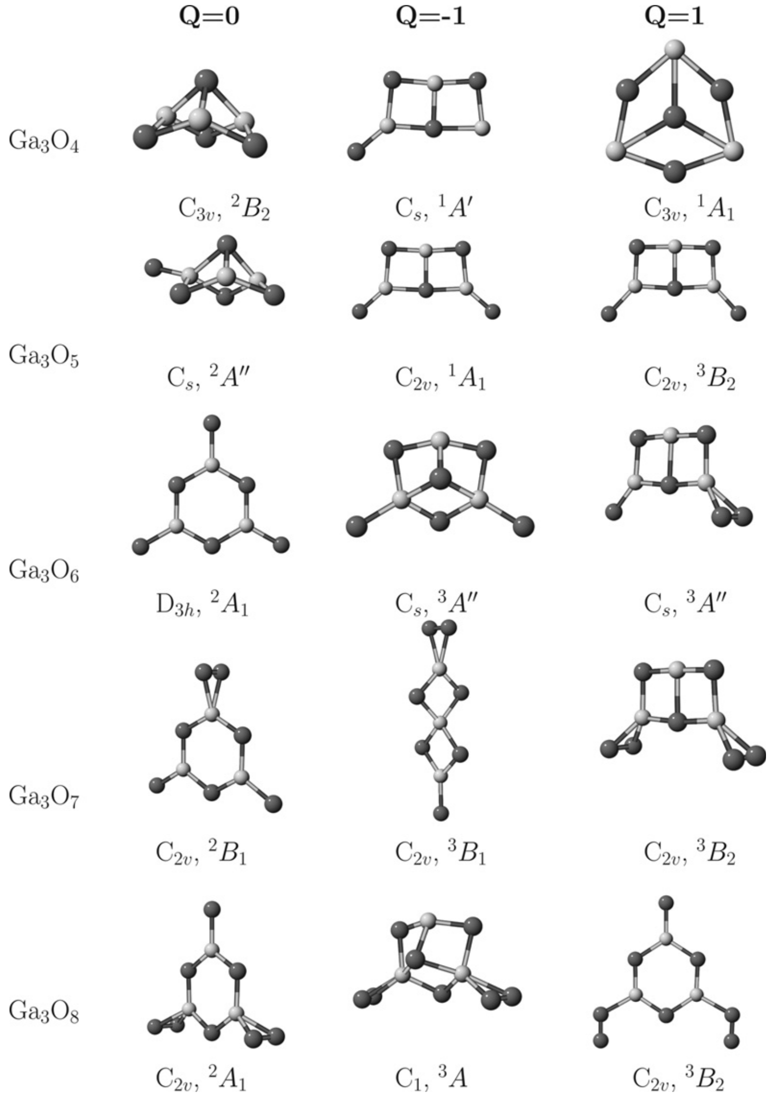

Fig. 2. Most stable structures of neutral and ionic Ga_3O_n ($n = 4$–8). Smaller (lighter shade) spheres represent gallium atoms while while larger (darker shade) ones represent oxygen atoms.

shared by the gallium atoms. The lowest energy isomer in $Ga_3O_8^+$ has a hexagonal ring structure similar to the neutral isomer; however, the two O_2 units are bonded asymmetrically (that is, with a Ga–O bond and an O–O bond), whereas in the neutral case they were symmetrically bonded (two Ga–O bonds and an O–O bond).

To understand the structural changes induced by the sequential oxidation as well as the addition (or removal) of an electron, many structural indices may be defined to classify the different structures. We may group them into four families. First, pyramid-like structures with terminal O or O_2 units (Ga_3O_4, Ga_3O_5, $Ga_3O_6^-$, and $Ga_3O_8^-$); they can be seen as a non-planar ring Ga_3O_3 structure with an O on top of the Ga, forming an irregular tetrahedron with the other three O atoms. Second, window-pane-like structures ($Ga_3O_4^-$, $Ga_3O_5^-$, $Ga_3O_5^+$, $Ga_3O_6^+$, and $Ga_3O_7^+$), in which the Ga_3O_3 subunit is planar consisting of two bonded squares sharing an edge. Third, hexagonal-like structures ($Ga_3O_4^+$, Ga_3O_6, Ga_3O_7, Ga_3O_8 and $Ga_3O_8^+$), where the Ga_3O_3 unit is a planar, almost regular alternating hexagon. And finally, $Ga_3O_7^-$ displays a chain-like structure with two tetrahedrally co-ordinated Ga and a tri-coordinated Ga. It is to be noted here that the bond length in the Ga_3O_3 backbones of the first three families remains nearly the same. Based on the choice of $\overline{R}_{BB}$ as the average $R_{Ga–O}$ in the Ga_3O_3 backbones, we find $\overline{R}_{BB}$ to be about 1.89 Å in pyramid-like structures, while that for window-pane, it's about 1.86 Å; hexagonal and chain-like structures both have 1.88 Å for $\overline{R}_{BB}$, though we find slight deviations due to positive (or negative) charge states of the clusters.

3.2. Stability

The stability of neutral and ionic clusters with respect to the constituent atoms is characterized by the binding energy (BE). Fig. 3 displays the BE/atom values (in eV) as a function of O/Ga ratio. Here, the values for Ga_3O,

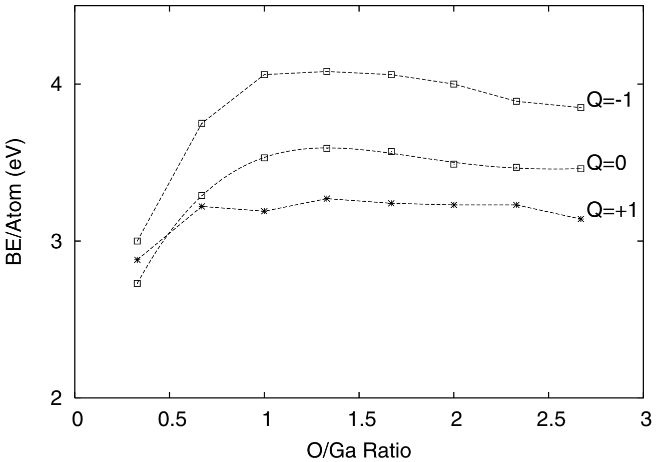

Fig. 3. Binding energy per atom of the most stable neutral and ionic Ga_3O_n clusters ($n = 1$–8). First three data points are taken from our previous work [4].

Ga_3O_2 and Ga_3O_3 are taken from our previous study [4]. Values for neutral clusters increase with O/Ga ratio up to Ga_3O_4 and tend to remain almost constant with a value of about 3.5 eV. The BE/atom values for ionic clusters follow a trend similar to the neutral cluster exhibiting the expected behavior: anionic ones being more stable and cationic ones less stable, compared to the respective neutral counterparts. While computing the binding energy of ionic clusters, the added electron was assigned to oxygen and the removed electron was assigned to gallium, in accordance with Pauling's electronegativity values (O: 3.5 and Ga: 1.6).

Presented in Table 2 are the fragmentation energies of the most stable neutral and ionic clusters considered in this study via either the loss of an oxygen atom or the oxygen molecule. Zero-point energy vibrational energy contributions have been neglected and we have used the following definition: $E_{\mathrm{Fragmentation}} = E_{\mathrm{Cluster}} - E_{\mathrm{Fragment1}} - E_{\mathrm{Fragment2}}$. Fragment 2 is either O or O_2, and the cluster is said to be stable with respect to fragments, if the fragmentation energy is negative (total energy, in hartree, of O is −75.06062 and O_2 is −150.32004). Neutral and ionic clusters show a preference for the O_2 channel, though from the values in Table 2, we find that all clusters are stable against both fragmentation channels considered. Fragmentation is easier when losing O_2 molecules, except in the smaller clusters: Ga_3O_2, Ga_3O_3 and $Ga_3O_3^-$, and $Ga_3O_4^-$.

Stability of the lowest energy isomers of neutral, anionic and cationic clusters was further investigated by analysis of vibrational frequencies, computed under the harmonic approximation. Almost all modes correspond to Ga–O related displacements and the existence of frequencies corresponding to O–O stretching (>1000 cm^{-1}) confirms the tendency of Ga_3O_7, Ga_3O_8 (neutral as well as charged) and $Ga_3O_6^+$ to prefer the formation of O–O bonds. The values of vibrational frequencies can be obtained from the authors upon request.

3.3. Electronic properties

We have calculated adiabatic electron affinity (AEA) and ionization potential (AIP, VIP) for the lowest energy isomers found in this study. The following definition was employed for determining these quantities: $\mathrm{EA} = E_{Q=0} - E_{Q=-1}$ and $\mathrm{IP} = E_{Q=+1} - E_{Q=0}$. The vertical detachment energy (VDE) can be defined as the difference in energy between anionic and neutral clusters, when both are at the optimized geometry of the anion. AEA is defined similarly, but with both clusters at their respective optimized geometries. VIP is defined as the energy difference between cationic and neutral clusters, when both are at the optimized geometry of the neutral cluster. AIP follows a definition similar to AEA, and is the energy difference between cationic and neutral clusters, both at their respective optimized geometries.

In Table 3, we present AEA, VDE, AIP and VIP values as a function of O/Ga ratio. We observe that all these four quantities show an oscillatory trend. As a result, chemical hardness [9], defined as $\eta = (\mathrm{IP} - EA)/2$ (IP and EA are the first vertical ionization energy and electron affinity), also inherits a similar oscillatory trend. The observed trend can be explained on the basis that oxygen-rich clusters have electron efficiency and thus present high EA and IP values. In this table, we also present vertical attachment energy (VAE), defined as the energy difference between the neutral and anionic clusters, with both at the optimized geometry of the neutral cluster. Though this is unattainable through any experiment, it nevertheless provides a lower limit to

Table 2
Fragmentation energies (eV) of neutral and ionic clusters via loss of oxygen atom and oxygen molecule

System	O/Ga	$Q = 0$		$Q = -1$		$Q = +1$	
		O	O_2	O	O_2	O	O_2
Ga_3O	0.33	−7.20	–	−6.50	–	−8.20	–
Ga_3O_2	0.66	−5.50	−7.30	−6.70	−7.80	−4.60	−7.40
Ga_3O_3	1.00	−4.70	−4.90	−5.60	−6.90	−3.00	−2.20
Ga_3O_4	1.33	−3.94	−3.27	−4.23	−4.42	−3.75	−1.38
Ga_3O_5	1.66	−3.43	−1.96	−3.95	−2.77	−3.00	−1.37
Ga_3O_6	2.00	−2.85	−0.86	−3.49	−2.02	−3.18	−0.77
Ga_3O_7	2.33	−3.34	−0.78	−2.86	−0.94	−3.18	−0.95
Ga_3O_8	2.66	−3.34	−1.27	−3.52	−0.98	−2.30	−0.07

Negative value of the energy means the cluster is stable. Values for Ga_3O_n ($n = 1-3$) are taken from our previous work [4].

Table 3
Vertical attachment energy (VAE), vertical detachment energy (VDE) adiabatic electron affinity (AEA), ionization potential (VIP, AIP), chemical hardness (η) and HOMO–LUMO gap; values in eV

System	O/Ga	VAE	VDE	AEA	AIP	VIP	η	H–L
Ga_3O	0.33	0.74	0.98	0.88	5.40	5.95	2.49	2.31
Ga_3O_2	0.66	1.91	2.25	2.08	6.34	7.67	2.71	2.34
Ga_3O_3	1.00	2.88	3.06	2.95	8.04	8.10	2.52	1.55
Ga_3O_4	1.33	2.87	6.92	3.23	8.23	8.27	0.68	2.52
Ga_3O_5	1.66	2.94	4.30	3.75	8.66	10.19	2.95	3.25
Ga_3O_6	2.00	1.97	5.54	4.39	8.32	11.23	2.85	3.63
Ga_3O_7	2.33	3.31	5.38	3.92	8.48	13.38	4.00	3.32
Ga_3O_8	2.66	1.93	5.22	4.11	9.53	10.26	2.52	3.34

Values for Ga_3O_n ($n = 1-3$) are taken from our previous work [4].

AEA, in much the same way that VDE provides an upper limit. Table 3 also contains HOMO–LUMO gap values for the most stable neutral isomers. Structural differences between the five systems considered in this study leads to an oscillatory trend of this quantity with the increase in O/Ga ratio.

We now compare the calculated results on Ga_3O_n clusters with those on Al_3O_n clusters to gain an insight into the chemistry of the oxygen-rich clusters when we go from aluminium to gallium. We observe that the lowest energy isomers of neutral Ga_3O_n (n: 6–8) resemble the corresponding alumina clusters [5]. Some of the anionic isomers also bear similarity to their alumina counterparts. For neutral Ga_3O_4, the ground state is similar to the one reported for Al_3O_4 by Martinez et al. [10] The anionic lowest energy isomer is similar to the second lowest energy isomer of $Al_3O_4^-$, reported by Martinez et al. [10]. Al_3O_5 sequence, as reported by Martinez et al. [11] does not have a structure similar in appearance to the lowest energy isomer of Al_3O_4. However, the second lowest energy isomer of $Ga_3O_5^-$ corresponds to the most stable of Al_3O_5 structures. Second and third isomers for $Ga_3O_5^-$ appear exactly as in the $Al_3O_5^-$ case.

In the absence of experimental values, we compare VDE values of Ga_3O_n ($n = 4,5$) with the results from photo-electron spectroscopy measurements on alumina clusters, [12,13] and note that our values follow the expected trend. Comparing AEA and VDE values for Ga_3O_n ($n = 6–8$) with corresponding alumina ones [5] the values decrease with an increase in O/Ga ratio, except AEA for Ga_3O_8, similar to alumina clusters.

On a comparative note, the oxygen-rich clusters of alumina and gallia are at a nearly equal footing; they are similar when it comes to tendency to form O–O bonds and trend of electronic properties, yet there are subtle differences when it comes to the structure of the lowest energy isomers.

4. Conclusions

In the DFT study of sequential oxidation of gallium oxide clusters using B3LYP/6-31 G(d, p), we find that the most stable isomers display up to four different backbones of constituent atoms. Also, all neutral isomers, $Ga_3O_4^-$, $Ga_3O_4^+$, and $Ga_3O_5^-$ are found in the respective lowest spin state while all other are found in triplet state. Anionic clusters are found to be more stable than the neutral clusters, and neutral ones are, in turn, more stable than the cationic ones. BE/atom for neutral as well as charged systems stays approximately constant with the increase in oxygen-to-metal ratio. Electron affinity, ionization potential and HOMO–LUMO gap values exhibit an oscillatory trend.

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References

[1] S. Sharma, M.K. Sunkara, J. Am. Chem. Soc. 124 (2002) 12288.
[2] S. Gowtham, A. Costales, R. Pandey, J. Phys. Chem. B 108 (2004) 17295.
[3] G. Meloni, S.M. Sheehan, D.M. Neumark, J. Chem. Phys. 122 (2005) 074317.
[4] S. Gowtham, M.D. Deshpande, A. Costales, R. Pandey, J. Phys. Chem. B 109 (2005) 14836.
[5] S. Gowtham, K.C. Lau, M.D. Deshpande, R. Pandey, A.K. Gionotto, G.S. Groenewold, J. Phys. Chem. A 108 (2004) 5081.
[6] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, Gaussian 98, Gaussian, Inc., Pittsburgh PA, 1998.
[8] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[9] R.G. Pearson, Chemical Hardness — Applications from Molecules to Solids, Wiley-VCH Verlag, Germany, 1997, ISBN 978-3-527-29482-4.
[10] A. Martinez, F.J. Tenorio, J.V. Ortiz, J. Phys. Chem. A 107 (2003) 2589.
[11] A. Martínez, F. Tenorio, J.V. Ortiz, J. Phys. Chem. A 105 (2001) 8787.
[12] S.R. Desai, H. Wu, C.M. Rohlfing, L. Wang, J. Chem. Phys. 106 (1997) 1309.
[13] H. Wu, X. Li, X.B. Wang, C.F. Ding, L.S. Wang, J. Chem. Phys. 109 (1998) 449.