A Theoretical Study of Lithium-Doped Gallium Clusters by Density Functional Theory

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The geometrical structures, stabilities, and electronic properties of Ga_nLi ($n = 1-13$) clusters were investigated within the density functional theory (DFT). The impurity lithium atom enhances the stability of Ga_nLi ($n = 1-13$) clusters, especially Ga_nLi ($n = 9-13$) compared to Ga_n ($n = 9-14$), that is at either apex position or side position. The dissociation energy, second-order energy differences, and the energy gaps between highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO) indicate that the Ga_7Li, Ga_9Li, and $Ga_{11}Li$ clusters are more stable within the studied cluster range. Moreover, the variation of the average bond length of $Ga-Li$ is due to the surface effect, and the binding strength increases resulting from the increase of charge amount.

Key words: Geometrical Structures; Stability; Clusters; Density Functional Theory.

1. Introduction

Clusters are often considered as a bridge between isolated atoms and bulk matter with fascinating physical and chemical properties [1]. The properties are not only size dependent, but also vary with different atoms doped into the clusters. This is significant especially for the material sciences since it allows one to control and manipulate properties of the material. Hence, understanding their physics and chemistry has become an intensive research area.

For gallium clusters, the clusters are studied as pure structure or impurity doped at various sizes within different quantum computational models [2 – 19]. In bulk materials, a small percentage of impurity is known to affect the properties. The effect is even more pronounced in clusters due to the finite size of the system. The lithium atom is one of the alkalis employed as an impurity in the host structure of the clusters [20 – 25]. It is valuable to study lithium doped gallium clusters to find out how the lithium atom affects the properties of the gallium cluster and adding that no systematic theoretical investigation on lithium doped gallium clusters was reported. For the Ga-Li system, Saint et al. reported phase diagram and electrochemical performance of the Li_2Ga_7 [26]. Thermodynamic descriptions of the $Ga_{14}Li_3$, Ga_7Li_2, Ga_9Li_5 were reported by Yuan et al. [27], and for these crystal structure data are available [28, 29]. On the other hand, the system is significant for battery applications [30]. In this paper, a systematic investigation of Ga_nLi ($n = 1-13$) clusters using the density functional theory (DFT) is reported. Ga_n ($n = 2-14$) is also provided for the comparison purposes. The computational method is described briefly in the following section. In Section 3, the results and discussion are presented. The conclusion is drawn finally.

2. Computational Method

The calculations were performed using the density functional theory with B3LYP exchange-correlation function and lanl2dz basis set as implemented in the Gaussian 09 program [31]. The lowest energy structures of the Ga_n ($n = 2-14$) clusters were obtained considering the possible initial configurations in geometry optimization guided by previous studies on gallium clusters. For the Ga_nLi ($n = 1-13$) clusters, the ground state geometries were investigated through replacing a lithium atom by a gallium atom either in the configuration used for the optimization of gallium clusters or in the optimized host structure of gallium clusters. The structures were optimized without symmetry restrictions with the standard integration grid followed by harmonic vibrational frequency calculations in order to verify true minima on their

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potential surfaces. Also, the same calculation method was exploited for geometry optimizations and for the frequency calculations. In the geometry optimization, the convergence thresholds are $4.5 \cdot 10^{-4}$ a.u. for the maximum force, $3 \cdot 10^{-4}$ a.u. for the rootmean-square (RMS) force, $1.8 \cdot 10^{-3}$ a.u. for the maximum displacement, and $1.2 \cdot 10^{-3}$ a.u. for the RMS displacement. The self-consistent field (SCF) electronic structure calculations were carried out with a convergence criterion of 10^{-6} a.u. on the total energy. In addition, the various spin multiplicities were not taken into account.

For accuracy of the computational method, GaLi and Ga_2 dimers were calculated. The GaLi dimer has a bond length of 2.92 Å with dissociation energy (20.4 kcal/mol) that are reasonably in agreement with the reported bond length (2.865 Å) and dissocation energy (22.3 kcal/mol) of GaLi [32]. For the Ga_2 dimer, the bond length and dissociation energy are obtained as 2.862 Å and 1.16 eV. The present dissociation energy is in agreement with the reported values of 1.10 eV (experimental), 1.18 eV or 1.12 eV [33 – 35]. The bond length can also be compared to the literature values of 2.73 Å or 2.719 Å [36, 37]. On this base, the calculation method is reliable to explain the properties of the Ga_nLi ($n = 1 – 13$) clusters.

3. Results and Discussion

3.1. Geometrical Structures

The lowest energy structures and some low lying isomers for Ga_nLi ($n = 1 – 13$) clusters are given in Figure 1 together with the lowest energy structures of Ga_n ($n = 2 – 14$) clusters where (a_0) and (a) represent the lowest energy structures for Ga_n and Ga_nLi. The symmetry, the spin multiplicity, the total energy, the relative energy, the average bond length of $Ga – Li$, and gapHL are summarized in Table 1 for the Ga_nLi clusters where the symmetry, the total energy, the spin multiplicity, and gapHL of Ga_n clusters are also provided.

For Ga_3, an equilateral triangle and an isosceles triangle were suggested as the lowest energy structures [37, 38]. The present calculation indicates that the lowest energy structure of Ga_3 is an isosceles triangle. For Ga_2Li, the lowest energy structure is also an isosceles triangle where the lithium atom is at the apex, and the average bond length of $Ga – Li$ is 2.982 Å. The linear structure (Fig. 1.3b) is less stable by 0.22 eV. A square is turned out to be the most stable structure of the Ga_4 cluster while the ground state of Ga_3Li prefers a tetrahedral structure with the average bond length of 2.981 Å for $Ga – Li$ and the lithium atom at the apex. The second isomer of this cluster is a linear one (Fig. 1.4b) and less stable by 0.54 eV. In the case of Ga_5, the lowest energy configuration is a pentagon. A buckled and a pentagon were reported as the ground state structures of this cluster [38, 39]. The optimized ground state of Ga_4Li is a lithium capped square having the lithium atom at the apex with an average bond length of 3.072 Å for $Ga – Li$. The isomer (Fig. 1.5b) is less stable by 0.33 eV. As for the Ga_6 cluster, the lowest energy structure is a prism, in that replacement of the gallium atom with a lithium atom results in the lowest energy structure of Ga_5Li. In this structure, the lithium atom is at the apex, and the average bond length of $Ga – Li$ is 2.941 Å. The lithium capped buckled structure (Fig. 1.6b) is another isomer and less stable by 0.04 eV. The Ga_7 cluster has a distorted capped trigonal prism as the lowest energy structure. For Ga_6Li, the optimized ground state structure is a lithium capped prism with an average bond length of 2.924 Å for $Ga – Li$. The low lying isomer (Fig. 1.7b) is less stable by 0.64 eV compared to the ground state structure. The lowest energy configuration of Ga_8 is a rhombic prism. A lithium atom was replaced by the gallium atom in this rhombic prism, and a bicapped prism is obtained as the ground state of the Ga_7Li where the lithium atom is at the apex, and the average bond length of $Ga – Li$ is 2.887 Å. The isomer (Fig. 1.8b) is another optimized structure and less stable by 0.54 eV. For Ga_9, the most stable structure is a bicapped prism that is different from the pentagonal structure reported in [39]. Ga_8Li has a lithium capped distorted rhombic prism to be the lowest energy structure with the average bond length of 2.878 Å for $Ga – Li$. The second isomer (Fig. 1.9b) is less stable by 0.26 eV. The lowest energy geometry of Ga_{10} develops a pentagonal arrangement of atoms. For the Ga_9Li cluster, two isomers were optimized. The isomer (Fig. 1.10a) has the lowest energy while the isomer (Fig. 1.10b) is less stable by 0.24 eV compared to ground state. The lowest energy structure has the lithium atom at face, and the average bond length of $Ga – Li$ is 2.886 Å.

The Ga_{11} cluster has the lowest energy structure that appears to be the gallium atoms capped octahedron.

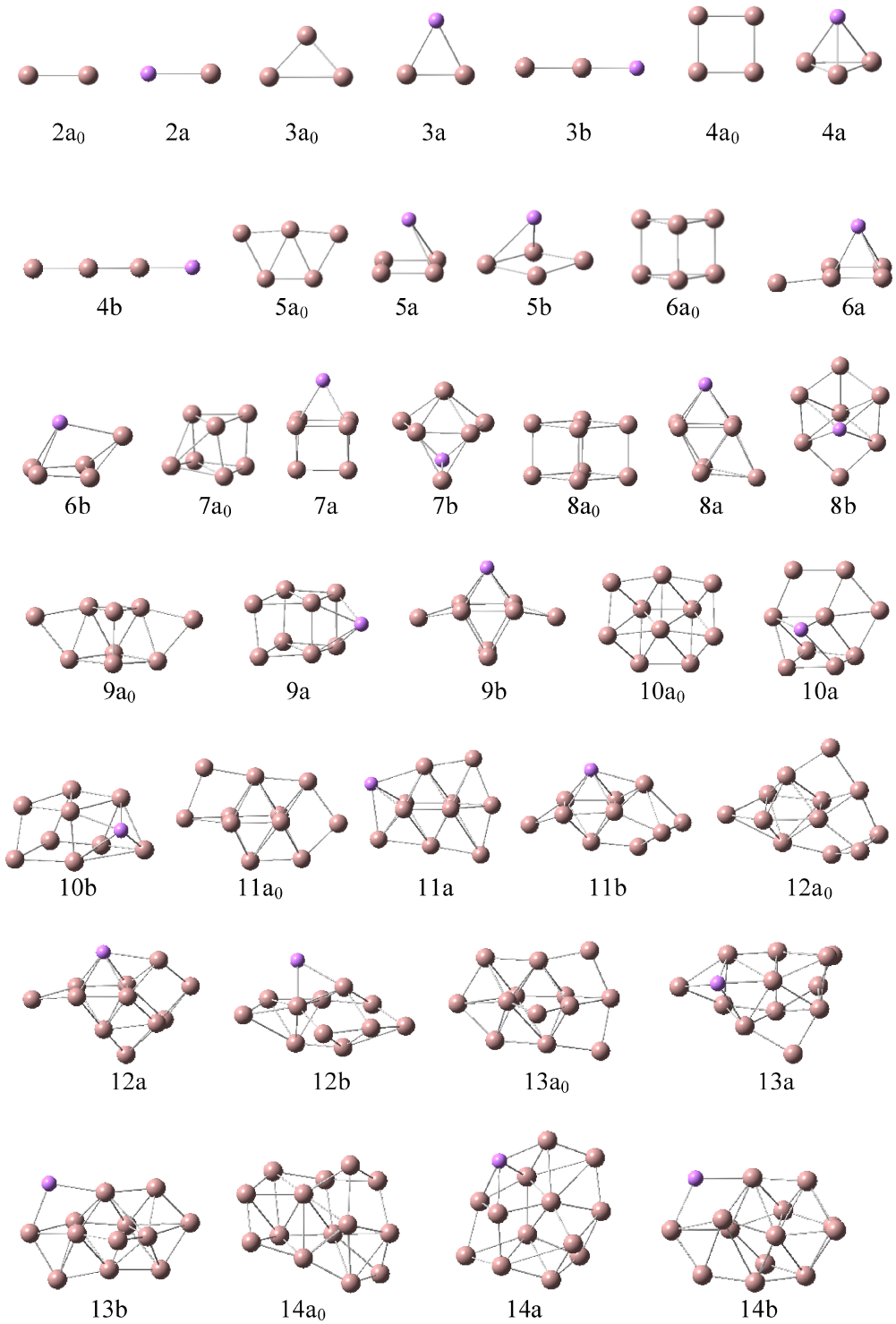

Fig. 1 (colour online). Lowest energy structures and some low lying isomers for Ga_nLi ($n = 1-13$) clusters together with the lowest energy structures of Ga_n ($n = 2-14$) clusters where the purples are Li atoms.

Clusters		Sym.	Multi	E_t (a.u.)	ΔE (eV)	r (Ga – Li) (Å)	gapHL (eV)
Ga_2	($2a_0$)	$D_{\infty h}$	3	−4.06501084			0.3426
Ga_3	($3a_0$)	C_{2v}	4	−6.12727162			0.0457
Ga_4	($4a_0$)	C_s	3	−8.2033317			0.0568
Ga_5	($5a_0$)	C_s	2	−10.2727839			0.1085
Ga_6	($6a_0$)	C_1	1	−12.3569031			1.8577
Ga_7	($7a_0$)	C_1	2	−14.4453061			0.5363
Ga_8	($8a_0$)	C_1	1	−16.5239785			1.8147
Ga_9	($9a_0$)	C_1	2	−18.5836941			0.1918
Ga_{10}	($10a_0$)	C_1	3	−20.653594			0.2955
Ga_{11}	($11a_0$)	C_1	2	−22.7300639			0.1404
Ga_{12}	($12a_0$)	C_1	1	−24.8103914			1.6922
Ga_{13}	($13a_0$)	C_1	2	−26.8808164			0.2816
Ga_{14}	($14a_0$)	C_1	1	−28.9671632			1.7137
GaLi	(2a)	$C_{\infty v}$	1	−9.533887706		2.92050	1.6531
Ga_2Li	(3a)	C_{2v}	2	−11.60006832		2.98245	0.1695
	(3b)	$C_{\infty v}$	2	−11.59184672	0.223		
Ga_3Li	(4a)	C_1	3	−13.67650648		2.98108	0.6473
	(4b)	$C_{\infty v}$	3	−13.65679993	0.536		
Ga_4Li	(5a)	C_1	2	−15.75793846		3.07261	0.0797
	(5b)	C_1	2	−15.74598283	0.325		
Ga_5Li	(6a)	C_1	1	−17.82627491		2.94175	1.7328
	(6b)	C_1	1	−17.82481581	0.039		
Ga_6Li	(7a)	C_1	2	−19.91433731		2.92473	0.0228
	(7b)	C_1	2	−19.89069176	0.643		
Ga_7Li	(8a)	C_1	1	−21.99903913		2.88772	2.0999
	(8b)	C_1	1	−21.97937394	0.535		
Ga_8Li	(9a)	C_1	2	−24.06831419		2.87883	0.7026
	(9b)	C_1	2	−24.05890875	0.255		
Ga_9Li	(10a)	C_1	1	−26.14809587		2.88692	2.1159
	(10b)	C_1	1	−26.13916045	0.243		
$Ga_{10}Li$	(11a)	C_1	2	−28.21528272		2.86714	0.3913
	(11b)	C_1	2	−28.20403444	0.306		
$Ga_{11}Li$	(12a)	C_1	1	−30.2945624		2.88845	1.7597
	(12b)	C_1	1	−30.2906565	0.106		
$Ga_{12}Li$	(13a)	C_1	2	−32.36253569		2.87677	0.14525
	(13b)	C_1	2	−32.35890228	0.098		
$Ga_{13}Li$	(14a)	C_1	1	−34.44268785		2.87266	1.5322
	(14b)	C_1	1	−34.44062732	0.056		

Table 1. Symmetry, spin multiplicity (multi), total energy E_t including the zero-point energy, relative energy ΔE, average bond length of Ga – Li, and gapHL summarized for the Ga_nLi clusters along with the symmetry, the total energy including the zero-point energy, the spin multiplicity, and gapHL of Ga_n.

The ground state of $Ga_{10}Li$ is similar to the structure of Ga_{11} with the lithium atom at the side and has the average Ga – Li bond length of 2.867 Å. The low lying isomer (Fig. 1.11b) is less stable by 0.31 eV. The lowest energy geometry of Ga_{12} cluster possesses a structure having the octahedron interlinked to the tetragonal prism with the capped two atoms. For $Ga_{11}Li$, the ground state structure is an octahedron interlinked to a trigonal prism with the capped two atoms. The lithium atom is at the apex in this structure, and the average bond length of Ga – Li is 2.867 Å. A pentagon pyramidal structure with the capped atoms is the lowest energy structure of the Ga_{13} cluster. The isomer (Fig. 1.13a) with the lithium atom at face is the lowest energy configuration of the $Ga_{12}Li$ cluster, and the average bond length of Ga – Li is 2.876 Å. The geometrical structure of the isomer (Fig. 1.13b) is similar to Ga_{13} and less stable by 0.10 eV compared to the ground state one. For the Ga_{14} cluster, the lowest energy configuration is a combination of a rhombic prism with a trigonal prism having two capped atoms. The isomer (Fig. 1.14a) is the lowest energy structure that capped the lithium atom at the side, and the average bond length of Ga – Li is 2.872 Å. The second isomer (Fig. 1.14b) is less stable by 0.06 eV. One notices here that the optimized lowest energy structures of the Ga_n ($n = 11-14$) clusters are different from the structures reported by Song and Cao [39].

In summary, the lithium atom alters the ground state geometries of Ga_n clusters apart from Ga_{11}, and the Ga_nLi ($n = 4-13$) clusters are in 3D. This impurity prefers either apex position or side position, but not

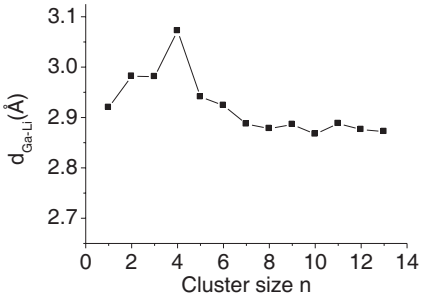

Fig. 2. Average bond lengths of $Ga-Li$ for Ga_nLi ($n = 1-13$) clusters.

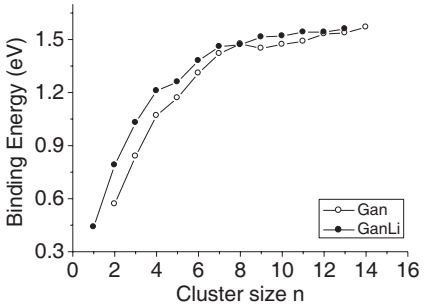

Fig. 3. Binding energy per atom for Ga_nLi ($n = 1-13$) and Ga_n ($n = 2-14$) clusters.

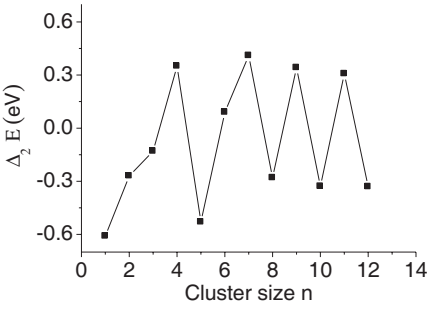

Fig. 4. Second-order energy difference of Ga_nLi ($n = 1-12$) clusters.

inside of the host structure: that is due to the ionic radius of the lithium atom. Regarding the bond length, the average bond length of $Ga-Li$ decreases rapidly in the range of $4 \leq n \leq 8$ and then the change is almost steady as given in Figure 2. In cluster physics, the explanation of many observed properties that scales as the ratio of surface to volume is attributed to the surface effect [40]. Hence, variation of the average bond length for Ga_nLi ($4 \leq n \leq 13$) clusters can be due to the surface effect.

3.2. Stabilities and Electronic Properties

The stability of clusters is described through the binding energy per atom (E_b), the dissociation energy (ΔE), and the second-order energy differences ($\Delta_2 E$). The stability is considered only for the lowest energy structures. The expressions used for the stability calculations are as follows:

$$E_b(Ga_nLi) = (nE[Ga] + E[Li] - E[Ga_nLi])/(n+1), \quad (1)$$

$$\Delta E[Ga_nLi] = E[Ga_{n-1}Li] + E[Li] - E[Ga_nLi], \quad (2)$$

$$\Delta_2 E[Ga_nLi] = E[Ga_{n+1}Li] + [Ga_{n-1}Li] - 2E[Ga_nLi], \quad (3)$$

where E is the total energy including the zero-point energy for the corresponding system. The binding energy per atom for Ga_nLi ($n = 1-13$) is presented in Figure 3 and also for the Ga_n ($n = 2-14$) clusters. The binding energy of the Ga_nLi clusters increases up to $n = 8$ and then increases slowly as cluster size grows. For the Ga_n clusters, the binding energy also possesses the similar behaviour within studied range. This indicates that the stability of these systems enhance with the increase of cluster sizes. However, there is a binding energy difference between the lithium doped gallium clusters and the host structure of the gallium clusters pointing out that doping of the lithium atom reduces the stability of the Ga_n ($n = 2-7$) clusters, but the stability is enhanced afterwards since the binding energy of Ga_nLi ($n = 9-13$) is slightly higher than that of the Ga_n ($n = 9-14$) clusters.

In Figure 4, the second-order energy difference $\Delta_2 E$ for the Ga_nLi ($n = 1-13$) clusters is plotted as a function of the cluster size. The maximum is found at $n = 4$, 6, 7, 9, and 11 implying that these clusters are more stable than their neighbouring clusters. It is worth to mention here that the second-order energy difference is directly compared to the experimental measurements of the relative abundance. The size dependence of the dissociation energy ΔE for these clusters is given in Figure 5. The peaks observed explore that the Ga_nLi ($n = 4, 6, 7, 9, 11, 13$) clusters have a higher stability than others.

For the electronic structures, HOMO-LUMO gaps and the charge transfer between the gallium atoms and the lithium atom were calculated. For the ground state of Ga_nLi ($n = 1-13$) clusters, the HOMO-LUMO energy gaps are given in Figure 6. The energy gap exhibits an odd–even oscillation, and the odd number

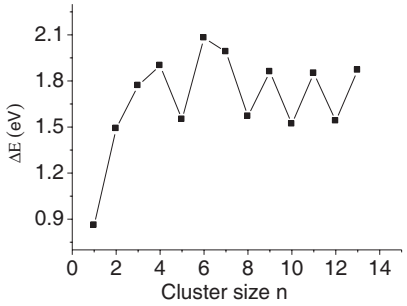

Fig. 5. Dissociation energy ΔE of Ga_nLi ($n = 1-13$) clusters.

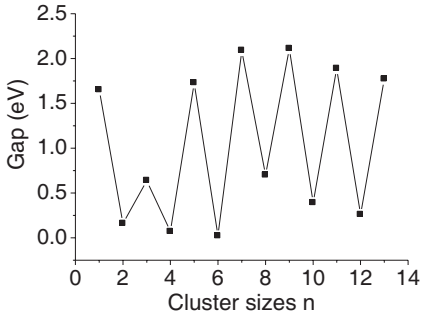

Fig. 6. HOMO-LUMO gap of Ga_nLi ($n = 1-13$) clusters.

clusters with higher peaks are chemically stable. The other clusters are chemically active due to the small HOMO-LUMO gap. One can compare the energy gaps with the second-order energy difference $\Delta_2 E$ and the dissociation energy ΔE for the clusters. It is seen that the odd–even oscillation from the HOMO-LUMO energy gap is consistent with the oscillation of $\Delta_2 E$ and ΔE for Ga_nLi ($n \geq 7$) clusters. The similar agreement was reported for the Ga_n ($n \geq 6$) clusters [39] and also for the Al-doped Ga_n ($n \geq 5$) clusters [41].

The charge transfer between gallium atoms and lithium atom were determined via natural bond analysis (NBO). The transfer takes place from the lithium atom to the gallium atoms due to electronegativity. The positive charge distribution of the lithium atom in the clusters is given in Figure 7. The lithium atom losses

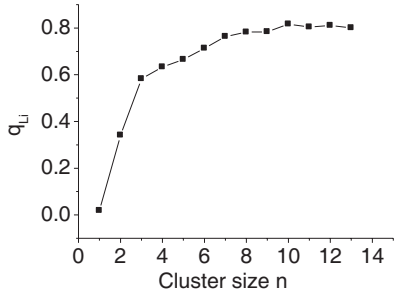

Fig. 7. Positive charge distribution of the Li atom in Ga_nLi ($n = 1-13$) clusters.

the charge rapidly up to $n = 3$, then the charge lost takes place slowly in the range of $n = 3-10$, and finally it becomes almost constant. This explores that the gallium atoms gain charges as the cluster size grows, and the charge amount becomes steady with $n \geq 10$. From the charge variation, the binding gets stronger for the Ga_nLi ($4 \leq n \leq 13$) clusters since the amount of charge increases in the clustering.

4. Conclusion

The impurity lithium enhances the stability of the Ga_nLi ($n = 1-13$) clusters and chooses either apex position or side position in the structures. Among the clusters, the Ga_nLi ($n = 9-13$) clusters are more stable compared to the Ga_n ($n = 9-14$) clusters. From the geometrical structure perspective, the Ga_nLi ($n = 3-13$) clusters are in 3D and their geometrical structure are different from the lowest energy structure of the Ga_n ($n = 4-14$) clusters except Ga_{11}. The agreement within the second-order energy difference, dissociation energy, and the HOMO-LUMO energy gap calculations points out that the Ga_7Li, Ga_9Li, and $Ga_{11}Li$ clusters have the higher stabilities. For the average bond length and the charge, the variation of the average bond length from $n = 4$ to $n = 13$ is due to the surface effect where the amount of charge increases slowly up to $n = 10$ showing that the binding strength increases.

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