A Density Functional Study of Li$_n$Cl ($n = 1-7$) Clusters

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The equilibrium geometries, relative stabilities, and electronic properties of Li$_n$Cl ($n = 1-7$) clusters were investigated within the density functional theory (DFT). The lowest energy structures reveal that the impurity chlorine atom prefers the apex position with the coordination number two except the Li$_6$Cl. From dissociation energy, second-order energy differences, and the energy gaps between highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO), Li$_n$Cl ($n = 1,3,5$) clusters are more stable within the studied cluster range. The binding energy per atom decreases as the cluster size increases, hence the clusters become more reactive when doped with the chlorine atom.

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

1. Introduction

Clusters have specific characteristics that are often between the bonding properties of molecules and that of a solid [1,2]. They therefore form the basis of intensive research in various fields such as material science, technological application as well as basic understanding of their physics and chemistry. The systems as bare or impurity doped are studied using the different quantum computational models. The impurity doped clusters have received particular attention recently due to application wise.

Among the alkali clusters, lithium clusters are one of the most studied systems at various sizes via different quantum computational models including density functional theory (DFT) and also the impurity doped ones [3 – 13]. The studies mainly consider equilibrium geometries, stability, energetics, and polarizability. To the best of knowledge, so far there is one theoretical work reported on the chlorine atom as an impurity to the lithium clusters [14]. In this study, molecular structures and stabilities for ClLi$_3$ and ClLi$_5$ were predicted. LiCl is important for battery applications [15] and is used to precipitate RNA from cellular extracts [16]. Besides, halogen atoms enhance catalytic activities [17] and also play an important role in electrochemistry [18]. Regarding the chlorine atom as an impurity, some of the studies are Ag$_n$Cl$^{0,\pm1}$ ($n = 2-7$) [19], Pd$_n$Cl ($n = 1-6$) [20], Cs$_n$Cl$_{n-1}$ ($n = 6-18$) [21]. In this paper, a systematic investigation of Li$_n$Cl ($n = 1-7$) clusters using the density functional theory is reported. A brief description of the computational method is given in the following section. In Section 3, lowest energy structures together with some low-lying isomers, relative stabilities, and electronic properties are presented. The conclusion is then drawn.

2. Computational Method

The geometry optimizations of the clusters without symmetry constrain were carried out using DFT with B3LPY exchange-correlation function and $6-311g+(2d,2p)$ basis set as implemented in the Gaussian 09 program [22]. For the lowest energy structures of Li$_n$Cl ($n = 1-7$) clusters, possible initial configurations were considered in geometry optimization either adding a chlorine atom to the host structure or replacing a chlorine atom by a lithium atom in the host structure guided by previous studies on the lithium clusters. Each geometry optimization was followed by the harmonic frequency calculations with no imaginary indicating that the optimized geometries correspond to the local minima. In the optimization, different spin multiplicities were not taken into account and the converged threshold is 10^{-6} a.u. (atomic unit) for the energy change.

To establish the accuracy of the computational method, Li$_2$ and LiCl dimers were calculated. The LiCl dimer have a bond length of 2.023 Å and a vibrational frequency of 639.925 cm^{-1} that are fairly in agreement with experimental bond length (2.021 Å) and vibrational frequency (643 cm^{-1}) of LiCl [23].

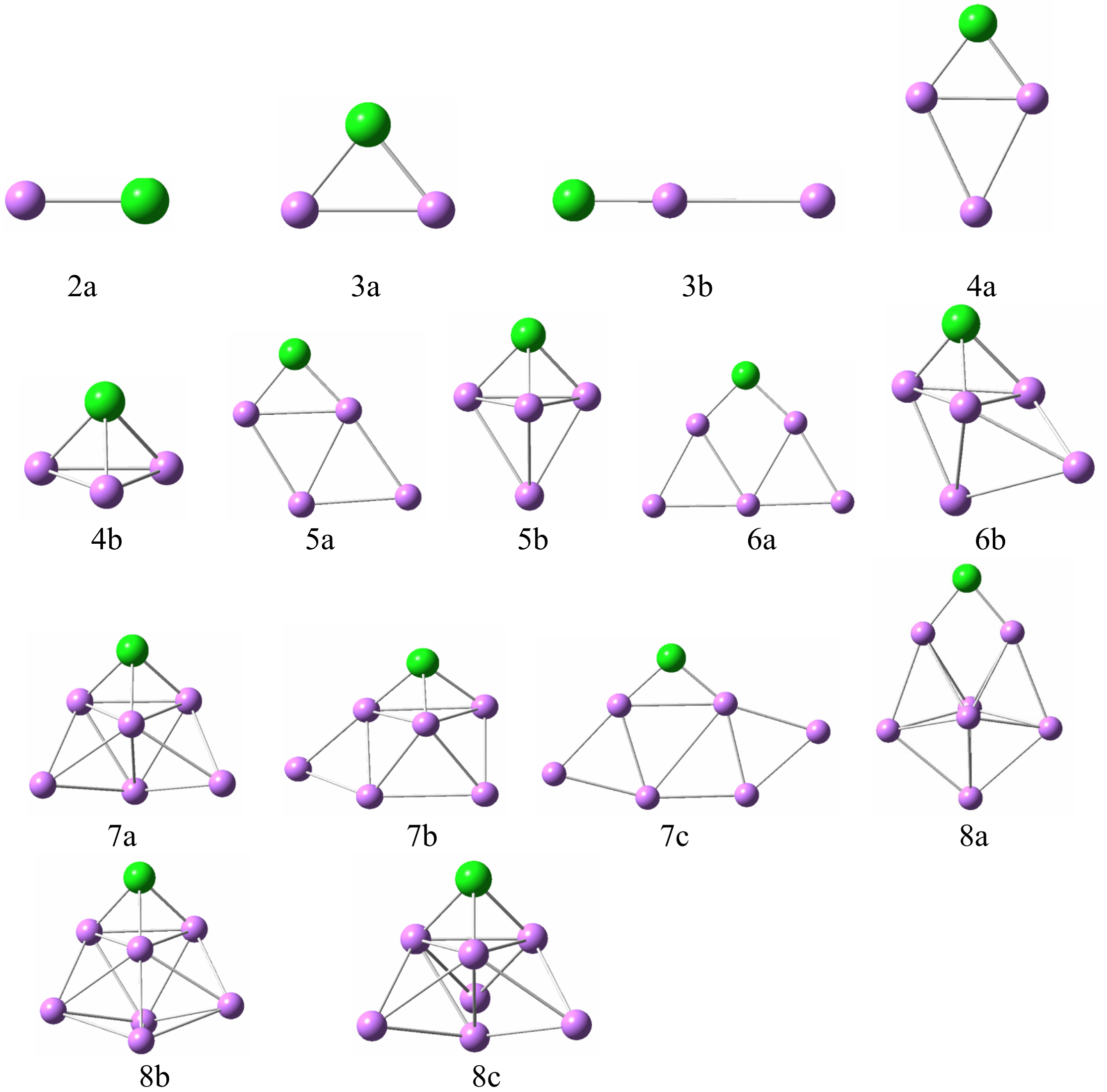

Fig. 1 (colour online). Lowest energy structures and some low lying isomers for the $\mathrm{Li}_n\mathrm{Cl}$ ($n = 1-7$) clusters; chlorine atoms are in green.

Agreement also exists for the calculated bond length (2.703 Å) of the Li_2 dimer with the experimental value of 2.67 Å [23]. Consequently, the calculation method is reliable to describe the properties of the $\mathrm{Li}_n\mathrm{Cl}$ ($n = 1-7$) clusters.

3. Results and Discussion

3.1. Geometrical Structures

The lowest energy structures and some low lying isomers for the $\mathrm{Li}_n\mathrm{Cl}$ ($n = 1-7$) clusters are presented in Figure 1. The structures labelled as ‘a’ are for the lowest structures in energy. For the $\mathrm{Li}_2\mathrm{Cl}$ cluster, the lowest energy structure is an isosceles triangle where the chlorine atom is at the apex, and the average bond length of Li–Cl is 2.176 Å. The linear structure is less stable by 0.807 eV compared to the ground state structure (Fig. 1.3b). The lowest energy structure of the $\mathrm{Li}_3\mathrm{Cl}$ cluster is a planar rhombus with the chlorine atom at the apex position, and the average bond length of Li−Cl is 2.186 Å. The planar rhombus structure having the chlorine atom at the apex position was reported as a ground state for the $\mathrm{Li}_3\mathrm{Cl}$ cluster [14]. The second isomer of this cluster turned out to be a tetrahedral structure with the 3D (Fig. 1.4b) and is less stable by 0.575 eV.

In the case of Li_4Cl, the optimized ground state structure is a capped planar rhombus with the chlorine atom at the apex (Fig. 1.5a), and the average bond length of Li−Cl is 2.185 Å. It was reported that the stable structure of the Li_5 is a pentagon [3,4], and also trigonal bipyramid structure was reported at ground state [5]. Hence, doping of the chlorine atom changes the geometry to the capped planar rhombus. A trigonal bipyramid structure having 3D is the second isomer of the Li_4Cl cluster and less stable by 0.136 eV than the ground state structure with the impurity at the apex position (Fig. 1.5b). The Li_5Cl cluster has the triangular prism as a lowest energy structure with the chlorine atom at the apex that was obtained through replacing the lithium atom by chlorine atom on the ground state geometry of the Li_6 cluster. The ground state of Li_6 was reported as a triangular prism [4, 6] and an octahedral structure [5]. The average bond length of Li−Cl is 2.184 Å. The second isomer is a capped trigonal bipyramid where the chlorine atom is at the apex (Fig. 1.6b) and less stable by 0.166 eV. A planer structure was predicted as the lowest energy structure for the Li_5Cl cluster [14].

As for the Li_6Cl cluster, three isomers were optimized given in Figure 1 (7a – 7c). The pyramidal structure has the lowest total energy (Fig. 1.7a). The chlorine atom is at the apex position in this structure, and the average bond length of Li−Cl is 2.311 Å. The lowest energy structure of the Li_7 cluster was found to be a pentagonal bipyramidal [4,5]. The isomer (Fig. 1.7b) is less stable by 0.253 eV compared to the ground state structure while the isomer (Fig. 1.7c) is higher in energy than the ground state by 0.345 eV. The chlorine atom is at the apex position within these isomers. Regarding Li_7Cl, the lowest energy structure is a 3D structure with the chlorine atom at the apex (Fig. 1.8a), and the average bond length of Li−Cl is 2.199 Å. The isomers, namely Li_7Cl (Fig. 1.8b), and Li_7Cl (Fig. 1.8c), have pyramidal structures where the chlorine atom is at the top. The isomers are higher in energy than the lowest energy structure by 0.016 eV and 0.042 eV, respectively. For Li_8, pyramidal [4, 6] and bicapped octahedral [4] structures were reported as ground state.

It is worth to mention that the average bond length of Li−Cl for all the clusters is given in Figure 2. The Li−Cl average bond lengths are similar for the clusters except for Li_6Cl, which may be due to the coordination of the chlorine atom. The chlorine atom is 3-coordinated for Li_6Cl and the coordination is two for the rest of the clusters.

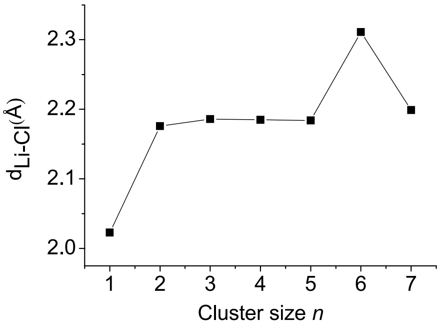

Fig. 2. Li−Cl average bond lengths (d_{Li-Cl}) for Li_nCl ($n = 1-7$) clusters.

3.2. Relative Stabilities and Electronic Properties

The stability of Li_nCl clusters is discussed on the basis of the binding energy per atom (E_b), the dissociation energy (ΔE) and the second-order energy differences ($\Delta_2 E$). The following expressions were used in the calculations:

$$E_b(Li_nCl) = (nE[Li] + E[Cl] - E[Li_nCl])/(n+1),$$
$$\Delta E[Li_nCl] = E[Li_{n-1}Cl] + E[Li] - E[Li_nCl],$$
$$\Delta_2 E[Li_nCl] = E[Li_{n+1}Cl] + E[Li_{n-1}Cl] - 2E[Li_nCl],$$

where E is the total energy of the corresponding system. For the electronic structure, the HOMO-LUMO gaps and charge transfer between the lithium atoms and a chlorine atom were calculated. The stability and the electronic structure features were considered for the lowest energy structure of the clusters. The size dependence of the binding energy per atom of the Li_nCl clusters is presented in Figure 3. It can be seen that the binding energy per atom decreases rapidly from $n = 1$ to $n = 4$ and then decreases slowly up to $n = 7$. This behaviour explores that the clusters are becoming more reactive. The small oscillations indicate that the odd number clusters are more stable than the even ones.

In cluster physics, the second-order energy difference ($\Delta_2 E$), and the dissociation energy (ΔE) are sensitive quantities measuring the relative stabilities of the clusters. The first one is often compared to the relative abundances determined from the mass spectroscopy findings while ΔE is the energy by which an atom is separated from the host structure. Figure 4 shows the second-order energy difference ($\Delta_2 E$) variation for the

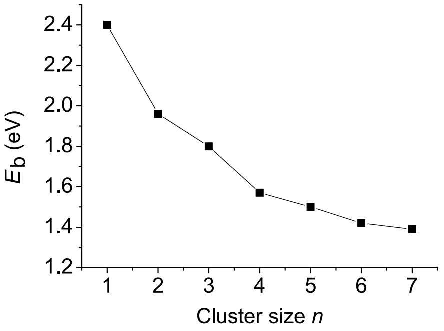

Fig. 3. Binding energy per atom of Li$_n$Cl ($n = 1-7$) clusters.

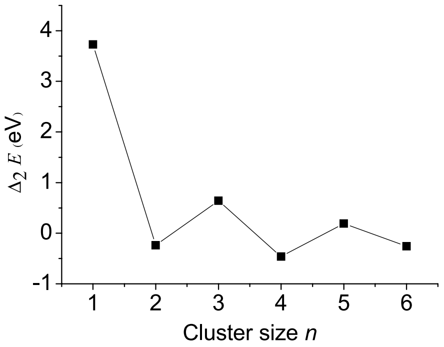

Fig. 4. Second-order energy difference variation for the Li$_n$Cl ($n = 1-6$) clusters.

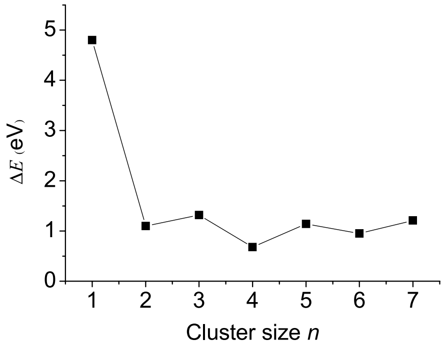

Fig. 5. Size dependence of dissociation energy (ΔE) for the Li$_n$Cl ($n = 1-7$) clusters.

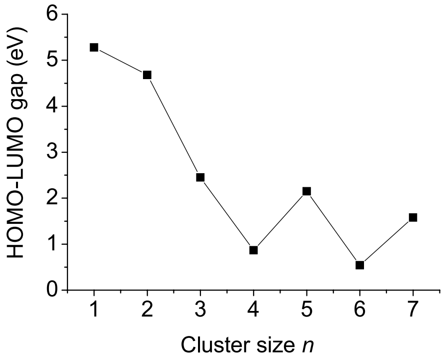

Fig. 6. The HOMO-LUMO energy gap of the Li$_n$Cl ($n = 1-7$) clusters.

cluster sizes. The peaks present the higher stability, hence the LiCl, Li$_3$Cl, and Li$_5$Cl clusters are more stable than the neighbouring clusters. The odd-even oscillations are also observed in the dissociation energy (ΔE) changes for the studied range as given in Figure 5. From the oscillation, the LiCl, Li$_3$Cl, Li$_5$Cl, and Li$_7$Cl clusters possess higher stability comparing to the others. Thus, the odd number clusters are more stable than the even number clusters.

The HOMO-LUMO gap is a parameter that provides information on the chemical stability of the clusters and a large energy gap corresponds to a high chemical stability. For the ground states of Li$_n$Cl($n = 1-7$) clusters, the HOMO-LUMO energy gaps are given in Figure 6. The energy gap decreases until $n = 4$ with the oscillations occurring afterwards. From the initial large energy gaps, the Li$_n$Cl ($n = 1-3$) clusters are chemically stable. Li$_5$Cl and Li$_7$Cl with higher peaks have also higher chemical stability. The other clusters are chemically active due to the small HOMO-LUMO energy gap.

The results from the second-order energy difference ($\Delta_2 E$) and the dissociation energy (ΔE) along with the HOMO-LUMO energy gap calculations point out that the Li$_n$Cl ($n = 1,3,5$) clusters have higher stability within the clusters range studied.

For the charge transfer, the charge transfer between the lithium atoms and the chlorine atom was determined via natural bond analysis (NBO). The charges of the chlorine atom in the clusters are -0.927 e, -0.944 e, -0.912 e, -0.906 e, -0.898 e, -0.890 e, -0.910 e, respectively, from LiCl to Li$_7$Cl. It appears that the charge transfer takes place from the lithium atoms to the chlorine atom as expected because of the electronegativity of the chlorine atom. The value of charge is around -0.910 e and varies with the clusters sizes.

4. Conclusion

The lowest energy structures of Li$_n$Cl ($n = 2-5$) clusters are in 2D, and transition from 2D to 3D occurs for the higher range. The impurity chlorine atom is at the apex position in the lowest structures and in the low lying isomers. Regarding the coordination and average bond length, the chlorine atom has a coordination number of 2 with similar average bond length, but the chlorine atom of Li_6Cl with a coordination number of 3 has a longer bond length. From the point of view of stability, second-order energy difference, dissociation energy, and HOMO-LUMO energy gap calculations show that the LiCl, Li_3Cl, and Li_5Cl clusters are more stable within the range of clusters studied. The decrease in the binding energy per atom points out that the doping of the chlorine atom causes the clusters to become more reactive.

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