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Density functional study of bromine-doped lithium clusters

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ABSTRACT

The geometrical structures, stabilities and electronic properties of Li_nBr ($n = 1–8$) clusters were investigated within the density functional theory. The impurity bromine atom enhances the stability of lithium clusters, however the stability decreases as the cluster size grows up. From the second order energy difference, dissociation energy and gapHL, the odd number clusters are more stable than the even number clusters, but LiBr is the most stable one. The bromine atom also modifies the ground state geometry of lithium clusters other than Li_4 and the geometry transition takes place from 2-D to 3-D at Li_6Br. In addition, the average bond length of Li–Br in the structures depends on the coordination number of bromine atom.

1. Introduction

Clusters are nano-sized materials between the atoms and the bulk with unique physical and chemical properties. The properties are different from those bulk materials and vary with the cluster sizes and also impurity doping. The systems are therefore subject of the research area both experimentally and theoretically.

Among the alkali clusters, lithium clusters are one of the most studied systems at various sizes via different computational methods including the density functional theory (DFT). In the DFT studies briefly, Gardet et al. reported electronic properties of the lithium clusters up to 20 atoms [1]; Jones et al. studied the small-sized Li_n ($n = 3–10$) clusters [2]; Fournier et al. implemented Kohn–Sham theory with local spin density and gradient-corrected energy functionals for the lithium clusters Li_n ($n = 5–20$) [3]. Jose and Gadre exploited the molecular electrostatic potential (MESP)-guided method for Li_n clusters from $n = 4$ to 58 and optimized the small clusters via DFT [4]. Goel et al. explored the structure, binding and charge distribution of the Li_n and Li_n^+ ($n = 2–30$). Yepes and coworkers reported structural and chemical properties of charged and neutral lithium clusters consisting of atoms from 5 to 10 [6]. There are also number of other studies such as using configuration interaction methods [7–9], coupled clusters [10–12], MP2 level of theory [12,13], Hartree–Fock theory [14–16].

For the lithium clusters, halogens are used as an impurity-doped atom, for example; Li_nF ($n = 2–4$) [17], Li_nCl ($n = 1–7$) [18], Li_nI (n = 3,5) [19]. The structures are called superalkali providing that the ionization potential is lower than the corresponding metal atom and that are significant for the cluster based material. Regarding the bromine-doped lithium clusters, a few studies are available in the literature [20–24]. Hebant and Picard have investigated the relative stability of Li_2Br through density functional theory together with the thermodynamic calculations [25]. They found that Li_2Br has C_{2v} symmetry with the bond length of 2.38 Å for Li–Br and the bond angle of Li–Br–Li is 72.31°. Recently, Velickovic et al. observed the positively charged Li_nBr ($n = 2–7$) clusters and determined ionization energies [26]. To the best of knowledge, so far no systematic theoretical study on the bromine-doped lithium clusters, namely Li_nBr ($n > 2$), has been reported. On the other hand, LiBr is important for the battery applications [27] and is used for the cooling system [28,29].

In this paper, a systematic investigation of Li_nBr ($n = 1–8$) clusters using density functional theory (DFT) is reported. Li_n ($n = 1–9$) 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 given. The conclusion is than drawn.

2. Computational methods

All calculations presented here were carried out with Gaussian 09 program [30]. The geometry optimizations of Li_n ($n = 2–9$)

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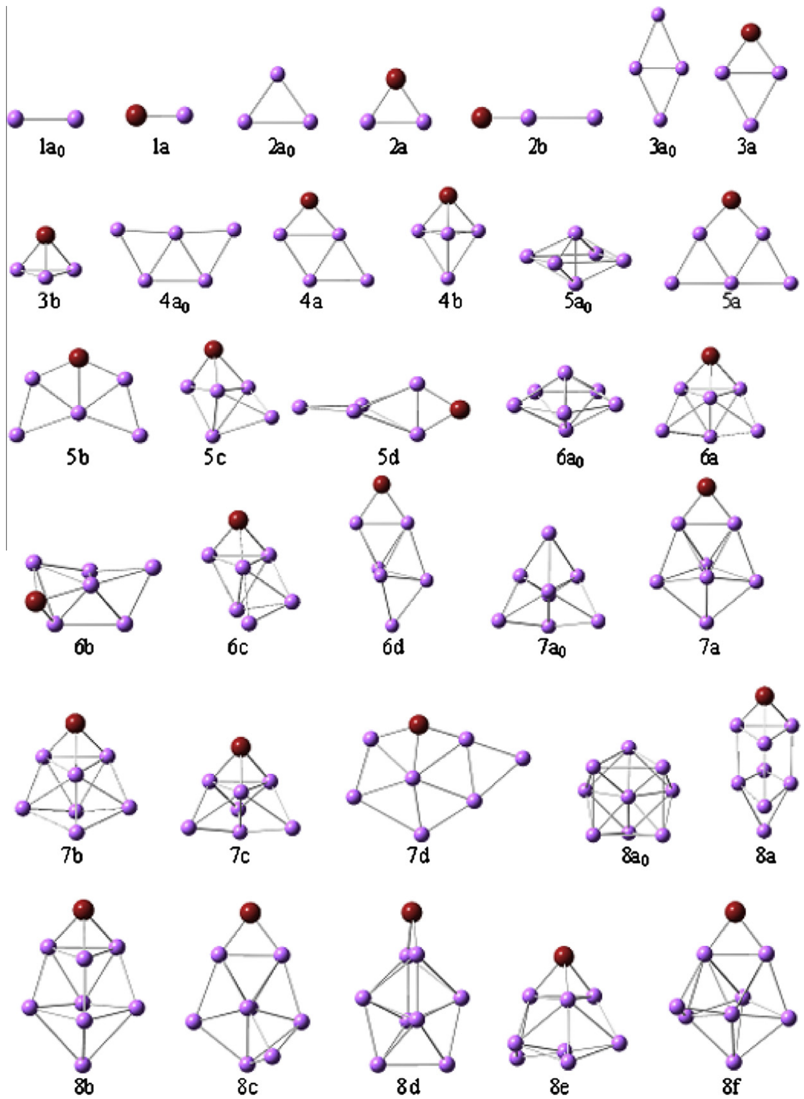

Fig. 1. The isomers of Li_nBr (n = 1–8) clusters together with the lowest energy structures of Li_n (n = 2–9) clusters; bromine atoms are in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

clusters were performed initially. The potential energy surfaces were produced via scanning angles formed by atoms or dihedral angles in the structures to generate the candidate structures at DFT/Lanl2dz level within the Berny algorithm. The structures from the potential energy surfaces were than optimized through DFT/B3LYP connection with 6-311g+(2d,2p) basis set [31,32]. The candidate structures for Li_nBr (n = 1–8) clusters were produced implementing the same approach used for the lithium cluster, the difference is that a lithium atom was replaced by a bromine atom one by one in each structure of the lithium clusters. The obtained structures were optimized at DFT/Lanl2dz level where the basis set includes the relativistic ECP. The optimization is followed by frequency calculation in order to verify true minima on the potential surfaces. Also, spin multiplicities with the different values were taken into account.

For the computational accuracy, LiBr and Li_2 dimers were calculated. The LiBr dimmer have a bond length of 2.268 Å with the vibrational frequency of 527.02 cm^{-1} that are reasonably in agreement with the experimental bond length of 2.170 Å and also vibrational frequency of 563 cm^{-1} for the LiBr [33]. The calculated bond length of 2.703 Å for the Li_2 is also consistent with the experimental value of 2.673 Å [33]. Hence, the calculation method is reliable to explain the properties of the Li_nBr (n = 1–8) clusters.

3. Results and discussion

3.1. Geometrical structures

The isomers of Li_nBr (n = 1–8) clusters together with the lowest energy structures of Li_n (n = 2–9) clusters are given in Fig. 1 where (a_o) and (a) represent the lowest energy structures for Li_n and Li_nBr. The symmetry, the spin multiplicity, the total energy, the relative energy, the gapHL of Li_nBr clusters and the symmetry, the total energy, the spin multiplicity, the gapHL for Li_n clusters are summarized in Table 1.

For Li_3, an isosceles triangle with the C_{2v} symmetry is found as the lowest energy structure. For Li_2Br, the lowest energy configuration is also an isosceles triangle with the C_{2v} symmetry where the bromine atom is at the apex position and the average bond length of Li–Br is 2.448 Å. A triangular structure with the C_{2v} symmetry was reported for the Li_2Br [25]. The isomer (Fig. 1.2b) is less stable by 0.643 eV. Li_4 cluster has a planar rhombus geometrical structure with D_{2h} symmetry. The lowest energy structure of Li_3Br is also planar rhombus one with C_{2v} symmetry. In this structure, the bromine atom is at the apex and the average bond length of Li–Br is 2.459 Å. The second isomer (Fig. 1.3b) is less stable by 0.547 eV. In the case of Li_5, the ground state structure is the w-shaped planer

Table 1
The isomer, symmetry, spin multiplicity (multi), relative energy (ΔE), total energy with zero point energy, and gapHL are given in Table 1 for the Li_nBr clusters along with the Li_n clusters.

Clusters	Isomer	Sym	Multi	Et (a.u)	ΔE (eV)	gapHL (eV)
Li_2	$1a_0$	$D_{\infty h}$	1	−15.01517		2.193
Li_3	$2a_0$	C_{2v}	2	−22.52548		1.263
Li_4	$3a_0$	D_{2h}	1	−30.05570		1.626
Li_5	$4a_0$	C_{2v}	2	−37.57553		1.430
Li_6	$5a_0$	D_{4h}	1	−45.11123		1.522
Li_7	$6a_0$	D_{5h}	2	−52.64515		1.132
Li_8	$7a_0$	T_d	1	−60.17446		1.942
Li_9	$8a_0$	C_{4v}	2	−67.69733		1.025
LiBr	1a	$C_{\infty v}$	1	−20.76496137	0.000	4.372
		$C_{\infty v}$	3	−20.62142551		
Li_2Br	2a	C_{2v}	2	−28.29137077	0.000	1.895
		C_s	4	−28.11254032		
Li_2Br	2b	$C_{\infty v}$	2	−28.26772802	0.643	
		$C_{\infty v}$	4	−28.09911364		
Li_3Br	3a	C_{2v}	1	−35.82980285	0.000	2.452
		C_{2v}	3	−35.79931985		
Li_3Br	3b	C_{3v}	1	−35.80967136	0.547	
Li_4Br	4a	C_s	2	−43.34472578	0.000	1.683
		C_{2v}	4	−43.30512369		
	4b	C_1	2	−43.33980495	0.133	
		C_1	4	−43.30721008		
Li_5Br	5a	C_1	1	−50.87644707	0.000	2.166
		C_1	3*	−50.84150199		
	5b	C_1	1	−50.87428693	0.058	
		C_1	3	−50.86177086		
	5c	C_s	1	−50.86896013	0.203	
		C_s	3	−50.86177729		
	5d	C_1	1	−50.86264163	0.375	
		C_1	3*	−50.85486496		
Li_6Br	6a	C_s	2	−58.39833328	0.000	1.363
		C_{3v}	4	−58.38444531		
	6b	C_1	2	−58.39151737	0.185	
		C_{3v}	4	−58.38444259		
	6c	C_1	2	−58.39151691	0.186	
		C_{3v}	4	−58.38446195		
	6d	C_1	2	−58.39019999	0.221	
		C_1	4	−58.37702265		
Li_7Br	7a	C_{2v}	1	−65.93208541	0.000	1.579
		C_{2v}	3	−65.91662433		
	7b	C_s	1	−65.93154176	0.014	
		C_s	3	−65.91663822		
	7c	C_1	1	−65.93019003	0.051	
		C_s	3	−65.91484719		
	7d	C_1	1	−65.91621861	0.431	
		C_1	3	−65.90180954		
Li_8Br	8a	C_s	2	−73.45786090	0.000	1.317
		C_s	4	−73.43296613		
	8b	C_1	2	−73.45566204	0.059	
		C_s	4	−73.43406017		
	8c	C_1	2	−73.45485144	0.081	
		C_s	4	−73.43294257		
	8d	C_1	2	−73.45341601	0.120	
		C_1	4*	−73.43268399		
	8e	C_1	2	−73.45214760	0.155	
		C_1	4	−73.43348069		
	8f	C_1	2	−73.45168208	0.168	
		C_1	4	−73.42951579		

Star (*) is for the transition state.

with the C_{2v} symmetry while the bromine atom capped planar rhombus having C_s symmetry is the optimized ground state structure of Li_4Br and the average bond length of Li–Br is 2.449 Å. The low-lying isomer of this cluster is less stable by 0.133 eV (Fig. 1.4b). As for the Li_6, a trigonal prism with the D_{4h} symmetry is the most stable structure. This is an agreement with previous calculations [6,12]. However, Gardet et al. [1] and Goel et al. [5] suggested that the most stable structure of Li_6 possess the C_{5v} symmetry. A trigonal prism with the bromine atom at the top is turned out as the ground state of Li_5Br among the optimized structures and the average bond length of Li–Br is 2.442 Å. The low-lying isomer (Fig. 1.5b) is less stable by 0.058 eV compared to the ground state structure.

For Li_7, a pentagonal bipyramid belonging to the D_{5h} point group comes out as the lowest energy structure that is consistent with the literature [5,6]. The lowest energy configuration of the Li_6-

Br is a trigonal pyramid with the bromine atom at the top, and the average bond length of Li–Br is 2.598 Å. Another isomer (Fig. 1.6b) is less stable by 0.185 eV. The ground state of Li_8 is a pyramidal structure with T_d symmetry. The similar structure is reported by Gardet et al. and Yepes et al. for this cluster [1,6]. For Li_7Br cluster, four isomers were obtained. The isomer (Fig. 1.7a) has the lowest energy and the isomers given in Fig. 1.7b and d are less stable by 0.014 eV, 0.051 eV, 0.431 eV. The lowest energy structure has the bromine atom at apex position with the average bond length of 2.467 Å for the Li–Br. Li_9 cluster has a cubic like structure with the C_{4v} symmetry. A doping of bromine atom to the Li_9 cluster results in an antiprism as the lowest energy geometry of Li_8Br with the average bond length of 2.592 Å for Li–Br. The isomer (Fig. 1.8b) is higher in energy than the lowest energy structure.

It is worth to point out that the bromine atom modifies the ground state structure of the lithium clusters for considered region except the Li_4. The geometry transition from 2-D to 3-D occurs for doped lithium clusters at Li_6Br and for lithium clusters at Li_6. The transition is due to the formation of cage critical points [34]. One also notices that Li_6Br (5a), Li_6Br (5d) and Li_8Br (5d) have single negative frequencies at 56.41 cm^{-1}, 55.65 cm^{-1}, 18.93 cm^{-1} for the higher spin cases presenting that these structures correspond to the transition state. Regarding the bond length of Li–Br, the bond length becomes longer with the increasing of coordination number of bromine atom.

3.2. Stabilities and electronic properties

The stability of clusters is discussed through the binding energy per atom (E_b), dissociation energy (ΔE) and second-order energy differences (Δ_2E) considering the lowest energy structures. The expressions used in the calculations are as follows:

$$E_b[Li_nBr] = (nE[Li] + E[Br] - E[Li_nBr])/(n+1) \quad (1)$$

$$\Delta E[Li_nBr] = E[Li_{n-1}Br] + E[Li] - E[Li_nBr] \quad (2)$$

$$\Delta_2E[Li_nBr] = E[Li_{n+1}Br] + [Li_{n-1}Br] - 2E[Li_nBr] \quad (3)$$

where E is the total energy including the zero-point energy for the related system. The binding energy per atom for Li_nBr (n = 1–8) and Li_n (n = 2–9) clusters is given in Fig. 2. The binding energy of Li_nBr (n = 1–8) is higher than the lithium clusters indicating that the doped bromine atom enhances the stability of lithium clusters. However, the doped clusters become reactive as the cluster size grows up since the binding energy decreases. The decrease in the binding energy can be due to the surface effect. For Li_n (n = 1–9) clusters, the stability increases smoothly up to n = 7 and then increase slowly. Another feature from binding energy curves is the initial difference of both systems that exhibits the strong binding of small doped clusters.

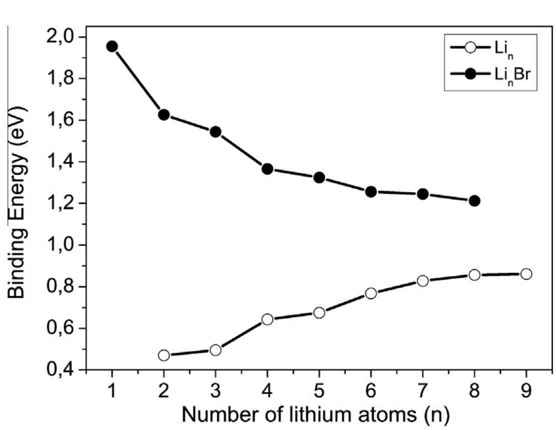

Fig. 2. The binding energy per atom for Li_nBr (n = 1–8) and Li_n (n = 2–9) clusters.

In cluster physics, the second-order energy differences (Δ_2E) and the dissociation energy (ΔE) determines the relative stability of the clusters. The second-order energy difference (Δ_2E) of Li_nBr (n = 1–8) clusters is plotted as a function of the cluster sizes in Fig. 3. The higher peaks are associated with odd number clusters. The clusters are therefore more stable than others. The dissociation energy (ΔE) of Li_nBr (n = 1–8) clusters given in Fig. 4 also points out that the odd number clusters are more stable than the even

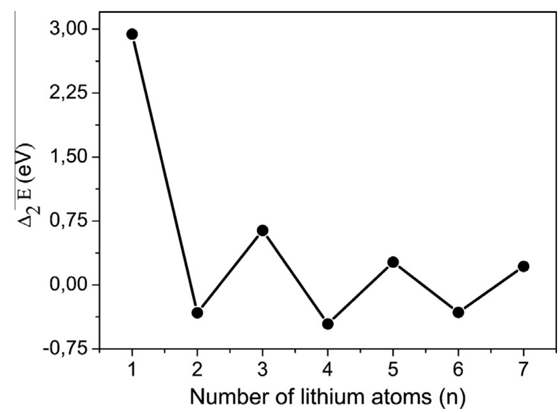

Fig. 3. The second-order energy difference of the Li_nBr (n = 1–8) clusters.

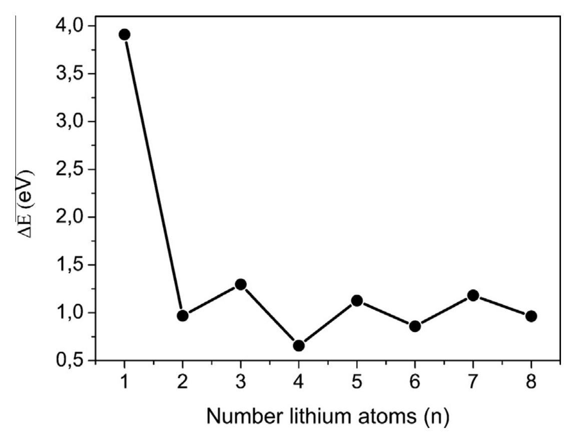

Fig. 4. The dissociation energy of the Li_nBr (n = 1–8) clusters.

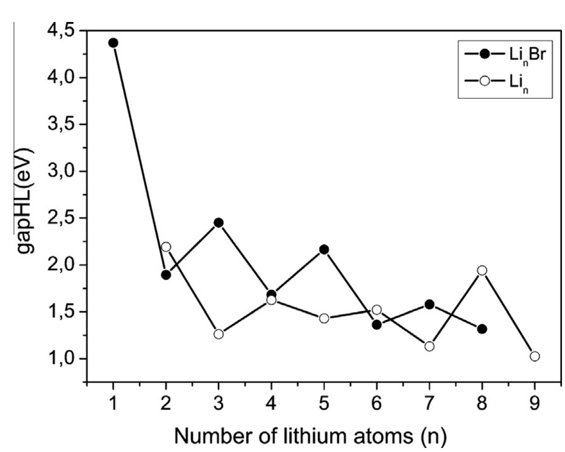

Fig. 5. The HOMO–LUMO gap of the Li_nBr (n = 1–8) clusters.

number clusters. The higher stability results from the electron pairing effect.

For the electronic structure stability, HOMO–LUMO gaps are calculated for the lowest energy structures of Li_nBr (n = 1–8) and Li_n (n = 2–9) clusters. From Fig. 5, the odd number of doped clusters possesses higher stability than the even number clusters and that is in agreement with the result of second-order energy differences (Δ_2E) and the dissociation energy (ΔE). Moreover, eight valance electrons of the LiBr leads to a maximum value of gapHL, hence the cluster can be magic number cluster. On the other hand, the sharp peaks of Li_2 and Li_8 clusters illustrate the magic numbers. The study by Harbola reported the Li_2 and Li_8 clusters as the magic number clusters [35]. The higher stability of Li_n (n = 2–9) clusters appears at n = 2, 4, 6 and 8.

4. Conclusion

The bromine doped lithium clusters have higher stability than the lithium clusters that is the effect of bromine atom. However, the stability of Li_nBr (n = 1–8) clusters decreases with increase of the sizes. Based on the second order energy difference, dissociation energy and gapHL calculations, LiBr is the most stable one while Li_nBr (n = 3, 5, 7) clusters are more stable than the Li_nBr (n = 2, 4, 6, 8). The bromine atom is at the apex position in the structures and the geometry makes the transition from 2-D to 3-D at Li_6Br. The average bond length of the Li–Br varies in respect to the coordination number of bromine atom.

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