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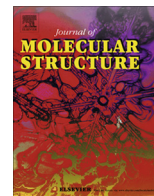**18** PUBLICATIONS **142** CITATIONS

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Stochastic search, fragmentation, electronic and reactivity properties of neutral and cationic hydrogenated Li$_6$ clusters

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HIGHLIGHTS

- We calculated the lowest-energy isomer of neutral and cationic Li$_6$H$_n$ (n = 0–7) clusters.
- Stochastic search method based on the density functional theory was employed.
- The fragmentation channels of Li, H, LiH, H$_2$ and Li$_2$H$_2$ forms were investigated.
- In neutral and cationic clusters is too high for the reversible hydrogen storage.
- The second isomer of neutral Li$_6$H$_6$ cluster is corresponding to a 3 × 2 × 2 compact structure.

GRAPHICAL ABSTRACT

We have reported the second isomer of neutral Li$_6$H$_6$ clusters, which very close to a 3 × 2 × 2 compact structure, is corresponding to one-quarter of a 3 × 3 × 3 compact lattice structure (Li$_{14}$H$_{13}$).
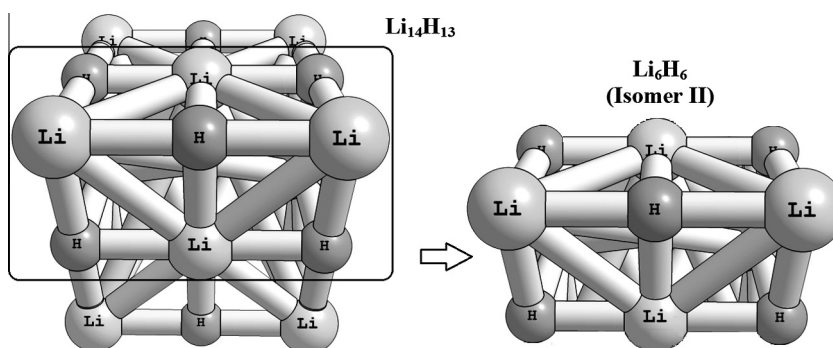
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ABSTRACT

In this study we investigated the lowest energy structures of neutral and cationic Li$_6$H$_n$ (n = 0–7) clusters using ab initio calculations based on DFT and CCSD(T) methods. We used the stochastic search method to obtain the global minimum on the potential energy surface of hydrogenated lithium clusters. For the lowest-energy isomers of the clusters, the relative stabilities, electronic and reactivity properties are presented depending on the binding energies, second energy difference, chemical hardness, chemical potential, softness, electrophilicity index, ionization potentials, electron affinities and HOMO–LUMO energy gaps. We also studied the fragmentation energies of neutral and cationic hydrogenated lithium clusters. In particular, the fragmentation energies of cationic clusters are compared with experimental data. The results are in good agreement with most available experimental findings.

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1. Introduction

The storage of hydrogen is technologically important because hydrogen is thought to be a promising solution for both the world's increasing energy consumption and for global warming. Hydrogen can be stored as a gas, liquid or a solid combined with a metal hybrid. Furthermore, the hydrogen storage materials must possess some important characteristics such as dependability, feasibility and reversibility as well as a high weight percentage of hydrogen. Hydrogen is being stored as a metal hydride at low pressures; however, it holds more volume than liquid hydrogen or the compressed gaseous form.

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Because lithium is the lightest metal element, compared to the other elements of this group, investigations of its bonding have an important role in cluster chemistry [1,2]. Therefore, lithium clusters have been extensively studied by many theoretical and experimental methods in recent years [3–7]. Since lithium clusters have a smaller weight percentage than other clusters, they have been used to store hydrogen efficiently [8].

We investigated lithium hydrides in the form of lithium clusters. Hydrogenated lithium clusters are an important model for simple electron-deficient ionic metal compounds. [9,10] Moreover, they have important applications in fusion reaction [11,12]. A detailed study of their electronic structure is necessary to predict and understand the geometrical variations of their structures. It is well known that significant changes in the electronic properties of the clusters are observed when the number of metal atoms increases in them. Some experimental studies about hydrogenated lithium clusters are therefore of great interest to investigate the interaction of hydrogen with a metal atom [13–16]. In particular, Antoine et al. carried out two experimental studies about the dissociation pathways and energies of cationic $Li_nH_m^+$ clusters. In the first experiment, by using a reflectron mass spectrometer, they reported [13] that LiH and Li_2H_2 molecules for $(LiH)_nLi_m^+$ ($m = 0, 1$ and 3) clusters exhibit the fragmentation behavior In the later study, they observed [14] a decay only fragmentation of Li atom and Li_2 molecules for $Li_nH_m^+$ ($1 \leqslant m \leqslant 6$, $n \leqslant 22$ and $(n-m) > 3$) clusters. However, these fragmentation channels may completely vary depending on the number of hydrogen and lithium atoms.

There are some theoretical and experimental studies about lithium and hydrogenated lithium clusters in the literature [17–27]. However, most of them [17–21] are concentrated on the neutral, pure lithium clusters, small Li_nH_m clusters ($n \leqslant 4$) or less hydrogenated clusters ($m \leqslant 2$), there are also limited studies [22–27] on larger hydrogenated lithium clusters. To the best of our knowledge, no theoretical or experimental study about neutral and cationic hydrogenated Li_6 clusters exists in the literature. Therefore, the present work aims, in particular, to investigate the neutral and cationic Li_6 clusters in detail. Also, neutral and cationic hydrogenated Li_6 clusters have never been searched for the global minimum of clusters. Moreover, the fragmentation energies and channels of clusters, and reactivity properties are discussed and investigated in detail.

The objective of the present work is to carry out a systematic analysis of the neutral and cationic Li_6 clusters with varying hydrogen content using the stochastic search method [28]. Furthermore, the manner in which hydrogenation changes the structural, electronic and reactivity properties of neutral and cationic Li_6 clusters is also investigated. The remainder of this paper is organized as follows: In the next section, computational methods will be described. After that the results and discussions of the computations will be presented. Finally, the conclusions of this research will briefly be discussed.

2. Computational methods

One of the important points in studies of clusters is the determination of the most stable isomers. As the number of atoms in a cluster increases, the number of possible isomers increases. Well-developed computer codes allow researchers to determine the geometry of the clusters, their isomers, and relative stability in up to a hundred atoms. It is well known that the most accurate way of studying the stability of clusters is to find all of their isomers on the potential energy surface and make a comparison of their energies. There are many ways to find isomers this include genetic algorithms [3,29], stochastic search [30–34], the Monte-Carlo method [35], etc. In this work, we performed an extensive search to obtain the global minimum on the potential energy

surface of neutral and cationic Li_6H_n ($n = 0–7$) clusters using the stochastic search method written in our group by Atiş. This method was first developed to search for the lowest energy structures of clusters by Saunders [28]. In this method, each atom of an initial structure is kicked randomly to move within a sphere of radius R. Thus, the system generates random values between $-R$ and $+R$ for displacements along the x, y, and z axes. An atom kicked in such a way falls within a cube with a side length of 2R instead of within a sphere of radius R. In order to have kicked positions which fall within a sphere instead of a cube, one need only to calculate the moved distance. If it is greater than R, this process is rejected and a new set of three random displacements is chosen. To prevent the fragmentation of atoms, atom neighborhoods are checked at each step, then these new atom coordinates are sent to the Gaussian-09 program [36] as an input file. For quick preliminary calculation, the Density Functional Theory (DFT) and 6-31G basis set are used to optimize the randomly kicked structure. The above mentioned steps are performed 400 times for each size, quite a large number of structures for neutral and cationic Li_6H_n ($n = 0–7$) clusters are obtained. After the searching processes, the same isomers are determined by comparing their geometrical structures and energies, and they are eliminated for further calculations. The selected different isomers are reoptimized using the quadratically convergent Self Consistent Field (SCF) procedure and the popular B3LYP hybrid functional [37] with a relatively higher basis set 6-311++G(2d,2p), where double plus adds the diffuse function to the hydrogen and Li atoms, in addition to the two d-functions for the lithium atom and two p-functions for the hydrogen atom.

We performed single point calculations of these clusters as well as the lowest isomers for every stoichiometry at the CCSD(T)/6-311++G(2d,2p) level of theory using their optimal B3LYP/6-311++G(2d,2p) geometries. The ab initio calculations are performed considering the singlet spin state for an even number of hydrogen atoms and a doublet for an odd number of hydrogen atoms, which are attached to neutral Li_6 clusters and vice versa in the cationic clusters.

3. Results and discussion

By choosing the isomers from the search process up to 30–50 kcal/mol energy, the geometries are reoptimized and frequencies are calculated using B3LYP with polarized split-valence basis sets 6-311++G(2d,2p). In order to get more reliable results, we performed CCSD(T)/6-311++G(2d,2p) single point energy calculations by using previous optimal B3LYP/6-311++G(2d,2p) geometries. We have only reported the two lowest energy isomers for each hydrogenated size. The isomers are ordered according to their relative energies with respect to the most stable isomer, and presented in Fig. 1. Molecular structure visualization is done using the MOLDEN 3.4 program [38].

3.1. Structural properties and stability

Since there is no imaginary frequency for the stationary points, the optimized structures are accepted as real minima. As seen in Fig. 1, the isomers are ordered based on the CCSD(T) level of theory and the relative energies of the B3LYP level of theory are also given in the parentheses. The energy difference between the two lowest neutral Li_6 clusters is about 2.46 kcal/mol. While the first isomer has a bipyramidal structure, the second isomer has a quasiplanar structure. Alexandrova and Boldyrev also obtained these two isomers [3]. They calculated the energy difference between these isomers to be 4.2 kcal/mol by using their search method, the Gradient Embedded Genetic Algorithm (GEGA), at the B3LYP level of theory. Moreover, they reported the same stable isomers for the cationic
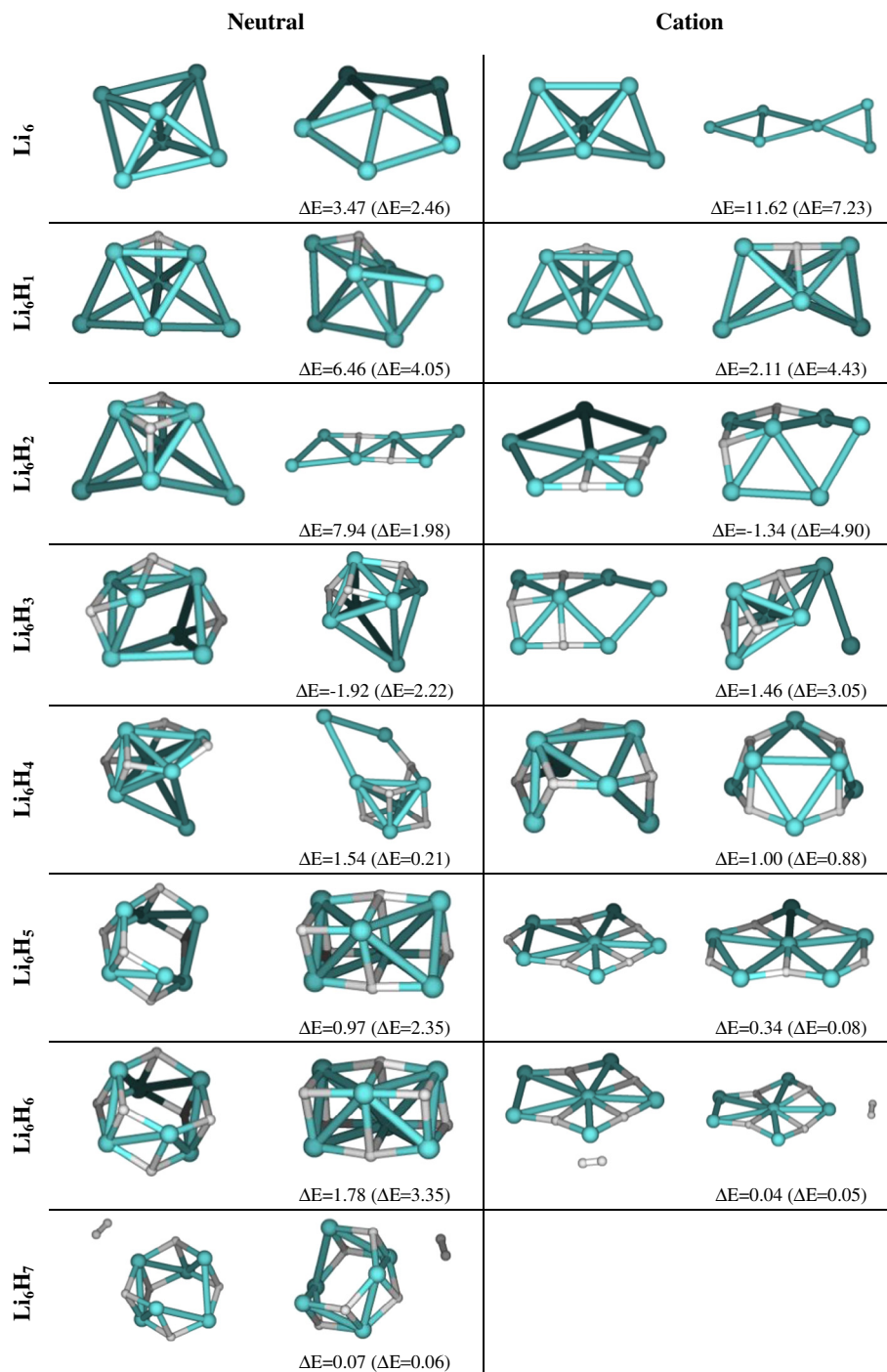
Neutral   **Cation**

Fig. 1. Lowest isomers for neutral and cationic Li$_6$H$_n$ (n = 0−7) with relative energies (kcal/mol) at CCSD(T)/6-311++G(2d,2p) without parentheses, at B3LYP/6-311++G(2d,2p) in parentheses.

Li$_6$ cluster as presented in this study. This supports the reliability of our search method. For neutral Li$_6$H$_1$ cluster, the energy difference within two isomers is 4.05 kcal/mol, as seen in Fig. 1. These structures can also be viewed as having a hydrogen capped trigonal bipyramid as a subunit. They are in agreement with the results in the literature [23,24,26,27]. Both of the Li$_6$H$_1$ cationic isomers have a three-dimensional (3D) structural form which possesses C$_s$ symmetry. The most stable structure of the neutral Li$_6$H$_2$ cluster results from the first isomer of the Li$_6$H$_1$ having a hydrogen atom added to it. Its second isomer has a planar geometry. The Li$_6$H$_2$ cationic isomers have a planar and quasiplanar geometry, respectively. To the best of our knowledge, for cationic hydrogenated

clusters, only the cationic Li$_6$H$_1$, Li$_6$H$_2$ and Li$_6$H$_5$ clusters are presented by Bonačić-Koutecký et al. [23] and Bertolus et al. [22]. However, the other cationic Li$_6$H$_n$ clusters have not been reported yet. Also, the neutral Li$_6$H$_3$ clusters are presented first of all. The neutral Li$_6$H$_3$ cluster is presented with the two most stable structures and the energy difference between them is 2.22 kcal/mol. It is worthwhile to note that the order of cationic Li$_6$H$_2$ and neutral Li$_6$H$_3$ isomers is switched when the energies are calculated by the B3LYP and CCSD(T) level of theory. The most stable isomer of the cationic Li$_6$H$_3$ cluster has a quasiplanar geometry and results from the second isomer of the Li$_6$H$_2$ having a hydrogen atom added to it. In the Li$_6$H$_4$ cluster, the first neutral isomer has 0.21 kcal/mol
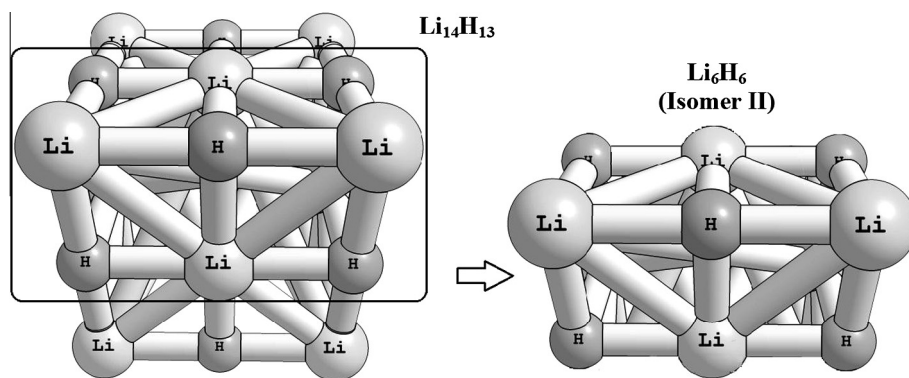
Fig. 2. The second isomer of neutral Li_6H_6 clusters which is very close to a $3 \times 2 \times 2$ compact structure.

lower energy than the second isomer. The first isomer has been reported in the literature [24,25]. For the neutral Li_6H_4 cluster, the first isomer with an umbrella-type is similar to the second isomer of the neutral Li_6H_3 cluster. The most stable structures of the neutral and cationic Li_6H_5 cluster are in good agreement with the results in the literature [22,24]. For the neutral Li_6H_6 cluster, the most stable isomer has a hexagonal unit cell. The second isomer has a rectangular structure, and it has 3.35 kcal/mol higher energy than the most stable isomer. Obviously, the first and second isomer of the neutral Li_6H_6 cluster grow from the first and second isomer of the Li_6H_5 by adding a hydrogen atom. The first and second isomers were found by Bertolus et al. [22]. We should also mention that the absolute ratio of existence is proportional to the energy difference relative to the most stable isomer, ΔE, at a given equilibrium temperature by assuming the Boltzmann distribution [39–41].

The ab initio calculations confirm that the small alkali halide clusters have approximately the structure of a small piece of bulk [14,42,43]. As seen from Fig. 2, we emphasize that the second isomer of neutral Li_6H_6 clusters, which is very close to a $3 \times 2 \times 2$ compact structure, corresponds to one-quarter of a $3 \times 3 \times 3$ compact lattice structure [44].

Hydrogen molecules separated from the rest of the cluster were observed in the neutral Li_6H_7 and cationic Li_6H_6. After higher level optimization, the distance between the H_2 molecule detached from the cluster and the rest of clusters, that is the neutral Li_6H_5 and cationic Li_6H_4 clusters, is about 2.08 Å.

Just like neutral hydrogenated Li_5 clusters, neutral hydrogenated Li_6 clusters prefer a three-dimensional geometry [45]. As seen from Fig. 1, the 3D structures are from an energy point of view favorable for all the studied neutral and cationic Li_6H_n ($n = 0–7$) clusters, whereas some cationic clusters ($n = 2,3,5,6$) present a planar or quasiplanar structure in the most stable configurations.

We have calculated the Li–H average nearest-neighbor distance (ANND) in order to investigate the evolution of the nearest-neighbor distance, and the results are plotted in Fig. 3(a). All of the neutral and cationic Li_6H_n ($n = 1−6$) clusters show that the Li–H bond lengths in these isomers are in the acceptable range of these atom types [46]. As seen from Fig. 3(a), the Li–H ANNDs in neutral and cationic clusters generally remain stable at about 1.81–1.82 Å and 1.79–1.80 Å, respectively. The Li–H ANNDs of cationic clusters, which exhibit a generally planar and quasi-planar structure, are usually lower than those of neutral clusters, which mostly exhibit 3D structures. Although the Li–H ANNDs of neutral clusters in hydrogenated Li_5 clusters are generally lower than those of anionic clusters [45], Li–H ANNDs of neutral clusters in hydrogenated Li_6 clusters are generally higher than that of cationic clusters.

The transition towards solid state can be observed in the sizes we have studied. The best example is the neutral Li_6H_6 cluster. The interatomic distances calculated for the first isomer of the
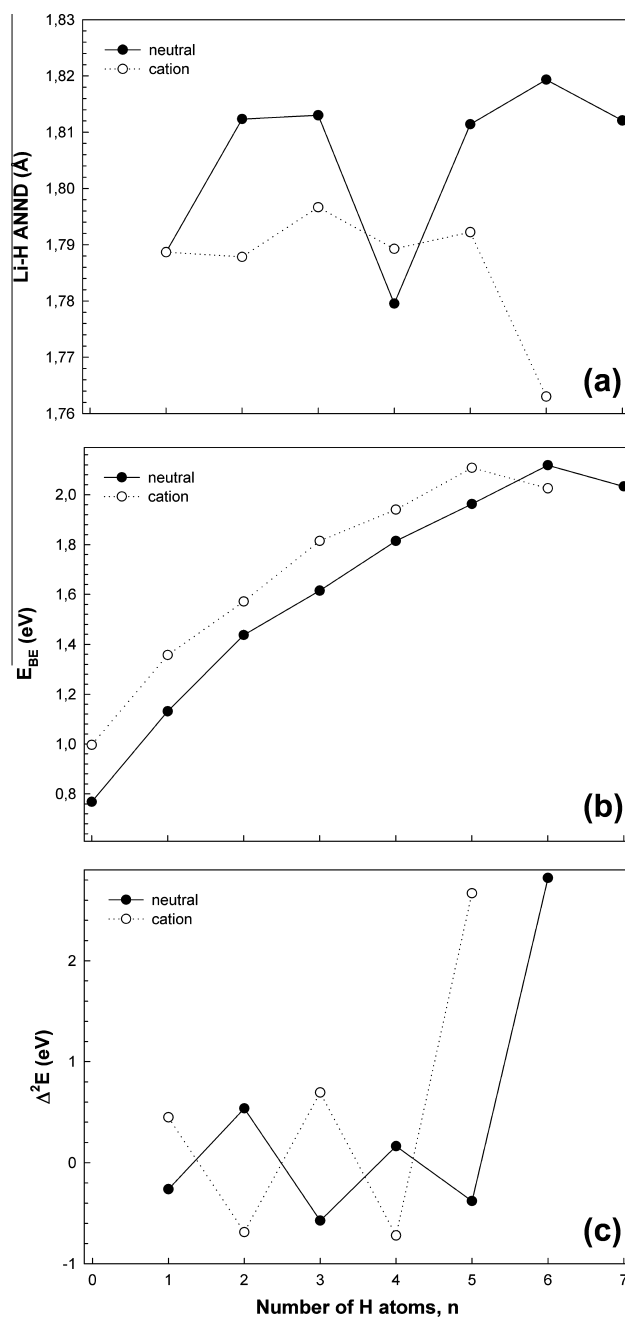

Fig. 3. For neutral and cationic Li_6H_n ($n = 0−7$) clusters (a) Li–H ANND, Li–H average nearest neighbor distance (b) E_{BE}, the binding energy per atom (c) $\Delta^2 E$, second energy differences.

neutral Li_6H_6 cluster are between 1.78 and 1.82 Å. The experimental Li–H lattice parameter [35] is 4.08 Å, which makes the Li–H distance equal to 2.04 Å. Moreover, Bertolus et al. [22] have calculated the interatomic distances between 1.82 and 1.86 Å for Li_4H_4, Li_6H_6, and $Li_{14}H_{13}^+$. For ionic clusters, the interatomic distances in the bulk are larger than in the isolated molecule. This can be explained by the fact that the number of first neighbors is larger, so that atoms must be further away in order to reduce electrostatic repulsion [47].

The binding energy per atom (E_{BE}) and second energy difference are investigated in order to evaluate the structural stabilities. The E_{BE} values for neutral and cationic clusters are calculated as follows:

$$E_{BE} = [6 \times E(Li) + n \times E(H) - E(Li_6H_n)]/(n+6) \quad (1)$$

$$E_{BE}^+ = [5 \times E(Li) + E(Li^+) + n \times E(H) - E(Li_6H_n)+]/(n+6) \quad (2)$$

The behavior of the E_{BE} in neutral and cationic hydrogenated Li_6 clusters is shown for the B3LYP method and is seen in Fig. 3(b). The E_{BE} of cationic clusters is higher than that of neutral clusters. This implies that it becomes more stable than its neutral counterparts when a cluster gives an electron. Obviously, the addition of hydrogen atoms to the Li_6 clusters generally increases the stability and it continues to increase until Li_6H_6 for neutral clusters and until Li_6H_5 for cationic clusters. The experimental binding energy per atom for neutral and cationic Li_6 clusters has been reported in the literature [4] and our results are in good agreement, as seen in Table 1. For neutral and cationic Li_6 clusters, the E_{BE} values 0.77 eV and 1.00 eV agree well with the experimental values 0.88 eV and 1.08 eV, respectively. For hydrogenated Li_6 clusters, there are no experimental results related to binding energies. Therefore, the computed binding energies are compared with the theoretical results whenever possible. The binding energies of neutral Li_6H_n ($n = 1, 2, 4, 6$) and cationic Li_6H_n ($n = 1, 2$) clusters obtained using B3LYP method are in good agreement with previous theoretical re-

sults [23–25], as shown in Table 1. The E_{BE} values of neutral clusters in hydrogenated Li_6 clusters are lower than those of cationic clusters (except for Li_6H_5).

In the cluster chemistry, the second energy difference of clusters is also another sensitive quantity that reflects the stability of clusters. The second energy difference (Δ^2E) is calculated by using the total energy values as follows:

$$\Delta^2E = E(Li_6H_{n+1}) + E(Li_6H_{n-1}) - 2E(Li_6H_n) \quad (3)$$

where $E(Li_6H_{n+1})$, $E(Li_6H_{n-1})$, and $E(Li_6H_n)$ denote the total energy of the Li_6H_{n+1}, Li_6H_{n-1}, and Li_6H_n clusters, respectively. Fig. 3(c) shows the second energy difference as a function of cluster size by using the B3LYP method. The values of Δ^2E exhibit an odd–even oscillation behavior and a sharp peak occurring for cationic Li_6H_5 and neutral Li_6H_6 clusters indicates the stability of this group.

3.2. Electronic and reactivity properties

Some electronic and reaction properties such as ionization potential, electron affinity, HOMO–LUMO energy gap, chemical potential, softness and hardness are investigated and compared with experimental and theoretical values [5,25,26,48]. The ionization potentials (IPs) are plotted for neutral clusters in Fig. 4(a) together with the highest occupied molecular orbital energies ($-E_{HOMO}$). The IPs can be defined in two different ways. They are either adiabatic ionization potentials (AIP) or vertical ionization potentials (VIP). The IPs can be calculated as follows:

$$AIP = E(optimized\ cation) - E(optimized\ neutral) \quad (4)$$

$$VIP = E(cation\ at\ optimized\ neutral\ geometry) \\ - E(optimized\ neutral) \quad (5)$$

The IP values exhibit odd–even oscillations with maxima at $n = 0, 2, 4, 6$. The IP values of even-numbered clusters are generally higher than their neighboring odd-numbered systems. Electron removal is more difficult from the doubly occupied molecular orbital than from the singly occupied molecular orbital because of the

Table 1
The binding energies per atom (E_{BE}), ionization potentials (AIP, VIP, IP_{exp}) and electron affinities (AEA, VEA, VDE).

Size	E_{BE} (eV/atom)		AIP	VIP	IP_{exp}	AEA	VEA	VDE
	Neutral	Cation	(eV)					
Li_6H_0	0.77	1.00	4.25	4.57	4.20[c]	0.83	0.73	0.96
	0.88	1.08[a]	4.10[b]	4.63[b]	–	–	–	–
Li_6H_1	1.13	1.36	4.04	4.27	4.08[f]	0.75	0.61	1.03
	1.02	1.24[d]	3.75[d]	3.96[d]	–	–	–	–
Li_6H_2	1.44	1.57	4.42	4.71	4.37[f]	0.38	0.35	0.44
	0.74	0.89[d]	4.11[d]	4.42[d]	–	–	–	–
Li_6H_3	1.61	1.81	4.43	4.57	–	0.63	0.60	0.65
Li_6H_4	1.81	1.94	4.36	5.23	–	0.19	0.18	0.27
	1.65	–	–	4.80[e]	–	–	–	–
Li_6H_5	1.96	2.11	4.04	4.79	4.50[e]	0.14	0.09	0.22
	1.78	–	–	4.46[e]	–	–	–	–
Li_6H_6	2.12	2.03	7.80	8.16	–	0.05	0.05	0.05
	2.11	–	7.12[g]	8.16[g]	–	–	–	–
Li_6H_7	2.03	–	4.01	4.75	–	0.12	0.07	0.20

[a] Ref. [4].
[b] Ref. [5].
[c] Ref. [47].
[d] Ref. [23].
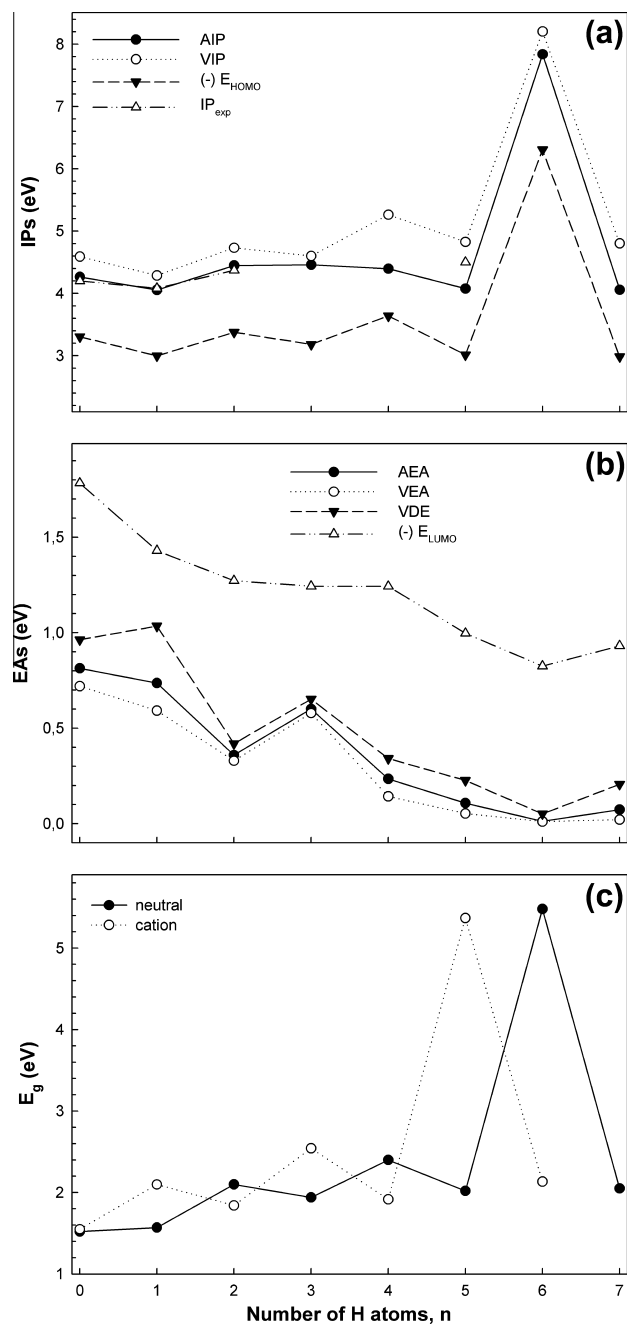[e] Ref. [24].
[f] Ref. [26].
[g] Ref. [25].

Fig. 4. The electronic properties (a) AIP, adiabatic ionization potentials; VIP, vertical ionization potentials; IP_{exp}, experimental ionization potential; $-E_{HOMO}$, HOMO energies (eV); (b) VEA, vertical electron affinities; $-E_{LUMO}$, LUMO energies; (c) E_g, HOMO–LUMO energy gap for neutral and cationic Li_6H_n ($n = 0–7$) clusters.

electron pairing effect. The electrons in doubly occupied molecular orbital have larger effective charge than in singly occupied orbital due to screening is weaker for electrons in the same orbital than inner shell electrons. Experimental ionization potentials [26] (IP_{exp}) for neutral Li_6H_n ($n = 0, 1, 2, 5$) clusters have been reported and our results are in good agreement, as seen in Fig. 4(a). For the Li_6H_1 cluster, the AIP of 4.03 eV agrees well with the experimental [26] values of 4.08 eV. In addition, the AIP value of the Li_6H_2 cluster (4.42 eV) is slightly higher than the available experimental value of 4.37 eV obtained by Vezin et al. [26]. For the Li_6H_5 cluster, the calculated AIP of the most stable isomer (4.04 eV) is in agreement

with the experimental [24] value of 4.50 eV, as seen in Table 1. As can be seen from Fig. 4(a), VIPs are higher than the AIPs due to energy compensation as a result of orbital relaxation on ionization.

The clusters with smaller electron affinities indicate that they are less reactive in accepting extra electrons and they are more stable. The adiabatic electron affinity (AEA), vertical electron affinity (VEA) and vertical detachment energy (VDE) on hydrogenated lithium clusters are reported for the first time in this study by using the B3LYP method. The electron affinities (EAs) can be calculated as follows:

$$AEA = E(\text{optimized neutral}) - E(\text{optimized anion}) \tag{6}$$

$$VEA = E(\text{optimized neutral}) - E(\text{anion at optimized neutral}) \tag{7}$$

$$VDE = E(\text{neutral at optimized anion}) - E(\text{optimized anion}) \tag{8}$$

The values and the graphs of the EAs are presented in Table 1 and in Fig. 4(b) together with the lowest unoccupied molecular orbital energies ($-E_{LUMO}$). The EAs decrease until $n = 2$ with the addition of hydrogen to the Li_6 clusters, but they show a peak at $n = 3$. After that they continue to decrease up to $n = 6$. The values of AEA, VEA and VDE are pretty close (except for $n = 1$). The EAs of the Li_6H_6 cluster are the lowest and imply that it hardly acquires an electron. According to the Koopmans' theorem [49], the ionization potential and the electron affinity of a cluster can be approximated by orbital energies for HOMO and LUMO, respectively. The theoretical results seen in Fig. 4(a) and (b) are compatible with this theorem. It is clear from this figure that the calculated IPs and EAs exhibit a similar trend with the $-E_{HOMO}$ and $-E_{LUMO}$ values, respectively ($-E_{HOMO} \approx VIP$, $-E_{LUMO} \approx VEA$). The energy gap between HOMO and LUMO (E_g) is an important quantity to reflect the chemical activity of clusters. If an electron is added to a cluster, it resides alone in the low-lying LUMO level or becomes the most weakly bound electron in the HOMO level of that cluster; therefore, the extra charge cannot produce large-scale changes either in geometry or in electronic states. It is natural to expect that the value of the HOMO–LUMO gap for both cationic and neutral clusters should be close to each other with a slight deviation depending on the open or closed shell electronic configurations. The E_g values exhibit an odd–even oscillation, as shown in Fig. 4(c). The values of the energy gap for the neutral Li_6H_n clusters with even hydrogen numbers ($n = 2, 4, 6$) are larger than those of odd ones (1, 3, 5) and vice versa for cationic ones. As seen in Fig. 4(c), the local peaks are found at $n = 5$ and 6 in cationic and neutral clusters, respectively. This means that the chemical stabilities of these clusters are stronger than those of the other clusters and their chemical activities are also comparatively weaker than the others.

Fig. 5 presents the global chemical descriptors [50–54] such as the chemical hardness (η), softness (σ), chemical potential (μ), and electrophilicity index (ω). These parameters for the most stable isomers of neutral hydrogenated Li_6 clusters are calculated by using the B3LYP/6-311++G(2d,2p) level of theory and Koopmans' theorem. Therefore, further estimates of η, σ, μ and ω quantities are defined follows:

$$\eta = (VIP - VEA)/2 \tag{9}$$

$$\sigma = 1/(VIP - VEA) \tag{10}$$

$$\mu = -(VIP + VEA)/2 \tag{11}$$

$$\omega = \mu^2/2\eta \tag{12}$$
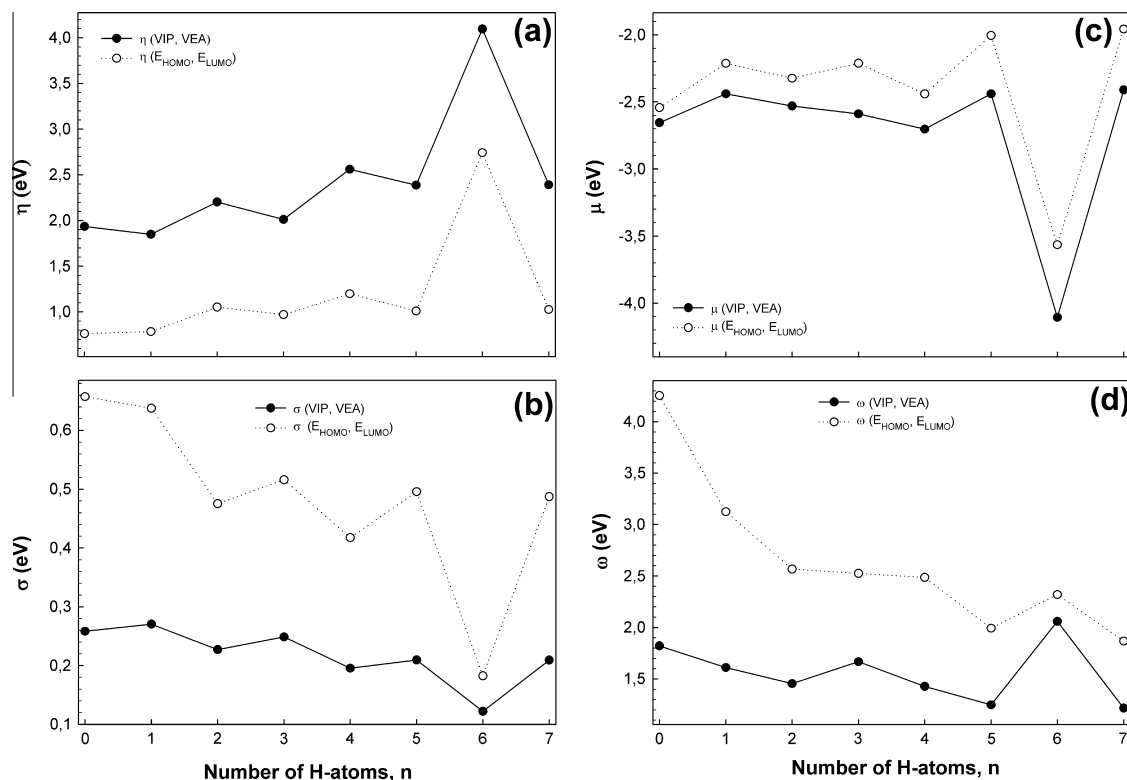
Fig. 5. The global reactivity descriptors (a) η, chemical hardness (b) σ, softness (c) μ, chemical potential (d) ω, electrophilicity index.

According to the principle of maximum hardness [55] (PMH), higher hardness indicates a more stable cluster. Fig. 5(a) and (b) clearly show that the neutral Li_6H_6 cluster is the hardest and its softness is the lowest. The chemical potential (μ) values lie in the energy range -1.9 and -4.2 eV, in particular the lowest value is seen at $n = 6$ in Fig. 5(c). This is another indicator that the neutral Li_6H_6 cluster has the strongest bond structure. The chemical potential of the molecule determines the direction of the charge transfer since an electrophile specifies it is capable of accepting electrons from a donor; therefore, its energy decreases upon the addition of an electron. The global reactivity index, ω, is defined via η and μ by Parr et al. [52]. This positive definite index is given in Fig. 5(d).

3.3. Fragmentation of Li_6H_n clusters

We examine the energies of five possible fragmentation pathways in order to explore the possible dissociation channels of Li_6-H_n ($n = 0-7$) clusters, as follows:

(i) $E(Li_6H_n) \rightarrow E(Li_6H_{n-j}) + E(H_j)$, (for neutral and cationic at $j = 1, 2$).
(ii) $E(Li_6H_n) \rightarrow E(Li_5H_n) + E(Li)$, (for neutral and cationic forms).
(iii) $E(Li_6H_n) \rightarrow E(Li_5H_{n-1}) + E(LiH)$, (for neutral and cationic forms).
(iv) $E(Li_6H_n) \rightarrow E(Li_4H_n) + E(Li_2)$, (for only cationic forms).
(v) $E(Li_6H_n) \rightarrow E(Li_4H_{n-2}) + E(Li_2H_2)$, (for only cationic forms).

The fragmentation energy can be defined as the required energy to dissociate a large molecule into smaller pieces (fragments). The fragmentation energies (E_{frag}) for neutral and cationic clusters are calculated by using the B3LYP/6-311++G(2d,2p) and CCSD(T)/6-311++G(2d,2p) levels of theory and the results are shown in Tables 2 and 3 as a function of the number of hydrogen atoms. The fragmentation energies of the H_2 molecule are always lower than those of the H atom, indicating that the Li_6H_n clusters prefer to subtract the H_2 molecule rather than H atom. From the energy point of view, the fragmentation of Li generally seems to be the lowest channel in Table 2. The fragmentation of cationic clusters has three different channels, i.e., Li, Li_2 and LiH. As seen in Table 2, the B3LYP and CCSD(T) methods give the average fragmentation energies of LiH and H_2 of the cationic clusters which are very close to each other with values of 1.95 eV and 1.89 eV, respectively. The cationic clusters generally fragment as an Li atom. The B3LYP calculation predicts that the cationic Li_6H_3 cluster prefers the Li_2 fragmentation instead of the Li atom but their values are also very close to each other. However, as for the CCSD(T) method, the lowest fragmentation channel is still Li. The cationic Li_6H_5 cluster prefers the LiH fragmentation (1.80 eV). The experimental result shows that fragmentation of LiH is easier than that of Li_2H_2. For example, Antoine et al. [14] studied $(LiH)_nLi_m^+$ ($m = 0, 1$ and 3; $n \leqslant 15$) clusters. They found that the fragmentation energies of an LiH or Li_2H_2 molecule are close to 2 eV, which is in good agreement with our results. Furthermore, they also reported that the fragmentation energy of LiH or Li_2H_2 is twice the energy necessary to dissociate an Li atom or Li_2 molecule in a metal rich lithium hydride cluster [13]. In the B3LYP method, we found the average fragmentation energies of Li and Li_2 to be 1.04 and 1.46 eV, respectively, which are in good agreement with experimental studies [13]. We also calculated these values by using

Table 2
The fragmentation energies (E_{frag}) and process of the neutral and cationic Li_6H_n ($n = 0$–6) clusters using B3LYP and CCSD(T) methods.

Neutral Fragmentation Channels					B3LYP E_{frag} (eV)	CCSD(T) E_{frag} (eV)	Cation Fragmentation Channels					B3LYP E_{frag} (eV)	CCSD(T) E_{frag} (eV)
Li_6	→	Li_5	+	Li	1.22	0.02	Li_6^+	→	Li_5^+	+	Li	1.10	0.90
							Li_6^+	→	Li_4^+	+	Li_2	1.46	1.24
Li_6H_1	→	Li_5H_1	+	Li	1.10	0.59	$Li_6H_1^+$	→	$Li_5H_1^+$	+	Li	1.40	0.57
	→	Li_6	+	H	3.31	2.93		→	Li_6^+	+	H	3.52	2.59
	→	Li_5	+	LiH	2.01	1.47		→	Li_5^+	+	LiH	2.09	2.02
								→	$Li_4H_1^+$	+	Li_2	1.57	1.36
Li_6H_2	→	Li_5H_2	+	Li	1.26	0.45	$Li_6H_2^+$	→	$Li_5H_2^+$	+	Li	0.76	0.94
	→	Li_6H_1	+	H	3.58	2.73		→	$Li_6H_1^+$	+	H	3.07	3.09
	→	Li_5H_1	+	LiH	2.15	1.85		→	$Li_5H_1^+$	+	LiH	1.95	2.19
	→	Li_6	+	H_2	2.11	2.04		→	Li_6^+	+	H_2	1.82	2.06
								→	$Li_4H_2^+$	+	Li_2	1.45	1.60
								→	Li_4^+	+	Li_2H_2	1.81	2.10
Li_6H_3	→	Li_5H_3	+	Li	0.63	0.58	$Li_6H_3^+$	→	$Li_5H_3^+$	+	Li	1.39	0.59
	→	Li_6H_2	+	H	3.04	2.84		→	$Li_6H_2^+$	+	H	3.76	2.53
	→	Li_5H_2	+	LiH	1.77	1.82		→	$Li_5H_2^+$	+	LiH	2.00	1.99
	→	Li_6H_1	+	H_2	1.84	1.95		→	$Li_6H_1^+$	+	H_2	2.06	1.99
								→	$Li_4H_3^+$	+	Li_2	1.34	1.19
								→	$Li_4H_1^+$	+	Li_2H_2	2.16	2.15
Li_6H_4	→	Li_5H_4	+	Li	1.26	0.52	$Li_6H_4^+$	→	$Li_5H_4^+$	+	Li	0.55	0.28
	→	Li_6H_3	+	H	3.61	2.56		→	$Li_6H_3^+$	+	H	3.07	2.62
	→	Li_5H_3	+	LiH	1.72	1.67		→	$Li_5H_3^+$	+	LiH	1.93	1.74
	→	Li_6H_2	+	H_2	1.87	1.77		→	$Li_6H_2^+$	+	H_2	2.05	1.53
								→	$Li_4H_2^+$	+	Li_2H_2	2.04	1.93
Li_6H_5	→	Li_5H_5	+	Li	1.09	0.89	$Li_6H_5^+$						
	→	Li_6H_4	+	H	3.45	3.09		→	$Li_6H_4^+$	+	H	3.79	2.98
	→	Li_5H_4	+	LiH	2.18	2.14		→	$Li_5H_4^+$	+	LiH	1.80	1.79
	→	Li_6H_3	+	H_2	2.28	2.02		→	$Li_6H_3^+$	+	H_2	2.08	1.97
								→	$Li_4H_3^+$	+	Li_2H_2	1.95	1.97
Li_6H_6	→	Li_5H_6	+	Li	4.18	2.83	$Li_6H_6^+$						
	→	Li_6H_5	+	H	3.83	2.88		→	$Li_6H_5^+$	+	H	1.12	0.94
	→	Li_5H_5	+	LiH	2.39	2.29							
	→	Li_6H_4	+	H_2	2.50	2.34		→	$Li_6H_4^+$	+	H_2	0.13	0.29

the CCSD(T) method as 0.66 and 1.35 eV for Li and Li_2, respectively. We can also illustrate this by following cycle as given in the study by Antoine et al. [14].

The experimental result shows that the fragmentation of LiH is easier than that of Li_2H_2. For example, Antoine et al. [14] studied $(LiH)_n Li_m^+$ ($m = 0$, 1 and 3; $n \leqslant 15$) clusters. This scheme presents

Table 3
The fragmentation energies of Li_2, H_2, LiH and $Li_2 + H_2$ for some cationic ($Li_6H_n^+$) clusters by using B3LYP and CCSD(T) methods.

Process	$n = 2$		$n = 3$		Exp.
	B3LYP	CCSD(T)	B3LYP	CCSD(T)	
D_1	1.45	1.60	1.34	1.19	1.40[a]
D_2	1.83	1.69	2.29	2.16	2.10[a]
2Δ	3.91	4.14	4.25	4.20	4.02[a]
$2D_{LiH}$	5.06	2.96	5.06	2.96	5.02[b]
$D_{H2} + D_{Li2}$	5.68	3.73	5.68	3.73	5.54[c,d]

All energies are in eV.
[a] Ref. [14].
[b] Ref. [58].
[c] Ref. [56].
[d] Ref. [57].

the fragmentation of Li_2, H_2, LiH and $Li_2 + H_2$ for cationic clusters, where n is the number of hydrogen atoms in cationic hydrogenated clusters and D_1 (or D_{Li2}), D_2 (or D_{H2}) and Δ (or D_{LiH}) are the fragmentation energies necessary to dissociate cationic clusters for Li_2, H_2 and LiH, respectively. We can report the $Li_6H_n^+$ ($n = 2$, 3) clusters due to probe the examination of the small hydrogenated lithium cluster in this study. Table 3 shows B3LYP/6-311++G(2d,2p), CCSD(T)/6-311++G(2d,2p) and the experimental results [14,56–58].

4. Conclusions

Using the stochastic search method, we studied the geometric structures and stabilities of neutral and cationic Li_6H_n ($n = 0$–7) clusters with B3LYP/6-311++G(2d,2p) and CCSD(T)/6-311++G(2d,2p) levels of theory. We should also mention that the higher level CCSD(T) method is the most accurate with the approximate inclusion of explicit electron correlation and can be regarded to provide a more reliable result. However, the B3LYP results are in better agreement experimentally than the CCSD(T) results. One explanation may be that the Becke hybrid functional uses accurate experimental data and the accuracy of the hybrid functional is dramatically better than any of the other existing functionals [59]. Our results show that although the most stable isomers of neutral hydrogenated Li_6 clusters prefer 3D structures, the most stable isomers of cationic hydrogenated Li_6 clusters generally prefer planar or quasi-planar geometries. The ab initio calculations confirm that the small alkali halide clusters have approximately the structure of a small piece of bulk [14,42,43]. We emphasize that the second isomer of neutral Li_6H_6 clusters, which is very close to a $3 \times 2 \times 2$ compact structure, corresponds to one-quarter of a $3 \times 3 \times 3$ compact lattice structure [47], as seen in Fig. 2.

The E_{BE} of cationic hydrogenated Li_6 clusters is higher than that of neutral clusters. The average Li–H bond lengths generally show an increasing trend when hydrogenated. Moreover, the ionization potentials and electron affinities are investigated in detail. The ionization potentials are in good agreement with theoretical and experimental results [5,23–26,48]. From the analysis of the electronic and reactivity properties, the neutral Li_6H_6 cluster is could be more stability than other cluster.

From the energetic point of view, the fragmentation of Li for neutral and cationic clusters seems to be in the lowest channel. The present results about fragmentation energies are in good agreement with experimental findings in the literature [13,14]. In addition, it is also seen that the monomer dissociation energy associated with Li_6^+ (1.10 eV) is in good agreement with the experimental value of 1.20 eV [4]. Since the loss of the H_2 molecule in clusters requires a total reorganization of the charge, fragmentation of H_2 is seen in bulk contrary to clusters. This probably indicates the presence of a barrier for the H_2 molecule in hydrogenated Li_6 clusters. The H_2 fragmentations of hydrogenated Li_6 clusters are exothermic. We should also mention that the fragmentation energies of hydrogenated Li_6 clusters are too high for reversible hydrogen storage systems.

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