Ab initio search for global minimum structures of neutral and anionic hydrogenated Li$_5$ clusters

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ARTICLE INFO

ABSTRACT

The structure and some electronic properties of neutral and anionic Li$_5$H$_n$ ($n = 0$–6) clusters have been studied by using the stochastic search method with the B3LYP/6-31G level of theory. After searching possible isomers, first few isomers with the lowest energy have been recalculated by the B3LYP/6-311G++(2d,2p) and CCSD(T)/6-311G++(2d,2p) level of theory. The method used in this study has been compared with the previously reported ab initio calculations, and its reliability has been confirmed. The anionic Li$_5$H$_n$ ($n = 0$–6) clusters are reported in this study for the first time. Our results show that in general, stability increases with increasing number of hydrogen atoms. The fragmentation energies of hydrogenated Li$_5$ clusters are easier to fragmentation the two hydrogen atoms than one hydrogen atom in hydrogenated clusters, and it is too high for the reversible hydrogen storage systems.

1. Introduction

Since cluster physics opens always new aspects, the electronic structure of clusters can be useful in finding the main reasons for their appearance. Metal clusters can absorb hydrogen in atomic form [1,2]. Recently, many scientific studies have been focused on hydrogenation of metals and it has been found that the metal hydrides appear to have some advantages such as the improvement of safety and reduced volume [3–5]. Lithium clusters present a good starting point for theoretical understanding of metal clusters. Moreover, because of a small number of electrons, the hydrogenated lithium clusters are important models for hydrogen storage materials [6], and for simple electron-deficient ionic metal compounds [7–9]. The hydrogenated lithium systems are of technological importance owing to their potential applications, including the fusion reaction such as deuterium–tritium reaction which is used in the first generation power reactors [10,11]. Experimental and theoretical studies based on lithium systems have been the subject of intense research for the last three to four decades [12–14].

To the best of our knowledge, neither the theoretical nor the experimental study about anionic hydrogenated Li$_5$ cluster exists in the literature. Therefore, the present work especially undertakes for the investigation of anionic Li$_5$ clusters. Besides, stable structures of the neutral hydrogenated Li$_5$ clusters have not been searched and reported as systematically as in this study. There are some theoretical and experimental studies in literature about lithium and hydrogenated lithium clusters [15–31]. However, most of them are concentrated on the neutral, pure lithium clusters or small Li$_n$H$_m$ clusters ($n \leqslant 4$), [15–25] and there are limited studies on the larger hydrogenated lithium clusters [26–31]. However, none of them includes any search algorithms for finding the global minimum of such clusters. Wheeler et al. [32] used only the Symmetry Adapted Stochastic Search (SASS) algorithm to find the lowest energy structures. Firstly, the lowest energy structures for some neutral and all of anionic hydrogenated Li$_5$ clusters will appear in literature.

The objective of the present work is to carry out a systematic analysis of the neutral and anionic Li$_5$ clusters with varying hydrogen content by using the stochastic search method [33], and is to investigate how hydrogenation changes the structure and electronic properties of Li$_5$ clusters. The Li$_5$H$_n$ ($n = 0$–6) clusters have not been investigated as systematically as by using a search method previously. Therefore, the lowest energy structures for neutral Li$_5$H$_4$ and Li$_5$H$_6$ and all of anionic clusters obtained in this study will be reported in the literature for the first time.

This work is organized as follows: In Section 2, computational methods will be described. After that, results and discussions of the computations will be presented. Finally, the conclusions of this research will be discussed briefly.

2. Computational methods

In this study, we have performed an extensive search on the potential energy surface of neutral and anionic Li$_5$H$_n$ ($n = 0$–6) clusters to find the low-lying energy structures, by using a program,

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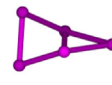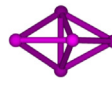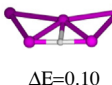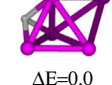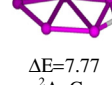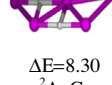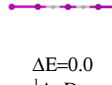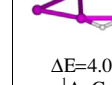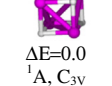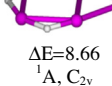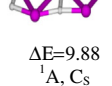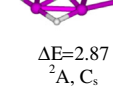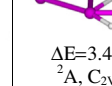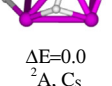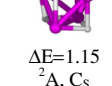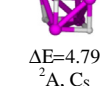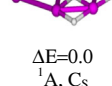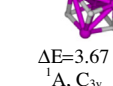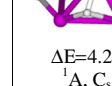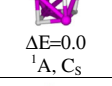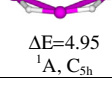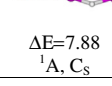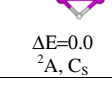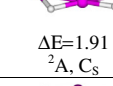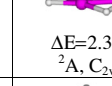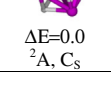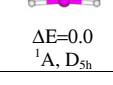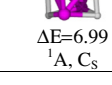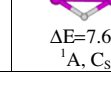
based on a stochastic search method, written by Atiş in our group. This method was first developed in order to search the lowest energy structures of clusters by Saunders [33], and used original or modified version of it in some studies [32,34]. In this method, each atom of an initial structure is kicked randomly to move within a sphere of radius R. Calculating such randomly moved positions is simple. One 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 a sphere of radius R. In order to have kicked positions fall within a sphere instead of a cube, one need only calculate the moved distance $\sqrt{x^2 + y^2 + z^2}$. If it is greater than R, this process is rejected and a new set of three random displacements is chosen against the scattering of atoms, atom neighborhoods is checked at each step. All of the lithium and hydrogen atoms are placed to origin as an initial geometry. Quantum chemical computations after each kick procedure are carried out by using the Gaussian-09 program [35]. For the global minimum search, the B3LYP method and 6-31G basis set were used in order to optimize the randomly kicked structure. After the searches had been completed, the isomers having same geometrical structures and energies were eliminated. The selected isomers were reoptimized by using the popular B3LYP hybrid functional [36] with a relatively higher basis set 6-311G++(2d,2p) where double plus adds the diffuse function to hydrogen and Li atoms, in addition to the 2d function for the lithium atom and 2p function for the hydrogen atom.

We should also mention that the ab initio calculations were performed by considering singlet–triplet and doublet–quartet for odd and even number of hydrogen atoms in the neutral clusters, respectively; and vice versa in the anions.

3. Results and discussion

3.1. Structure and geometry

We applied the stochastic search method so as to obtain global minimum structures of neutral and anionic hydrogenated pentaatomic lithium clusters Li_5H_n ($n = 0$–6) at B3LYP/6-311G++(2d,2p) level of theory. The three lowest energetic structures among the optimized geometries are given in Fig. 1. Also, the optimized energies are listed in Table 1 and Table 2 for the neutral and anionic clusters, respectively. Molecular structure visualization is plotted with the MOLDEN package [37]. Three stable isomers are found in neutral Li_5 clusters. The most stable isomer of the neutral Li_5 cluster has a triangular bipyramidal structure with a C_{2v} point group (Fig. 1). The second isomer of the neutral Li_5 cluster has a "W-shaped planar" geometry with the C_{2v} point group. The reported [16,20,29,38–40] most stable isomer of neutral Li_5 is the same as the second isomer, found in this study, (seen in Fig. 1). On the other hand, Alexandrova and Boldrev [15] have reported the same stable isomers for neutral Li_5, as presented in this study,

Fig. 1. Geometries, point groups, electronic states and relative energies (kcal/mol) of lowest energy structures of neutral and anionic Li_5H_n ($n = 0$–6) clusters calculated using 6-311++G(2d,2p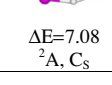) basis set at B3LYP level. The relative energies were calculated by subtracting the energy of most stable isomer from the related isomers' energy.

Table 1
The binding energy per atom (E_{BE}), experimental ionization potentials (IP_{exp}), adiabatic ionization potential (AIP), vertical ionization potential (VIP), adiabatic electron affinity (AEA), vertical electron affinity (VEA), vertical detachment energy (VDE), Homo–Lumo energy gap (E_g), chemical hardness (η), chemical potential (μ), softness (σ) and lowest frequencies (cm^{-1}) of neutral Li_5H_n clusters calculated using 6-311++G(2d,2p) basis set at B3LYP level.

Size	E_{BE} (eV/atom)	IP_{exp}. (eV)	AIP (eV)	VIP (eV)	AEA (eV)	VEA (eV)	VDE (eV)	E_g (eV)	η (eV)	μ (eV)	σ (eV)	f_{min} (cm^{-1})
Li_5	0.68	4.02	4.12	4.23	0.75	0.59	1.06	1.11	1.74	−2.49	0.29	127
	0.78[a]					0.59[e]			1.76[f]	−2.50[f]	0.28[f]	
Li_5H_1	1.14	4.12	4.33	4.89	0.50	0.21	0.57	2.11	2.19	−2.69	0.23	85
	1.05[b]		4.22[b]	4.78[b]								
Li_5H_2	1.46	4.00	4.04	4.35	–	0.41	–	1.77	2.05	−2.30	0.24	139
Li_5H_3	1.74	5.00	4.92	5.26	0.16	0.15	0.17	2.62	2.55	−2.71	0.20	161
	1.58[c]		4.93[d]	5.27[d]								
Li_5H_4	1.88	–	3.64	4.47	0.32	0.29	0.36	1.91	2.08	−2.39	0.24	66
Li_5H_5	2.05	–	6.26	8.07	0.10	0.09	0.14	5.25	3.98	−4.09	0.13	155
	2.05[d]		6.76[d]	8.07[d]								
Li_5H_6	1.93	–	7.60	5.70	0.56	0.35	0.13	2.77	2.57	−3.13	0.19	61

[a] Ref [41].
[b] Ref [26].
[c] Ref [27].
[d] Ref [28].
[e] Ref [20].
[f] Ref [17].

Table 2
Point group, electronic state, binding energy per atom (E_{BE}), second energy differences ($\Delta^2 E$), Homo–Lumo energy gap (E_g) and lowest frequencies (cm^{-1}) of the anionic Li_5H_n clusters.

Size	P.G.	E.S.	E_{BE} (eV/atom)	$\Delta^2 E$ (eV)	E_g (eV)	f_{min} (cm^{-1})
Li_5^-	D_{3h}	^1A	0.67	–	1.09	131
$Li_5H_1^-$	C_s	^2A	1.09	−0.24	0.92	103
$Li_5H_2^-$	$D_{\infty h}$	^1A	1.42	0.17	1.90	20
$Li_5H_3^-$	C_{3v}	^2A	1.65	−0.08	0.41	87
$Li_5H_4^-$	C_s	^1A	1.83	0.19	1.80	63
$Li_5H_5^-$	C_s	^2A	1.96	−0.31	1.50	67
$Li_5H_6^-$	D_{5h}	^1A	2.10	–	4.08	70

by using a search method based on gradient embedded genetic algorithm (GEGA) developed by them. They found the energy difference between the first and second stable isomers as 1.5 kcal/mol, whereas in this study it is found to be 0.88 kcal/mol (Fig. 1). The most stable isomer of hydrogenated Li_5 clusters generally prefers the three dimensional structure (Fig. 1). For a neutral Li_5H_1 cluster, three isomers are given in Fig. 1. The most stable isomer has a planar triangular structure with the C_{2v} point group. The second isomer has also a planar geometry and 0.10 kcal/mol higher in energy than the most stable isomer. In the literature, these two isomers were reported previously [26,31]. The energy difference between the first and third isomer is about 2.01 kcal/mol indicating the poor stability of the third isomer compared to the first isomer. Bonačić-Koutecký et al. [26] reported the same geometries (Table 1).

The energy difference between the first and the second isomer of neutral Li_5H_2 is found to be as 7.77 kcal/mol (Fig. 1). The third isomer of neutral Li_5H_2 has distorted W-shape planar structure, and its energy is 8.30 kcal/mol higher than that of the first isomer. By using symmetry adapted stochastic search algorithm (SASS), Wheeler et al. [32] reported fourteen lowest energy isomers together with relative energies. The first three most stable structures, presented in this work, are in excellent agreement with those reported by Wheeler et al. in both structure and relative energetics. The most stable configuration for neutral Li_5H_3 is a distorted cube with C_{3v} point group. In this group, the energy differences between the 1st–2nd, and 1st–3rd isomers are 8.66 kcal/mol and 9.88 kcal/mol, respectively. The most stable isomer of neutral Li_5H_3 is in agreement with the literature [27,28]. The other isomers of this group have not been previously reported in the literature. The most

stable isomer of Li_5H_4 has a three dimensional structure which is slightly (1.15 kcal/mol) more stable than the second isomer. This structure is also more stable than the structure reported by Gautam et al. [28]. The energy difference between the first and the third isomer is 4.79 kcal/mol. For neutral Li_5H_5, the most stable isomer has a chair-type structure with the C_s point group. The second most stable isomer has a ring structure and it is 4.95 kcal/mol higher energy than the most stable isomer. The third isomer of Li_5H_5 cluster is less stable than the first isomer with an additional 7.88 kcal/mol. In the search procedures of Li_5H_6 cluster, it has been found that hydrogen molecules is generally separated from the rest of the cluster, i.e., cluster are divided to Li_5H_4 and H_2. The structure called as the third isomer has been presented as an example of this situation. The acceptable most stable isomer of Li_5H_6 cluster can be described as a distorted three-sided cube with the C_s point group. The second isomer of Li_5H_6 has a ring structure, and the energy difference between the two isomers is 7.08 kcal/mol.

To the best of our knowledge, the anionic Li_5H_n cluster structures have not been reported previously in literature. The first three isomers of anionic Li_5H_n (n = 1–6) clusters are also given in Fig. 1. It should be noticed that the low lying energy state prefers the lowest spin multiplicity rather than higher spin multiplicity, except for the anionic Li_5 cluster. The most stable anionic Li_5H_1 and Li_5H_3 clusters are three-dimensional structures and a linear chain has been found as the most stable isomer of Li_5H_2. The others have a planar and quasi-planar structures. It is interesting that all of the hydrogenated anionic planar structures prefer to get a hydrogen at the center of the rectangular or pentagonal lithium rings. The hydrogen atom fills the space at the center of the wide lithium ring. The additional hydrogen atoms placed themselves at the outer of the lithium ring in the same plane. The best example is the star-like anionic pentagonal Li_5H_6 cluster.

3.2. Relative stabilities

The relative stabilities of Li_5H_n (n = 0–6) clusters can be examined by using energy parameters such as binding energy per atom (E_{BE}) and the second energy difference. The binding energy per atom can be calculated as follows:

$$E_{BE}(Li_5H_n) = [5 \times E(Li) + n \times E(H) - E(Li_5H_n)]/(n+5)$$

where n is the number of hydrogen atoms. The binding energy is calculated as an average over all atoms in the cluster. The binding energies per atom is given in Table 1 for neutral and Table 2 for
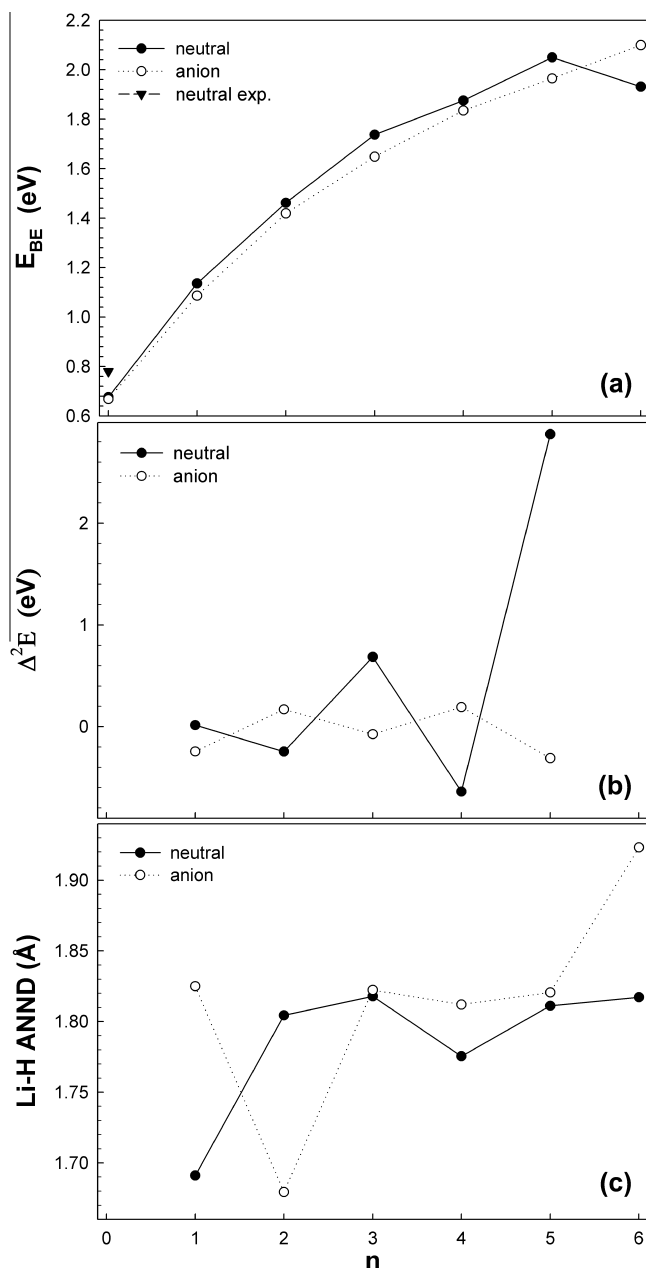
Fig. 2. For neutral and anionic Li_5H_n (n = 0–6) clusters (a) binding energy (eV/atom) per atom, (b) second energy differences (eV) and (c) Li–H average nearest neighbor distance (ANND) calculated using 6-311++G(2d,2p) basis set at B3LYP level.

anionic clusters, and plotted for the number of hydrogen atoms, in Fig. 2a.

For the neutral hydrogenated Li_5 clusters, the addition of hydrogen atoms to clusters increases the binding energy, and this trend continues until the point where the number of H atoms is equal to the number of Li atoms. After this point, a decrease in the binding energy occurs, which indicates the saturation of Li_5 with hydrogen. The highest value of binding energy is found for Li_5H_5. For Li_5 cluster, the binding energy per atom is 0.68 eV which is in agreement with the experimental value of 0.78 eV [41]. Unfortunately, there are no experimental results related to binding energy values for hydrogenated Li_5 clusters. Therefore, the computed binding energy values in this study are compared with theoretical results in the literature whenever possible. As seen in Table 1, the binding energies of Li_5H_1, Li_5H_3 and Li_5H_5 clusters are in good agreement with previous theoretical results [25,28,31].

Another way of testing the relative stabilities of the clusters is to calculate the second energy differences ($\Delta^2 E$) which have been calculated by using the total energy values as:

$$\Delta^2 E(Li_5H_n) = E(Li_5H_{n+1}) + E(Li_5H_{n-1}) - 2E(Li_5H_n)$$

where $E(Li_5H_{n+1})$, $E(Li_5H_{n-1})$, and $E(Li_5H_n)$ denote the total energy of the Li_5H_{n+1}, Li_5H_{n-1}, and Li_5H_n clusters, respectively. The $\Delta^2 E$ values for the lowest energy Li_5H_n clusters are plotted in Fig. 2b. The values of $\Delta^2 E$ exhibits the odd–even oscillating behavior and a sharp peak occurs at Li_5H_5 cluster indicating the highest stability of this group.

For the hydrogenated anionic lithium clusters, the increase in the binding energy continues up to $Li_5H_6^-$ due to the extra electron on the clusters. It is expected that an addition of one more hydrogen to the cluster, would decrease binding energy. The second energy difference plot (Fig. 2b) exhibits the odd–even oscillating behavior of anionic clusters. However, the energy difference among the anionic clusters is smaller than the neutral clusters. Unfortunately, due to lack of experimental data on these clusters in the literature, any comparison could not be done.

In order to investigate the evolution of the nearest-neighbor distance, we have calculated the Li–H average nearest-neighbor distance (ANND) (in Fig. 2c) As seen from Fig. 2c, the Li-H ANNDs generally remain stable about 1.80 when hydrogenated except sharp increase in the neutral Li_5H_2, sharp decrease in anionic Li_5H_2 clusters. The first isomer of neutral Li_5H_6 and anionic Li_5H_6 clusters show that the Li–H bond lengths in these isomers are in the acceptable range of these atom types although ANNDs of neutral Li–H clusters are generally lower than that of anionic clusters.

We should also mention that highly correlated CCSD(T)/6-311++G(2d,2p) energy calculations were also calculated on the previously optimized geometries by using B3LYP. This choice of methodology has proven very successfully in the treatment of Li clusters. However, the CCSD(T) method represents a marked departure from the B3LYP method in some cases for the single point energy analysis. As seen from Table 3, the first two B3LYP/CCSD(T) calculated energies are in reverse order for the neutral Li_5, Li_5H_4, Li_5H_5. Furthermore, both methods have given very different structures for the anionic Li_5H_1 and Li_5H_3, strictly speaking, the fourth isomer found in the B3LYP becomes the most stable isomer when calculated by CCSD(T) method. It is noticed that this fourth isomer is not seen in Fig. 1 because we have only reported the most stable three isomers. There is a remarkable agreement, with some exceptions, between our results and Yepes et al.'s results [40].

3.3. Ionization potentials and electron affinities

The ionization potential is defined as the amount of energy required to remove an electron from a neutral cluster. It is possible to define two types of ionization potentials, which are adiabatic ionization potentials (AIP), and vertical ionization potentials (VIP). AIP is the difference in zero-point vibrational energy between cationic and neutral clusters at their respective equilibrium geometries. VIP is defined as the energy difference between the ground state of neutral and cationic clusters, optimized by the geometry of the neutral clusters. The ionization potentials can be calculated as follows:

$$AIP = E(Li_5H_n)^+ \text{ optimized cation} - E(Li_5H_n)^0 \text{ optimized neutral}$$

$$VIP = E(Li_5H_n)^+ \text{ cation at optimized neutral}$$
$$- E(Li_5H_n)^0 \text{ optimized neutral}$$

Table 3
The binding energies per atom (eV/atom) for the most stable isomers of neutral and anionic clusters.

Size	Neutral				Anion		
	Symmetry	B3LYP	CCSD(T)	Refs.	Symmetry	B3LYP	CCSD(T)
Li_5	C_{2v}	0.6762	0.2858	0.78[a]	D_{3h}	0.6679	0.4488
	C_{2v}	0.6686	0.3333		C_{2v}	0.6572	0.3484
	C_2	0.6524	0.2966		C_{4v}	0.6523	0.3170
Li_5H_1	C_{2v}	1.1356	0.6707	1.05[b]	C_s	1.0860	0.7723
	C_{2v}	1.1349	0.6678		C_s	1.0774	0.8002
	C_s	1.1211	0.6147		C_1	1.0751	0.7873
	–	–	–		C_s	1.0706	0.8113
Li_5H_2	C_s	1.4621	0.9850		$D_{\infty h}$	1.4195	1.0601
	C_s	1.4139	0.9847		C_s	1.4002	0.9620
	C_1	1.4106	0.9655		C_s	1.3946	0.9934
Li_5H_3	C_{3v}	1.7375	1.2009	1.58[c]	C_{3v}	1.6485	1.2289
	C_{2v}	1.6906	1.1846		C_s	1.6329	1.2587
	C_s	1.6840	1.1732		C_{2v}	1.6299	1.2580
	–	–	–		C_{3v}	1.6215	1.2628
Li_5H_4	C_s	1.8756	1.3581		C_s	1.8349	1.3774
	C_s	1.8701	1.3584		C_{3v}	1.8172	1.3609
	C_s	1.8525	1.3400		C_s	1.8143	1.3333
Li_5H_5	C_s	2.0500	1.4932	2.05[d]	C_s	1.9649	1.5185
	C_{5h}	2.0285	1.4953		C_s	1.9566	1.5086
	C_s	2.0158	1.4727		C_{2v}	1.9549	1.5069

[a] Ref. [41].
[b] Ref. [26].
[c] Ref. [27].
[d] Ref. [28].
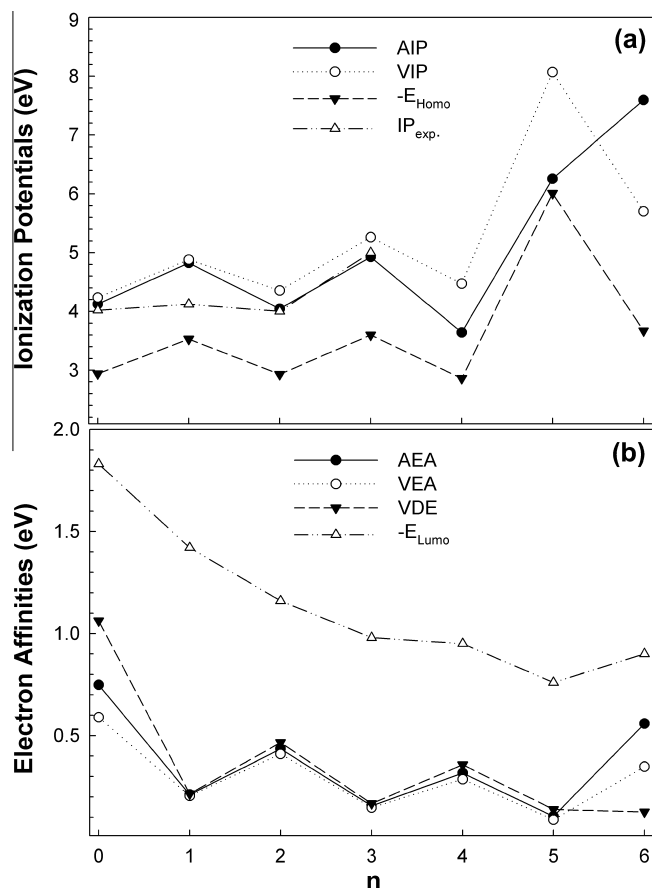
Fig. 3. For neutral Li_5H_n ($n = 0–6$) clusters (a) adiabatic ionization potentials, vertical ionization potentials, and Homo energies (eV) and (b) adiabatic electron affinities, vertical electron affinities, vertical detachment energies, and Lumo energies calculated using 6-311++G(2d,2p) basis set at B3LYP level.

For the neutral clusters; calculated AIP, VIP, and E_{Homo} are compared with experimental results in Table 1, and plotted as a function of hydrogen atom in Fig. 3.a. The AIP and VIP values of odd-numbered clusters are higher than their neighboring even-sized systems. As expected, removing an electron from the doubly occupied molecular orbital is more difficult than singly occupied molecular orbital. This can be explained through the electron-pairing effect. The electrons in doubly occupied molecular orbital have stronger effective core potentials as screening. In literature, there are experimental ionization potentials (IP_{exp}) up to the Li_5H_3 cluster and our results are in good agreement [16,18,26,29,39] with them as seen in Fig. 3a. For Li_5 cluster, the AIP of 4.12 eV agrees well with the experimental value [39] of 4.02 ± 0.1 eV. However, the AIP value of Li_5H_1 cluster (4.33 eV) is slightly larger than the available experimental value of 4.12 ± 0.1 eV obtained by Vezin et al. [29] and Bonačić-Koutecký et al. [16,18]. For Li_5H_2 cluster, with the best of our knowledge, this is the first time the calculated AIP of the most stable isomer (4.04 eV) has been reported, and it is in agreement with the experimental value [15] of 4.00 ± 0.08 eV. For, the Li_5H_3 cluster, this value has been calculated to be 4.92 eV which is also very close to the experimental value (5.00 ± 0.1 eV), found by Vezin et al. [29]. As seen from the above comparison, the AIP values presented in this work show good agreement with experimental values found in literature. As expected, due to energy compensation as a result of orbital relaxation on ionization, VIPs are higher than the AIPs, except for Li_5H_6. Because, as concluded section "Structure and geometry", the Li_5H_6 clusters is not a stable structure. The most of the Li_5H_6 cluster isomers had hydrogen molecules separated from the rest of the cluster.

The electron affinity is an amount of the energy required to add an electron to a neutral cluster to form a negative charged ion. Adiabatic electron affinity (AEA) is the energy difference between the neutral and the anionic clusters at their respective equilibrium geometries. Vertical electron affinity (VEA) is the energy difference between the ground state of the anionic and the neutral clusters at the equilibrium geometry of the neutral. Vertical detachment energy (VDE) is defined as the energy difference between the neutral cluster at the equilibrium geometry and anionic cluster at the ground state. More quantitatively, the AEA, VEA and VDE can be

Fig. 4. The figure shows a difference among the adiabatic electron affinity, vertical electron affinity, and vertical detachment energy calculated using 6-311++G(2d,2p) basis set at B3LYP level.

measured (Fig. 4). The electron affinities can be calculated as follows:

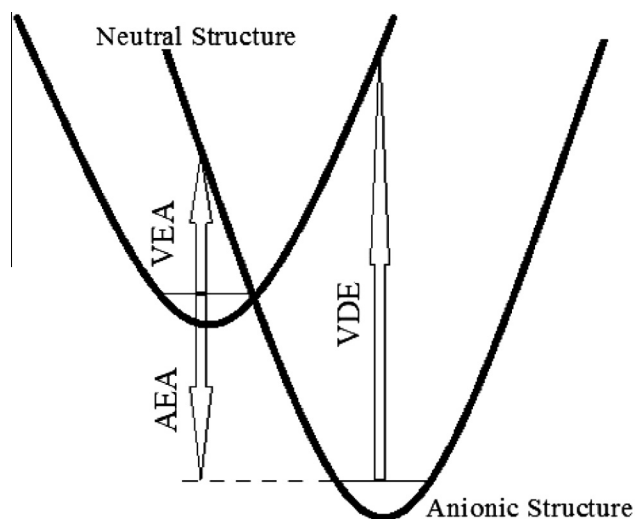$$\text{AEA} = E(\text{Li}_5\text{H}_n)^0 \text{ optimized neutral} - E(\text{Li}_5\text{H}_n)^- \text{ optimized anion}$$

$$\text{VEA} = E(\text{Li}_5\text{H}_n)^0 \text{ optimized neutral}$$
$$- E(\text{Li}_5\text{H}_n)^- \text{anion at optimized neutral}$$

$$\text{VDE} = E(\text{Li}_5\text{H}_n)^0 \text{ neutral at optimized anion}$$
$$- E(\text{Li}_5\text{H}_n)^- \text{optimized anion}$$

The electron affinities (EAs) on hydrogenated lithium clusters has been reported in detail in this study. The values and the graphs of AEA, VEA, and VDE are presented in Table 1, and in Fig. 3b, respectively, together with lowest unoccupied molecular orbital energies (E_{Lumo}). For Li_5H_2, the AEA and VDE values could not be calculated as seen in Table 1, and Fig. 3b. Because, the optimization of anionic form for neutral Li_5H_2 first isomer has given the imaginary frequency. At the other calculations, there was not any imaginary frequency. The addition of hydrogen to the Li_5 cluster decreases the electron affinity. The VEA value of Li_5H_n clusters exhibit even–odd oscillations with maximums at $n = 0, 2, 4$ and 6. The values of AEA and VDE decrease until the Li_5H_3 cluster. After that, it shows a peak at Li_5H_4. The Li_5H_3 cluster has eight valence electrons, and its electronic structure obeys to the cluster electronic shell model (CSM) [42]. According to the Koopmans' theorem [43], the electron affinity and the ionization potential of a cluster can be approximated by orbital energies for Homo and Lumo, respectively. As seen in Fig. 3, our results obey this theorem. It is clear from this figure that the calculated IP's exhibit the similar trend with the $-E_{Homo}$ values and the calculated EA's exhibit the similar trend with the $-E_{Lumo}$ values. The AEA and VDE can be measured experimentally by anion photoelectron spectroscopy. The VDE corresponds to the transition from the ground state of the anionic cluster to the identical geometry in the neutral cluster, and the values of VDE are expected to be higher than AEA values as seen in Fig. 4, where the reported values are in agreement with this expectation except for Li_5H_6 cluster (Fig. 3b).

3.4. Homo–Lumo energy, hardness, chemical potentials, softness, and vibrational frequencies

Hard structures have a large Homo–Lumo gap, and they resist changes in their electron number whereas soft structures have a small Homo–Lumo gap. Therefore, hard structures are more stable and less reactive than soft ones, especially in situations where the electron transfer is required for the reaction. The chemical potential signifies the direction of electron transfer, which flows from the high chemical potential to the lower one. A negative chemical potential is equal to the electronegativity [44]. Table 1 presents the values of hardness (η), chemical potential (μ), softness (σ), and Homo–Lumo energy gap for the neutral clusters. For the anionic clusters, only E_g is given in Table 2. According to Koopmans' approximation, frontier orbital energies are given by

$$-E_{Homo} \approx IP \text{ and } - E_{Lumo} \approx EA.$$

Therefore, further estimates of η, μ, σ, and E_g quantities are defined as:

$$\eta = (\text{VIP} - \text{AEA})/2$$

$$\mu = -(\text{VIP} + \text{AEA})/2$$

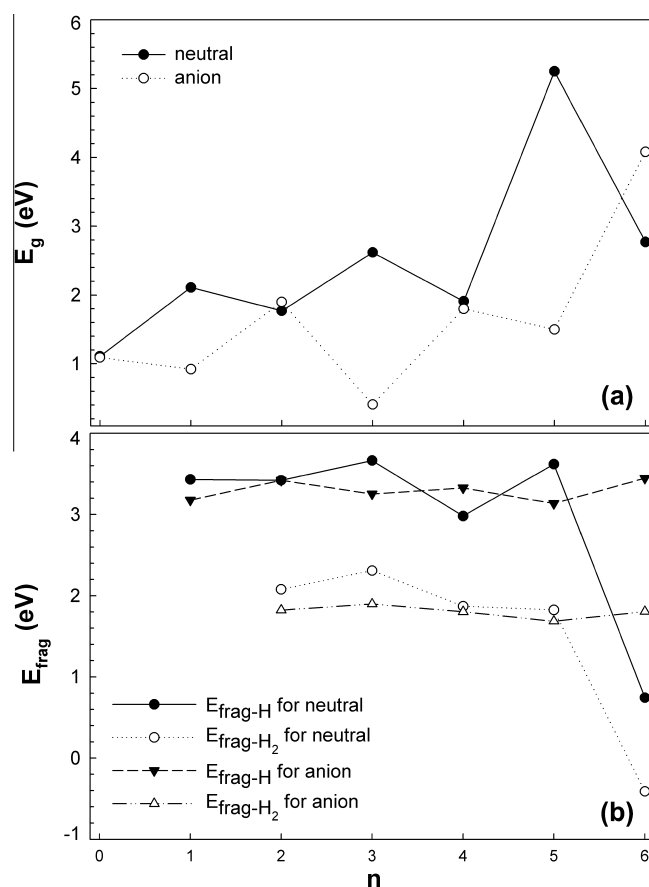$$\sigma = 1/(\text{VIP} - \text{AEA})$$

$$E_g = E_{Lumo} - E_{Homo}.$$

Fig. 5. For neutral and anionic Li_5H_n ($n = 0$–6) clusters (a) Homo–Lumo energy gap and (b) fragmentation energies of a single hydrogen atom calculated using 6-311++G(2d,2p) basis set at B3LYP level.

For Li$_5$H$_n$ (n = 0–6) clusters, the structures with odd-number hydrogen atoms, are closed shell structures so that they have higher hardness and stabilities than the others. As seen in Table 1, the E_g, η, μ and σ values show an oscillating behavior with increasing number of hydrogen. As seen from Fig. 5a, because of an extra electron, the oscillations in anionic clusters are opposite to neutral clusters E_g curve. Also, the E_g values are generally lower for anionic clusters than that of neutral ones. According to the principle of maximum hardness [45] (PMH) the larger hardness indicates the more stable cluster. Fig. 5a clearly shows that the neutral Li$_5$H$_5$ cluster is harder and anionic Li$_5$H$_5$ cluster is softer than neighboring clusters. Additionally, the neutral Li$_5$H$_5$ cluster has the highest VIP and η which are 8.07 eV and 3.98 eV, respectively (listed in Table 1). The maximum values in the results are in agreement with the binding energy per atom and second energy difference. This result is attributable to the weak chemical activity of the even-n neutral Li$_5$H$_n$ clusters with odd valence electrons. This situation is opposite for anionic clusters.

For the most stable isomers of neutral and anionic Li$_5$H$_n$ (n = 0–6) clusters, the vibrational frequencies were investigated at the B3LYP/6-311G++ (2d,2p) level of theory. As seen in Tables 1 and 2, there are no imaginary frequencies which indicate the transition state on the potential energy surface.

3.5. Fragmentation energies

The neutral and anionic Li$_5$H$_n$ (n = 1–6) clusters can dissociate into two product fragments, which are considered to be Li$_5$H$_n$ → Li$_5$H$_{n-j}$ + H$_j$ (1 ⩽ n ⩽ 6, j = 1, 2). The fragmentation energies for H and H$_2$ are calculated as:

$$E_{frag} = E(Li_5H_{n-j}) + E(H_j) - E(Li_5H_n).$$

The fragmentation energies (E_{frag}), calculated from total energies of the products, and reactants are shown in Table 4, together with fragmentation process, and they are plotted in Fig. 5b. For neutral clusters the fragmentation energies for H and H$_2$ remained stable with hydrogenation, almost up to Li$_5$H$_5$ cluster. There is not important variation in the hydrogen fragmentation energy along the series of the clusters. However, as seen in Fig. 5b, the fragmentation energy of neutral Li$_5$H$_6$ cluster increases which in turn reduces the stability. After that formation of H$_2$ begins to be observed. Accordingly, it is nearly impossible to add six hydrogen atoms on the neutral Li$_5$ cluster. This result is also supported by a decrease in the binding energy per atom of the neutral cluster curve.

For all structures, the fragmentation of H$_2$ molecules is easier than that of H. In this study, from the energetic point of view, the fragmentation of H$_2$ for neutral and anionic clusters shows to be the lower channel than that of H, and the fragmentation energy for the evaporation of an H$_2$ dimer are closed to 2 eV. This result is

good agreement with experimental results [1]. The Antoine et al. reported the fragmentation channels for (LiH)$_n$Li$_m^+$ (m = 0,1,3; n ⩽ 15) by using a reflectron mass spectrometer. They report that the fragmentation energies of LiH and H$_2$ are close and they found 2 eV. A simple Born–Haber cycle calculation shows that in the bulk, evaporation of a LiH molecule requires 2.32 eV whereas those of H$_2$ needs 1.88 eV in the same standard conditions [44]. The previous ab initio calculations on very small clusters predict energy barriers for the fragmentation of H$_2$ dimer [40]. Our results also predict these experimental and theoretical energy values as seen in Table 4.

As seen from Fig. 5b, except for the Li$_5$H$_6$, the fragmentation energy values are very close to each other. Additionally, the fragmentation energies of hydrogenated lithium structures are too high for the reversible hydrogen storage at room temperature, and at moderate pressures. It is about 3.5 eV for single hydrogen fragmentation and about 2 eV for hydrogen dimer fragmentation which must be in the range 0.2/0.6 eV/H$_2$ for the reversible hydrogen storage systems. Some groups try to decrease fragmentation energies of hydrogenated clusters by adding some extra elements [46–48].

4. Conclusions

The stochastic search method locates a large number of stationary points on a given potential energy surface. The structures obtained from calculations can be studied further at higher levels of theory. In this theoretical study, we applied search procedure for the low-lying isomers of neutral and anionic Li$_5$H$_n$ (n = 0–6) clusters by using a stochastic search method. The neutral and anionic Li$_5$H$_n$ (n = 0–6) clusters are systematically characterized, and the structural stability, binding energy, ionization potentials, electron affinities, hardness, softness, chemical potentials, Homo–Lumo energy gap, the lowest vibrational frequencies and fragmentation energies have been investigated at the B3LYP/6-311G++(2d,2p) level of theory. The neutral Li$_5$H$_5$ cluster has higher values of ionization potentials together with the largest Homo–Lumo energy gap and hardness. Thus, it is the most stable and hardest neutral cluster among the ones investigated in this study. For anionic clusters, Li$_5$H$_5$ has the lowest Homo–Lumo gap and softness. While neutral hydrogenated clusters generally prefer the three dimensional structure, most stable anionic clusters generally prefer the two dimensional structure. The average Li–H bond lengths remain constant around 1.80 Å when hydrogenated. The ionization potentials and electron affinities have been investigated in detailed for neutral clusters. In this way, it is the first time the chemical potentials, hardness, softness and fragmentation energies have been calculated for Li$_5$H$_n$ (n = 0–6) clusters. Furthermore, we also obtained information about the electronic properties of clusters which have not been reported previously for anionic clusters. The results obtained at the B3LYP/6-311G++(2d,2p) level of theory is in good agreement with available theoretical and experimental results, for neutral clusters. We have also calculated single point energies of clusters by using CCSD(T) and found that B3LYP gives both lower energies than CCSD(T). Unfortunately, there are no experimental and theoretical EA data for neutral Li$_5$H$_n$ clusters. Thus, it is hoped that our results will be confirmed by further experimental and theoretical studies. Moreover, we believe our EAs can help to interpret future photoelectron spectroscopic studies, for this cluster.

Above all it is the first time that anionic hydrogenated clusters have been reported in this study. However for the neutral clusters, the agreement in between our results and literature makes our results reliable for anionic clusters. In addition, the most stable structure of Li$_5$H$_6$ cluster has also been reported for the first time in this study and our most stable Li$_5$H$_4$ structure has lower energy than

Table 4
The fragmentation energies (E_{frag}) and process of neutral and anionic Li$_5$H$_n$ clusters.

Li$_5$H$_n^0$		Process	E_{frag} (eV)	Li$_5$H$_n^-$		Process	E_{frag} (eV)
Li$_5$H$_1$	→	Li$_5$ + H	3.43	Li$_5$H$_1^-$	→	Li$_5^-$ + H	3.18
Li$_5$H$_2$	→	Li$_5$H$_1$ + H	3.42	Li$_5$H$_2^-$	→	Li$_5$H$_1^-$ + H	3.42
	→	Li$_5$ + H$_2$	2.08		→	Li$_5^-$ + H$_2$	1.82
Li$_5$H$_3$	→	Li$_5$H$_2$ + H	3.67	Li$_5$H$_3^-$	→	Li$_5$H$_2^-$ + H	3.25
	→	Li$_5$H$_1$ + H$_2$	2.31		→	Li$_5$H$_1^-$ + H$_2$	1.90
Li$_5$H$_4$	→	Li$_5$H$_3$ + H	2.98	Li$_5$H$_4^-$	→	Li$_5$H$_3^-$ + H	3.33
	→	Li$_5$H$_2$ + H$_2$	1.87		→	Li$_5$H$_2^-$ + H$_2$	1.80
Li$_5$H$_5$	→	Li$_5$H$_4$ + H	3.62	Li$_5$H$_5^-$	→	Li$_5$H$_4^-$ + H	3.13
	→	Li$_5$H$_3$ + H$_2$	1.82		→	Li$_5$H$_3^-$ + H$_2$	1.69
Li$_5$H$_6$	→	Li$_5$H$_5$ + H	0.74	Li$_5$H$_6^-$	→	Li$_5$H$_5^-$ + H	3.45
	→	Li$_5$H$_4$ + H$_2$	−0.41		→	Li$_5$H$_4^-$ + H$_2$	1.81

found in literature [28]. The fragmentation energies of hydroge-nated Li_6 clusters are too high for the reversible hydrogen storage systems. Unlike other cluster, it has been observed that formation of hydrogen molecules took place for some Li_5H_6 isomers.

Acknowledgement

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