Journal of Cluster Science (2021) 32:507–516
https://doi.org/10.1007/s10876-020-01810-x

ORIGINAL PAPER

A Density Functional Investigation on Li_nI (n = 1–8) Clusters

Arslan Ünal[1] · **Ömer Ayın**[2]

Received: 17 December 2019 / Published online: 12 May 2020

Abstract
A density functional theory (DFT) investigation on isomeric structures of lithium-iodide clusters, and stabilities as well as electronic structure features of global equilibrium structures are reported. The relative energies and population values of structural isomers for Li_nI (n = 1–8) clusters are obtained at the B3LYP/Lanl2dz and B3LYP/6-311G(d,p) theory levels. The iodine atom prefers the apex position in the most stable structures within the coordination number two except Li_6I and Li_8I clusters. The binding energies, dissociation energies, second-order energy differences, HOMO–LUMO gaps, ionization and elimination energies of global minimum structures are calculated in order to get beneficial information about the stability and electronic properties of Li_nI (n = 1–8) clusters. The results of relative energies affirm an odd–even oscillation that Li_nI (n = 1, 3, 5, 7) clusters are more stable than neighboring clusters. The iodine atom also enhances the stability order of pure lithium clusters while the cluster size grows up this stability decreases, and lithium-iodide clusters become more reactive. The ionization and elimination energy results also show that Li_nI (n = 1–8) clusters can be classified as superalkalies due to owing lower ionization energies than Li atom and the interaction between pure lithium clusters and iodine atom can be realized as electrostatic bonding.

Keywords DFT · Cluster · Stability · Lithium · Iodine

Introduction

Small one halogen atom-doped lithium clusters, Li_nX ($n > 1$ and X = Cl, Br, F or I), are the subject of experimental and theoretical cluster physic studies in the last decade due to the possibility of their practical industrial and scientific applications as in lithium-based batteries, electrocatalysis, cooling systems, supersalts, non-linear optical sensors, high pressure electrides, desiccants and nanotubes [1–10]. It is well-known that the addition of an impurity to pure-lithium clusters can lead to fundamental changes in their structural geometries, stabilities, energetics, electronic properties, magnetic properties, polarizabilities, bonding natures and superatomic features [1–22]. In general, halogens are used an impurity-doped atom, for instance; Li_nCl [2, 5], Li_nBr [3, 14], Li_nF [4, 8, 15, 16] and Li_nI [9, 17, 18] clusters. These clusters are called hypermetalated (hypervalent or hyperlithiated) molecules, are thermodynamically stable due to a mix of covalent bonding between lithium atoms in lithium cage, and electrostatic bonding between anionic iodine atom and cationic lithium cage [15, 23]. In addition, a halogen atom-doped lithium clusters [2–5, 8, 15, 17] have lower ionization energies than lithium atom (5.39 eV), so these structures are called superalkali [24–26] and these clusters can have significant non-linear optical properties [4, 23, 27].

Nowadays, computational methodologies especially density functional theory (DFT) have played a crucial role in the understanding of modeling, physical and chemical properties of superalkali clusters, studying its different components and their interactions [2, 3, 7–9, 11, 13, 17, 18, 27, 28]. Regarding the one iodine-doped lithium clusters, a few systematic studies are reported. Veličković and coworkers have experimentally investigated the ionization energies of Li_nI (n = 2, 3) molecules by surface ionization mass spectrometry [29]. Đustebek et al. have calculated the equilibrium geometries of ground-state forms for neutral and positive charged Li_nI (n = 2–5) clusters and they have

---

✉ Arslan Ünal
arslan.unal@bilecik.edu.tr

[1] Department of Physics, Bilecik Şeyh Edebali University, 11210 Bilecik, Turkey

[2] Institute of Science and Technology, Bilecik Şeyh Edebali University, 11210 Bilecik, Turkey

also analyzed experimental and theoretical ionization energies of Li_nI (n = 2–6) [9, 18]. A theoretical study on geometry and stability of small lithium-iodide Li_nI (n = 2–6) clusters have researched by Milonavić and Jerosimić [17]. Botana et al. have examined the stability of crystalline Li_nI (n = 2–5) compound at high pressure [7]. To expand our understanding of the physical and chemical features of Li_nI (n = 1–8) clusters, we have performed a systematic series of calculations to predict the isomeric geometries, stabilities and electronic features using DFT framework.

Computational Details

The potential energy surfaces of Li_nI (n = 1–8) clusters were explored using the molecular cluster capabilities of the ASCEC program [30] which contain an adapted version of the Simulated Annealing optimization procedure. The annealing algorithm [31–33] was used to generate candidate structures after random walks of Hartree–Fock (HF) theory level in conjunction with the effective core potential on the basis set of Los Alamos National Laboratory 2 Double-Zeta (LANL2DZ) for lithium and iodine atoms. The hybrid Becke's three-parameter exchange functional accompanied by the Lee–Yang–Parr correlation functional (B3LYP) with LANL2DZ basis set was used to optimize and characterize the candidate isomers without any constraint by using analytical gradient method afforded by ASCEC. All of the isomers were subjected to geometry optimization procedure with following harmonic vibrational mode calculation, the aim of which was to found the presence of imaginary wavenumbers. The lack of imaginary frequencies in the vibrational analysis shows that the obtained structure corresponds to the local minima in potential energy surface of related isomer. Further refinement and characterization calculations of the located minima were conducted by means of B3LYP theory level in conjunction with all-electron 6-311G(d,p) basis set. The DFT calculations of lithium-iodide clusters were carried out using Gaussian 09 suite of programs [34]. Isomer populations were estimated by standard Boltzmann distribution analysis [35, 36]. The structural parameters of isomers in neutral or charged lithium clusters were obtained from previous studies [2, 11, 37–39] and were also tested using B3LYP/Lanl2dz and B3LYP/6-311G(d,p) levels of theory.

In order to testing the reliability of B3LYP/Lanl2dz and B3LYP/6-311G(d,p) theory levels, some electronic properties of Li–I and Li–Li dimers were initially calculated. The Li–I dimer equilibrium bond length, vibrational wavenumbers, dipole moment and ionization energy were calculated as 2.471 Å, 468 cm^{-1}, 7.66 Debye and 8.53 eV for B3LYP/Lanl2dz and 2.411 Å, 499 cm^{-1}, 7.35 Debye and 8.65 eV for B3LYP/6-311G(d,p), which are close the experimental data of Li–I (2.392 Å, 498 cm^{-1}, 7.43 Debye and 8.44 ± 0.03 eV or 8.6 ± 0.3 eV) [40–43]. The experimental bond length, vibrational wavenumbers and ionization energy for Li_2 molecule are 2.673 Å, 351 cm^{-1}, and 5.1127 eV [43–45]. The calculated values, 2.703 Å, 343 cm^{-1} and 5.299 eV for B3LYP/Lanl2dz and 2.705 Å, 343 cm^{-1} and 5.241 eV for B3LYP/6-311G(d,p) are also in good agreement with the experimental values. As a result, the levels of theory used in calculations are reliable to describe electronic structure properties and chemical stability of the Li_nI (n = 1–8) clusters when considering the performance on our previous one halogen atom doped lithium cluster studies [3, 8]. By comparing the computed values with the experimental data of Li–I and Li–Li dimers, it is found that the present results based on the B3LYP/6-311G(d,p) method are more dependable than B3LYP/Lanl2dz method.

Results and Discussion

Geometrical Structures

The equilibrium structures of optimized neutral stable isomers of Li_nI (n = 2–8) clusters were obtained by using B3LYP level of theory with Lanl2dz basis set, and the illustrations of the obtained isomers are set out in Fig. 1. Each isomer structures given in Fig. 1 hereafter are labeled *nm*, in which *n* is the number of lithium atoms, *a* represent the lowest energetically structure and *b*–*f* are denoted the stability order of isomers for each cluster. The symmetry, spin multiplicity, total electronic energy with zero point energy, Gibbs free energy, relative energy, HOMO–LUMO gap of lithium-iodide clusters and the population percentage for isomers of each cluster were calculated based on the optimized geometries by using B3LYP level of theory with Lanl2dz and 6-311G(d,p) basis sets are tabulated in Tables 1 and 2. As can be seen from Tables 1 and 2, whole examined isomeric structures have singlet or doublet multiplicity.

The most stable isomer of Li_2I cluster (2a) with 100% population rate, has an isosceles triangle structure in C_{2v} group symmetry, where the iodine atom is at the apex position. The average bond length of Li–I is calculated at 2.599 Å by B3LYP/6-311G(d,p) (I) and at 2.679 Å B3LYP/Lanl2dz (II) theory level. The triangular co-structure having the same symmetry is already reported for the Li_2Cl, Li_2Br, Li_2F and Li_2I molecules [2, 3, 8, 9, 17, 46]. The second low-lying isomer (2b) has a linear structure through the iodine atom located externally, and is less stable by 0.517 eV (I and II). The population analysis results show

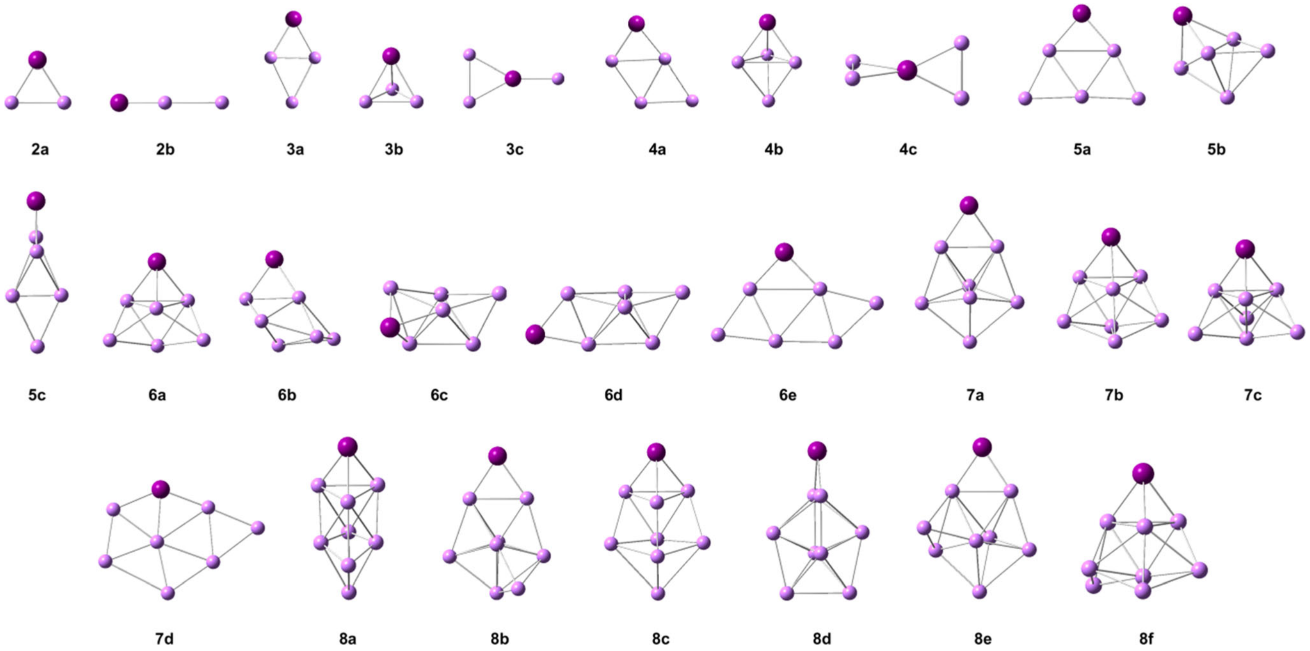

Fig. 1 The stable isomers of Li_nI (n = 2–8) clusters; iodine atoms are in dark purple

Table 1 The isomer, symmetry, spin multiplicity (multi), total energy with zero point energy (E_T), relative energy (ΔE), HOMO–LUMO gap (gapHL), Gibbs free energy (ΔG), relative Gibbs free energy (δΔG) and the population value (N_i) for the stable isomeric structures of lithium-iodide clusters (I)

Clusters	Isomers	Sym	Multi	E_T (a.u)	ΔE (eV)	gapHL (eV)	ΔG (a.u.)	δΔG (eV)	N_i (%)
Li I	1a	$C_{\infty v}$	1	− 18.980	0.000	4.036	− 19.003	0.000	100.00
Li_2I	2a	C_{2v}	2	− 26.502	0.000	1.954	− 26.530	0.000	100.00
	2b	$C_{\infty v}$	2	− 26.483	0.517	2.337	− 26.513	0.463	0.00
Li_3I	3a	C_{2v}	1	− 34.041	0.000	2.476	− 34.071	0.000	100.00
	3b	C_{3v}	1	− 34.020	0.571	1.966	− 34.051	0.544	0.00
	3c	C_{2v}	1	− 33.999	1.143	0.873	− 34.032	1.061	0.00
Li_4I	4a	C_s	2	− 41.556	0.000	1.674	− 41.590	0.000	99.50
	4b	C_1	2	− 41.550	0.163	1.253	− 41.585	0.136	0.50
	4c	C_s	2	− 41.514	1.143	1.039	− 41.553	1.007	0.00
Li_5I	5a	C_{2v}	1	-49.087	0.000	2.178	− 49.123	0.000	100.00
	5b	C_s	1	− 49.080	0.190	1.466	− 49.115	0.218	0.00
	5c	C_{2v}	1	− 49.074	0.354	1.639	− 49.111	0.327	0.00
Li_6I	6a	C_s	2	− 56.609	0.000	1.381	− 56.646	0.000	98.33
	6b	C_1	2	− 56.602	0.190	1.395	− 56.641	0.136	0.49
	6c	C_1	2	− 56.602	0.190	1.414	− 56.641	0.136	0.49
	6d	C_s	2	− 56.602	0.190	1.405	− 56.641	0.136	0.49
	6e	C_s	2	− 56.598	0.299	1.415	− 56.640	0.163	0.20
Li_7I	7a	C_{2v}	1	− 64.143	0.000	1.584	− 64.182	0.000	73.15
	7b	C_s	1	− 64.142	0.027	1.647	− 64.181	0.027	25.75
	7c	C_{3v}	1	− 64.140	0.082	2.037	− 64.178	0.109	1.10
	7d	C_1	1	− 64.124	0.517	1.572	− 64.169	0.354	0.00
Li_8I	8a	C_s	2	− 71.667	0.000	1.320	− 71.710	0.000	65.06
	8b	C_1	2	− 71.666	0.027	1.332	− 71.709	0.027	22.90
	8c	C_s	2	− 71.665	0.054	1.319	− 71.708	0.054	8.07
	8d	C_{2v}	2	− 71.664	0.082	1.269	− 71.707	0.081	2.86
	8e	C_1	2	− 71.663	0.109	1.294	− 71.706	0.109	0.98
	8f	C_1	2	− 71.662	0.136	1.256	− 71.704	0.163	0.13

Table 2 The isomer, symmetry, spin multiplicity (multi), total energy with zero point energy (E_T), relative energy (ΔE), HOMO–LUMO gap (gapHL), Gibbs free energy (ΔG), relative Gibbs free energy (δΔG) and the population value (N_i) for the stable isomeric structures of lithium-iodide clusters (II)

Clusters	Isomers	Sym	Multi	E_T (a.u)	ΔE (eV)	gapHL (eV)	ΔG (a.u.)	δΔG (eV)	N_i (%)
Li I	1a	$C_{\propto v}$	1	− 6927.134	0.000	4.300	− 6927.157	0.000	100.00
Li_2I	2a	C_{2v}	2	− 6934.657	0.000	1.961	− 6934.685	0.000	100.00
	2b	$C_{\propto v}$	2	− 6934.636	0.571	2.335	− 6934.665	0.544	0.00
Li_3I	3a	C_{2v}	1	− 6942.196	0.000	2.483	− 6942.226	0.000	100.00
	3b	C_{3v}	1	− 6942.174	0.599	1.913	− 6942.203	0.626	0.00
	3c	C_{2v}	1*	− 6942.150	1.253	0.847	− 6942.181	1.211	0.00
Li_4I	4a	C_s	2	− 6949.711	0.000	1.665	− 6949.745	0.000	99.83
	4b	C_1	2	− 6949.706	0.136	1.303	− 6949.739	0.163	0.17
	4c	C_s	2*	− 6949.665	1.264	1.172	− 6949.698	1.285	0.00
Li_5I	5a	C_{2v}	1	− 6957.242	0.000	2.179	− 6957.278	0.000	99.83
	5b	C_s	1	− 6957.237	0.136	1.466	− 6957.272	0.163	0.17
	5c	C_{2v}	1	− 6957.231	0.299	1.646	− 6957.267	0.299	0.00
Li_6I	6a	C_s	2	− 6964.767	0.000	1.399	− 6964.804	0.000	98.47
	6b	C_1	2	− 6964.760	0.190	1.401	− 6964.799	0.136	0.49
	6c	C_1	2	− 6964.760	0.190	1.431	− 6964.799	0.136	0.49
	6d	C_s	2	− 6964.760	0.190	1.409	− 6964.799	0.136	0.49
	6e	C_s	2	− 6964.755	0.327	1.402	− 6964.797	0.190	0.06
Li_7I	7a	C_{2v}	1	− 6972.303	0.000	1.592	− 6972.341	0.000	73.47
	7b	C_s	1	− 6972.301	0.054	1.638	− 6972.340	0.027	25.47
	7c	C_{3v}	1	− 6972.299	0.109	2.013	− 6972.337	0.109	1.06
	7d	C_1	1	− 6972.282	0.571	1.547	− 6972.326	0.408	0.00
Li_8I	8a	C_s	2	− 6979.829	0.000	1.333	− 6979.871	0.000	65.92
	8b	C_1	2	− 6979.826	0.082	1.348	− 6979.870	0.027	23.04
	8c	C_s	2	− 6979.826	0.082	1.324	− 6979.869	0.054	7.92
	8d	C_{2v}	2	− 6979.826	0.082	1.278	− 6979.868	0.082	2.75
	8e	C_1	2	− 6979.823	0.163	1.310	− 6979.866	0.136	0.33
	8f	C_1	2	− 6979.822	0.190	1.281	− 6979.864	0.190	0.04

Star (*) is for the n-order transition state

that the 2b structure should be very difficult to occur spontaneously in Li_2I cluster. The lowest energetically isomer structure (3a) of Li_3I cluster has a planar rhombus structure having the iodine atom is at the top position within C_{2v} group symmetry. The average bond length of Li–I is obtained at 2.607 Å (I) and 2.684 Å (II), and this isomeric structure with 100% population value is also obtained as a ground-state for Li_3X (X = Cl, Br, F and I) clusters [2, 3, 8, 17, 18]. The second low-lying isomer (3b) turns into a tetrahedral structure and is less stable by 0.599 eV (I) or 0.571 eV (II) than 3a isomer. The last low-lying isomer (3c) for this cluster turned out to be a planar structure in C_{2v} group symmetry, and lies about 1.253 eV (I) and 1.143 eV (II) above 3a isomer. However, 3c isomer is found first-order transition states on the potential energy surface (PES) of Li_3I cluster in the computation at B3LYP/6-311G(d,p) level of theory. In agreement with previous reports of one halogen atom doped lithium clusters [2, 3, 8, 17], a capped planar rhombus structure 4a in C_s symmetry is predicted to be the global minimum for Li_4I cluster along with 99.83% (I) and 99.50% (II) population value, and the Li–I average bond length is found 2.605 Å (I) and 2.672 Å (II). The second stable isomer 4b in C_1 structure and third stable isomer 4c in C_s structure are higher than isomer 4a by 0.136 eV (I), 0.163 eV (II) and 1.264 eV (I), 1.143 eV (II). The calculated population value of 4b structure (0.17% for I and 0.50% for II) showed that it may be found in a trace amount in Li_4F cluster. However, the similar state may not be observed about the formation of 4c structure. This structure is also observed as third-order transition state in the frequency calculation at B3LYP/6-311G(d,p) theory level. One halogen atom doped hexaatomic cluster in neutral states have been investigated in previous studies [2, 3, 8, 17, 18]. In this studies, Li_5X (X = Cl, Br, F and I) clusters have two or four stable isomers. In the most stable isomers, the halogen atom is at the apex position having 2D geometry conformation excluding Li_5F. Our results confirmed that lowest-energy isomer (5a) having a trigonal prism with the iodine atom at the top position is turned out as the ground state of Li_5I cluster among the other two isomers (5b and 5c). The predicted population value of 5a structure indicated that 5b and 5c isomeric structures may not be existed in Li_5I cluster. The average Li–I bond length is also calculated as 2.605 Å (I) and 2.665 Å (II). As for the Li_6I cluster, five isomers were obtained. The ground state of Li_6I cluster is 6a isomer with pyramidal geometric structure. The iodine atom is at the apex position in C_s symmetry as in the other Li_nX (X = Cl, Br, F) clusters [2, 3, 8, 17] and the average bond length of Li–I is 2.748 Å (I) and 2.834 Å (II). The next lowest energy isomers are 6b–6d structures, the iodine atom acts as an anionic atom with cationic boat form of Li_6^+ cluster [37, 39], which are only 0.19 eV (I and II) higher in energy. The last low-lying isomer, 6e, has a planar structure with the iodine atom is externally bounded in C_s symmetry and is 0.327 eV (I) or 0.299 eV (II) less stable than 6a structure. The population analysis confirm that 6a structure which has 98% value, is the lowest-energetically structure of Li_6I cluster. However, the other isomers may be found with very low probability in Li_6I cluster. The Li_7I cluster has the pyramidal prism in C_{2v} group symmetry (7a) as a lowest energy structure with the iodine atom at the top position that was obtained through replacing lithium atom by iodine atom on the ground state geometry of pyramidal structure Li_8 cluster [37, 47, 48]. The average bond length of Li–I is 2.627 Å (I) and 2.693 Å (II). The second and third low-lying isomers, 7b in C_s symmetry and 7c in C_{3v} symmetry, have pyramidal geometric structure with the iodine atom at the apex, are less stable by 0.054 eV (I), 0.027 eV (II) and 0.109 eV (I), 0.082 eV (II), respectively. The 7b isomer of Li_7I cluster obtained with the stochastic procedure and B3LYP/aug-cc-pVTZ (PP) method were also reported as the lowest-lying structural form by Milovanovic et al. [17]. The fourth low-lying isomer (7d) has a planar structure and is higher in energy than the lowest energy structure by 0.571 eV (I) or 0.517 eV (II). The calculated population value of 7a isomer shows that this geometric form is the ground state of Li_7I cluster and 7b geometric structure may be found in 1/4 ratio in this cluster. A doping of halogen atom to the Li_9 cluster results in an antiprism as the lowest energy structure for Li_8X (X = Cl, Br, F, I) clusters [2, 3, 8, 17]. The most stable isomer has a 3D structure with the iodine atom at apex in C_s symmetry, and the average bond length of Li–I is 2.748 Å (I) or 2.831 Å (II). The other local minima isomers, 8b-8f, have pyramidal geometric structures where the iodine atom is always at the top. The other isomers are less stable than the global minimum structure 8a in the range of 0.082 eV to 0.190 eV (I) and 0.027 eV to 0.136 eV (II). The population analysis value for 8a and 8b isomers of Li_8I cluster are 65% and 23% indicates that 8a is the most stable structure and the other isomers (excluding 8b isomer) have a very low probability of existence in Li_8I cluster. The most stable structure of Li_8I cluster were also obtained with the stochastic procedure and B3LYP/aug-cc-pVTZ (PP) method by Milovanovic et al. [17].

The average bond length of Li–I of most stable isomers for all clusters is given in Fig. 2. The Li–I average bond lengths are similar in lithium-iodide clusters except for Li_6I and Li_8I due to the coordination of the iodine atom. The iodine atom is 3-coordinated with lithium atoms in Li_6I and Li_8I whereas the coordination number is two for the rest of clusters. For this reason, the average bond length of Li–I is increasing through the coordination number of iodine atom.

Stabilities and Electronic Properties

The relative stabilities of Li_nI (n = 1–8) clusters can be examined on the basis of the binding energy per atom (E_b), dissociation energy (ΔE), second-order energy difference ($\Delta_2 E$) as well as HOMO–LUMO gap (*gapHL*) considering the global minimum structures.

The binding energy per atom calculations allow us to discuss the energetic and relative stability of the clusters as a function of the number of lithium atoms. The E_b for doped clusters is defined as $E_b[Li_nI]=(nE[Li]+E[I]-E[Li_nI])/(n+1)$, where n is the total number of lithium atom and E is the total molecular energy including the zero-point energy for the cluster, lithium and dopant atoms. The size dependence of E_b is shown as a function of the number of lithium atoms for Li_n and Li_nI clusters at Fig. 3. As seen from this figure, there is a quite clear distinction in the behavior of E_b for the ground state of pure lithium clusters

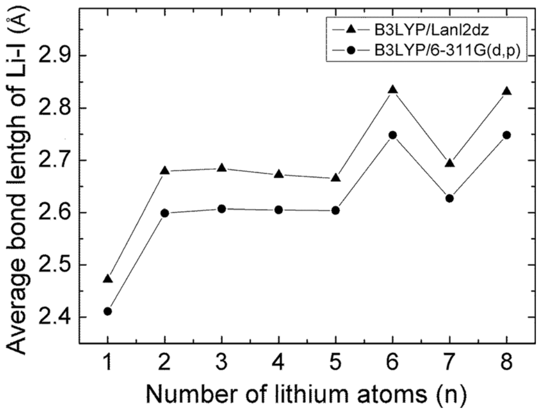

Fig. 2 The Li–I average bond length for Li_nI (n = 1–8) clusters

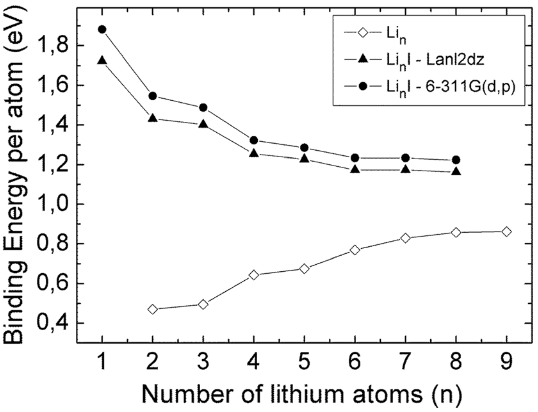

Fig. 3 The binding energy per atom of $\mathrm{Li}_n\mathrm{I}$ (n = 1–8) and Li_n (n = 2–9) clusters

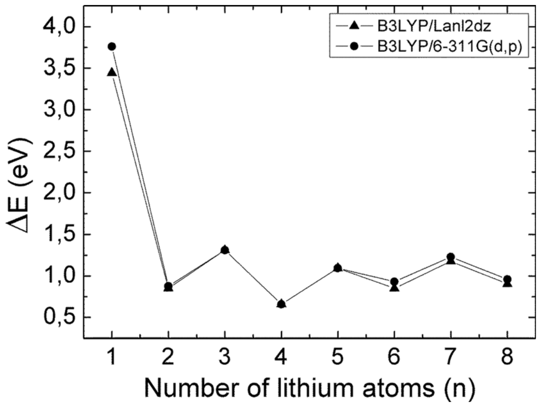

Fig. 4 The dissociation energy for $\mathrm{Li}_n\mathrm{I}$ (n = 1–8) clusters

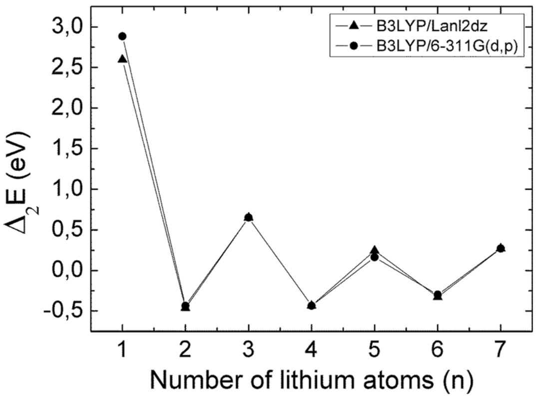

Fig. 5 The second-order energy difference variation of $\mathrm{Li}_n\mathrm{I}$ (n = 1–7) clusters

and lithium-iodide clusters. The dopant in lithium-iodide clusters leads to enhancing the stability of the host clusters because of having significantly higher binding energies per atom than pure lithium clusters. One also noticed that when the cluster size grows up, the E_b of host clusters increases smoothly up to n = 7 and then increases slowly [3, 17]. However, E_b of the lowest-energy lithium-iodide clusters decreased as the size n increased, but after n = 6 the decrease became smaller and stable. This decrease trend in the E_b explores that although iodine impurity doping can enhance the stabilities of lithium clusters, the effect is becoming weaker as successive Li atoms are added to a I atom. This is because that the I atom prefers sitting at a surface site to the center of the structures of $\mathrm{Li}_n\mathrm{I}$ clusters as shown in Fig. 1. The similar feature of binding energy curves is also observed in the small pure lithium clusters doped with one bromine [3] or one iodine atom [17].

In order to determine better outcomes for the relative stabilities of the clusters, we were calculated the dissociation energy, $\Delta E[\mathrm{Li}_n\mathrm{I}]= E[\mathrm{Li}_{n-1}\mathrm{I}]+ E[\mathrm{Li}] - E[\mathrm{Li}_n\mathrm{I}]$ and the second-order energy difference, $\Delta_2 E[\mathrm{Li}_n\mathrm{I}]= E[\mathrm{Li}_{n+1}\mathrm{I}]+ E[\mathrm{Li}_{n-1}I] - 2E[\mathrm{Li}_n\mathrm{I}]$. Here, $E[X]$ is the total energy of the X cluster with n lithium atoms. In general, a maximum signal in the dissociation energy and a correspondent maximum signal in the second-order energy difference prove out the stability of the cluster. The dissociation energy (ΔE) and second-order energy difference ($\Delta_2 E$) of $\mathrm{Li}_n\mathrm{I}$ (n = 1–8) clusters is plotted as function of the number of lithium atoms in Fig. 4 and Fig. 5. The peaks are correspond to the higher stability to neighboring clusters. From both figures, the electron pairing effect and odd–even oscillation pattern are clearly observed in the studied range. From the observed oscillation, LiI, $\mathrm{Li}_3\mathrm{I}$, $\mathrm{Li}_5\mathrm{I}$ and $\mathrm{Li}_7\mathrm{I}$ clusters are more stable than $\mathrm{Li}_2\mathrm{I}$, $\mathrm{Li}_4\mathrm{I}$, $\mathrm{Li}_6\mathrm{I}$ and $\mathrm{Li}_8\mathrm{I}$ clusters. Thus, closed shell clusters (low-spin multiplicity) are more stable than neighboring open shell clusters (high-spin multiplicity). The $\mathrm{Li}_n\mathrm{I}$ (n = 2–6) clusters are also confirmed to be thermodynamically stable toward dissociation [9, 17, 18].

The energy difference between the HOMO and LUMO molecular orbitals is referred to as energy gap, which is an important parameter that can determine the chemical stability of clusters [3, 49]. High chemical stable clusters have a large HOMO–LUMO gap, and low chemical stable clusters have a small HOMO–LUMO gap. The HOMO–LUMO gaps are given for the ground state structures of $\mathrm{Li}_n\mathrm{I}$ (n = 1–8) and Li_n (n = 2–9) clusters in Fig. 6. The higher chemical stability of Li_n (n = 2–9) clusters appears at even-numbered clusters and the highest peaks of Li_2 and Li_8 clusters characterize the magic numbers [2, 3]. For the one iodine atom doped clusters, the results exhibit odd–even oscillations indicating that the even-numbered clusters are relatively higher chemical stability than the neighboring odd-numbered clusters. The reason of these oscillation patterns is due to the closed shell clusters are generally more stable than open shell clusters. This pattern is also in agreement with the result of second-order energy differences and the dissociation energy.

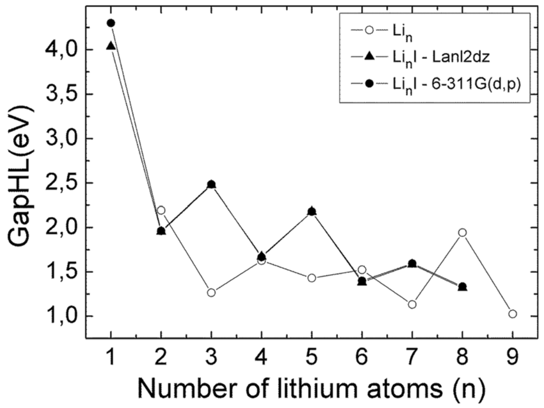

Fig. 6 The HOMO–LUMO gap of Li_nI (n = 1–8) and Li_n (n = 2–9) clusters

In order to getting more information about the stability of Li_nI clusters, ionization energies (IE), elimination energies (EEs) of I atom, LiI molecule and I^- anion were investigated. The IEs of Li_n and Li_nI clusters were computed as the difference in total electronic energy with zero point energy of neutral and cationic global local minimum structures. The EEs of I, LiI and I^- in Li_nI clusters were also computed as

$$EE[\mathrm{I}] = E[\mathrm{Li}_n] + E[\mathrm{I}] - E[\mathrm{Li}_n\mathrm{I}],\ EE[\mathrm{LiI}] = E[\mathrm{Li}_{n-1}] + E[\mathrm{LiI}] - E[\mathrm{Li}_n\mathrm{I}] \text{ and } EE[\mathrm{I}^-] = E\left[\mathrm{Li}_n^+\right] + E[\mathrm{I}^-] - E[\mathrm{Li}_n\mathrm{I}]$$

where $E[X]$ represents the total electronic energy of respective species including zero point energy correction. The IEs of pure lithium clusters and lithium-iodide clusters and EEs of lithium-iodide clusters were calculated by means of B3LYP/Lanl2dz (I) and B3LYP/6-311G(d,p) (II) theory levels are listed in Tables 3 and 4, respectively. The neutral and cationic global minimum structures of Li_nI (n = 2–8) clusters are also given in Fig. 7.

The IEs of one iodine atom doped lithium clusters and pure lithium clusters are in very good agreement with the corresponding experimental data [9, 17, 18, 37, 50]. As can be seen from Table 3 and Table 4, IE values of Li_n and Li_nI clusters are also lower than IE value of Li atom (5.392 eV) [25, 51]. Therefore, both clusters can be classified as superalkalies due to owing lower ionization energies than Li atom.

The EE results showed that Li_nI clusters are stable against dissociation of I atom, LiI molecule and I^- anion owing to having positive values. The positive values of EE[I] and EE[I^-] eliminations are about four times and about six times greater than the value of EE[LiI] further suggest that Li_nI (n = 2–8) clusters can be realized by the electrostatic interaction of Li_n clusters with I atom or preferably $Li_n^+ - I^-$ species.

Atomic charges of the most stable isomers for $Li_nI^{(0,+1)}$ (n = 2–8) clusters were analyzed by natural bond orbital (NBO) method at the B3LYP/6-311G(d,p) level. Tables 5 and 6 present the natural bond orbital (NBO) charges of ground-state Li_nI (n = 2–8) clusters and ground-state Li_nI^+ (n = 2–8). The atom numeration to identify Li atoms is shown in Fig. 7. As shown in Tables 5 and 6, it can be clearly seen that the iodine atom in neutral lithium-iodide clusters and in cationic lithium-iodide clusters possesses the negative charge, which are in the range of − 0.69e to − 0.57e and − 0.82e to − 0.53e, respectively. Except Li_6I and Li_8I clusters where the iodide atom has coordination number three with the inner (nearest to the central of I) lithium atoms, the charge of iodine atom in $Li_nI^{(0,+1)}$ (n = 2–8) clusters has a small decrease trend with the increasing of cluster size. Similar situation was observed by Ivanic et al. for Li_nX (n = 3 and 5; X = F or Cl) clusters

Table 3 Ionization energies (IEs) and elimination energies (EEs) of the lowest structures of lithium-iodide clusters (I)

Isomers	IE (eV)		Isomers	IE (eV)		EE (eV)		
	Calculated	Experimental		Calculated	Experimental[d]	I	LiI	I^-
Li	5.601	5.392[a]	Li I	8.525	8.440, 8.600	3.445	0.000	6.067
Li_2	5.252	5.140[b], 5.113[a]	Li_2I	4.652	4.690	3.380	0.849	5.700
Li_3	4.214	4.350[c], 4.080[a]	Li_3I	5.187	5.140	4.161	1.247	5.480
Li_4	4.539	4.700[a], 4.310[b]	Li_4I	4.434	4.860	3.746	1.374	5.427
Li_5	4.128	4.020[a]	Li_5I	4.654	4.620	4.050	1.395	5.347
Li_6	4.233	4.200[a]	Li_6I	4.249	4.960	3.678	1.454	5.158
Li_7	3.955	3.940[a]	Li_7I	4.512	–	3.680	1.408	4.913
Li_8	4.173	4.160[a]	Li_8I	4.191	–	3.536	1.139	5.006

[a] Ref. [37]
[b] Ref. [50]
[c] Ref. [14]
[d] Ref. [17]

Table 4 Ionization energies (IEs) and elimination energies (EEs) of the lowest structures of lithium-iodide clusters (II)

Isomers	IE (eV)		Isomers	IE (eV)		EE (eV)		
	Calculated	Experimental		Calculated	Experimental[d]	I	LiI	I^-
Li	5.616	5.392[a]	Li I	8.652	8.440, 8.600	3.741	0.000	8.820
Li_2	5.241	5.140[b], 5.113[a]	Li_2I	4.621	4.690	3.730	0.872	8.435
Li_3	4.214	4.350[c], 4.080[a]	Li_3I	5.170	5.140	4.522	1.293	8.200
Li_4	4.539	4.700[a], 4.310[b]	Li_4I	4.294	4.860	4.105	1.422	8.107
Li_5	4.130	4.020[a]	Li_5I	4.510	4.620	4.392	1.453	7.986
Li_6	4.245	4.200[a]	Li_6I	4.081	4.960	4.120	1.558	7.828
Li_7	3.957	3.940[a]	Li_7I	4.461	–	4.167	1.582	7.588
Li_8	4.166	4.160[a]	Li_8I	4.135	–	4.083	1.377	7.713

[a] Ref. [37]

[b] Ref. [50]

[c] Ref. [14]

[d] Ref. [17]

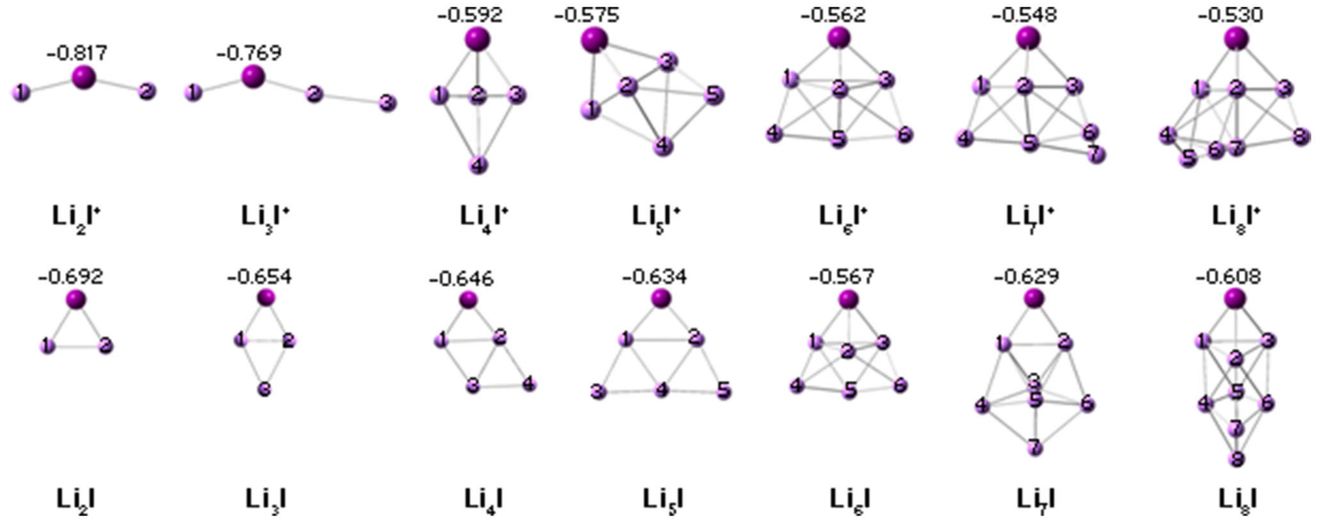

Fig. 7 The ground-state structures of Li_nI (n = 2–8) and Li_nI^+ (n = 2–8) clusters; iodine atoms are in dark purple and lithium atoms are numbered

Table 5 Natural bond orbital (NBO) charge of ground-state Li_nI (n = 2–8) clusters

Cluster	I	Li-1	Li-2	Li-3	Li-4	Li-5	Li-6	Li-7	Li-8
Li_2I	− 0.692	**0.346**	**0.346**						
Li_3I	− 0.654	**0.291**	**0.291**	0.072					
Li_4I	− 0.646	**0.377**	**0.099**	0.030	0.141				
Li_5I	− 0.634	**0.218**	**0.218**	0.178	− 0.159	0.178			
Li_6I	− 0.567	**0.216**	**− 0.248**	**0.216**	0.331	− 0.279	0.331		
Li_7I	− 0.629	**0.357**	**0.357**	− 0.524	0.347	− 0.524	0.347	0.269	
Li_8I	− 0.608	**0.376**	**0.290**	**0.376**	− 0.755	0.246	− 0.755	0.436	0.392

The Li atoms bonding to iodine atom denoted are in bold

[52] and by Milovanovic et al. for $Li_nI^{(0,+1)}$ (n = 2–6) clusters [17]. The lithium atoms have positive net charge in the Li_nI (n = 2–4) and Li_nI^+ (n = 2–5) clusters. The bonding in Li_nX ($n > 1$, X = halogen atom) clusters could be described as electrostatic interaction between negatively charged X-ion and positively charged lithium cage [9, 17, 18, 23, 52]. However, lithium atom/atoms which is/are the center of Li_n moiety in the other neutral or cationic

Table 6 Natural bond orbital (NBO) charge of ground-state Li$_n$I$^+$ (n = 2–8) clusters

Cluster	I	Li-1	Li-2	Li-3	Li-4	Li-5	Li-6	Li-7	Li-8
Li$_2$I$^+$	− 0.817	**0.908**	**0.908**						
Li$_3$I$^+$	− 0.769	**0.884**	**0.324**	0.561					
Li$_4$I$^+$	− 0.592	**0.419**	**0.420**	**0.419**	0.334				
Li$_5$I$^+$	− 0.575	**0.510**	**0.210**	**0.210**	0.206	0.439			
Li$_6$I$^+$	− 0.562	**0.367**	**− 0.051**	**0.367**	0.444	-0.009	0.444		
Li$_7$I$^+$	− 0.548	**0.406**	**0.111**	**0.138**	0.513	− 0.554	0.434	0.500	
Li$_8$I$^+$	− 0.530	**0.234**	**− 0.068**	**0.459**	0.316	0.573	0.504	− 1.025	0.537

The Li atoms bonding to iodine atom denoted are in bold

lithium-iodide clusters have negative net charge. The reason of this charge distribution in Li$_n$I (n = 5–8) and Li$_n$I$^+$ (n = 6–8) clusters could be due to the symmetries of clusters.

Conclusion

The global minimum structures of Li$_n$I (n = 2–5) clusters are in two-dimension geometry configuration, and the geometry transition takes place from two-dimension to three-dimension at Li$_6$I cluster. The dopant iodine atom is at the apex position in lowest or low-lying structures except 3c, 4c and 7d isomers. The average bond length of Li–I in the structures depends on the coordination number of iodine atom. The iodine atom has a coordination number of two with similar average bond length, but the iodine atom of Li$_6$I and Li$_8$I with a coordination number of three has a longer bond length. Regarding the binding energy per atom, we have found that the Li$_n$I (n = 2–8) clusters are higher than the pure lithium clusters, however, they decrease with the increase of the lithium atom number (volume of molecular bulk) contrary to the case of Li$_n$ clusters. For this reason, small iodine-doped lithium clusters have higher stability than the pure lithium clusters. On the other hand, the binding energy per atom of Li$_n$I (n = 2–8) clusters have smaller value than Li$_n$X (X = Cl, Br, F and n = 2–8) clusters. From the point of view of dissociation energy, second order energy difference and HOMO–LUMO gap calculations show that a typical odd–even oscillation. The Li$_n$I (n = 1, 3, 5, 7) clusters are more stable than the Li$_n$I (n = 2, 4, 6, 8), however, LiI is the most stable than the other clusters. The results of ionization and elimination energy point out that Li$_n$I (n = 2–8) clusters belong to the class of superalkali due to having lower ionization energies than lithium atom. The electrostatic interaction between the pure small lithium cluster and the effect of iodine atom can be thought of forming between a positive lithium cage and a iodine anion.

References

1. D. Linden *Handbook of Batteries*, 2nd ed (McGraw-Hill, New York, 1995).
2. Ş. Şentürk (2011). A Density Functional Study of Li$_n$Cl (n = 1–7) Clusters. *Z. Naturforsch. A* **66**, 372–376.
3. Ş. Şentürk, A. Ünal, and O. M. Kalfa (2013). Density functional study of bromine doped lithium clusters. *Comput. Theor. Chem.* **1023**, 46–50.
4. A. K. Srivastava and N. Misra (2015). Nonlinear optical behavior of Li$_n$F (n = 2–5) superalkali clusters. *J. Mol. Model.* **21**, 305.
5. M. Milovanović, S. Veličković, F. Veljković, and S. Jerosimić (2017). Structure and stability of small lithium-chloride Li$_n$Cl$_m^{(0,1+)}$ ($n \geq m$, n = 1–6, m = 1–3) clusters. *Phys. Chem. Chem. Phys.* **19**, 30481–30497.
6. A. K. Srivastava and N. Misra (2016). Remarkable NLO responses of hyperalkalized species: the size effect and atomic number dependence. *New J. Chem.* **40**, 5467–5472.
7. J. Botana, J. Brgoch, C. Hou, and M. Miao (2016). Iodine anions beyond -1: formation of Li$_n$I (n = 2–5) and its interaction with quasiatoms. *Inorg. Chem.* **55**, 9377–9382.
8. A. Ünal and B. Kotan (2018). A DFT based study of geometries, stabilities and electronic properties of Li$_n$F (n = 1–8) clusters. *Main Group Chem.* **17**, 267–272.
9. J. Đustebek, S. Veličković, S. Jerosimić, and M. Veljković (2011). Mass spectrometric study of the structures and ionization potential of Li$_n$I ($_n$ = 2, 4, 6) clusters. *J. Anal. Atomic Spectrom.* **26**, 1641–1647.
10. G. Lanaro and G. N. Patey (2017). Crystal structures of model lithium halides in bulk phase and in clusters. *J. Chem. Phys.* **146**, 154501.
11. L. Cheng and J. Yang (2013). Communication: new insight into electronic shells of metal clusters: Analogues of simple molecules. *J. Chem. Phys* **138**, 141101.
12. M. Zhang, J. Zhang, X. Feng, H. Zhang, L. Zhao, Y. Luo, and W. Cao (2013). Magnetic superatoms in VLi$_n$ (n = 1–13) clusters: a first-principles prediction. *J. Phys. Chem. A* **117**, 13025–13036.
13. H. Pauna, X. Shi, M. Huttula, E. Kokkonen, T. Li, Y. Lou, J. Lappalainen, M. Zhang, and W. Cao (2017). Evolution of lithium clusters to superatomic Li$_3$O$^+$. *Appl. Phys. Lett.* **111**, 103901.
14. S. R. Veličković, J. B. Đustebek, F. M. Veljković, and M. V. Veljković (2012). Formation of positive cluster ions Li$_n$Br (n = 2–7) and ionization energies studied by thermal ionization mass spectrometry. *J. Mass Spectrom.* **47**, 627–631.
15. N. L. Moreira, B. G. A. Brito, J. N. T. Rabelo, and L. Cândido (2016). Quantum Monte Carlo study of the energetics of small hydrogenated and fluoride lithium clusters. *J. Comput. Chem.* **37**, 1534–1536.
16. J. Đustebek, S. R. Veličković, F. M. Veljković, and M. V. Veljković (2012). Production of heterogeneous superalkali

clusters Li_nF (n = 2–6) by Knudsen cell Mass Spectrometry. *Dig. J. Nanomater. Biostruct.* **7**, 1365–1372.

17. M. Z. Milonavić and S. V. Jerosimić (2014). Theoretical investigation of geometry and stability of small lithium-iodide Li_nI (n = 2–6) clusters. *Int. J. Quantum Chem.* **114**, 192–208.
18. J. Đustebek, M. Milovanović, S. Jerosimić, M. Veljković, and S. Veličković (2013). Theoretical and experimental study of the non-stoichiometric Li_nI (n = 3 and 5) clusters. *Chem. Phys. Lett.* **556**, 380–385.
19. L. P. Ding, P. Shao, C. Lu, F. H. Zhang, Y. Liu, and Q. Mu (2017). Prediction of the iron-based polynuclear magnetic superhalogens with pseudohalogen CN as ligands. *Inorg. Chem.* **56**, 7928–7935.
20. P. Shao, B. L. Chen, L. P. Ding, D. B. Luo, C. Lu, and X. Y. Kuang (2017). Prediction of hypervalent molecules: investigation on M_nC (M = Li, Na, K, Rb and Cs; n = 1–8) clusters. *Phys. Chem. Chem. Phys.* **19**, 25289–25297.
21. L. P. Ding, P. Shao, C. Lu, F. H. Zhang, and L. Y. Wang (2017). Iron-based magnetic superhalogens with pseudohalogens as ligands: an unbiased structure search. *Sci. Rep.* **7**, 45149.
22. P. Shao, X. Y. Kuang, L. P. Ding, M. M. Zhong, and Y. R. Zhao (2014). Probing the structural and electronic properties of small aluminum dideuteride clusters. *J. Mol. Graph. Model.* **53**, 168–178.
23. P.v.R. Schleyer, Are CLi_6, NLi_5, OLi_4, Etc, Hypervalent? In New Horizons of Quantum Chemistry, Reidel, Dordrecht, 1986
24. G. L. Gutsev and A. I. Boldryev (1981). DVM-Xα calculations on the ionization potentials of MX_{k+1}^- complex anions and the electron affinities of MX_{k+1} “superhalogens”. *Chem. Phys.* **56**, 277–283.
25. G. L. Gutsev and A. I. Boldryev (1982). DVM Xα calculations on the electronic structure of “superalkali” cations. *Chem. Phys. Lett.* **92**, 262–266.
26. E. Rehm, A. I. Boldryev, and P. V. R. Schleyer (1992). Ab initio study of superalkalis. First ionization potentials and thermodynamic stability. *Inorg. Chem.* **3**, 4834–4842.
27. A. Ünal and S. Güvenir (2019). The investigation of optical properties of linear and non-linear fluorine-doped lithium clusters. *BSEU J. Sci.* **6**, 146–152.
28. Y. Li and D. Wu (2010). Theoretical study on static first hyperpolarizabilities of hypervalent compounds F_nLi_{n+1} (n = 1–3). *Gaodeng Xuexiao Huaxue Xuebao* **31**, 1811–1814.
29. S. Veličković, V. Djordjević, J. Cvetićanin, J. Đustebek, M. Veljković, and O. Nesković (2006). Ionization energies LinX (n = 2, 3; X = Cl, Br, I) molecules. *Rapid. Commun. Mass Spectrom.* **20**, 3151–3153.
30. J. Perez, A. Restrepo, ASCEC V-02: Annealing Simulado con Energia Cuantica. Property, development and implementation: Grupo de Quimica–Fisica Teorica, Instituto de Quimica, Universidad de Antioquia: Medellin, Colombia, 2008.
31. N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller, and E. J. Teller (1953). Equation of state calculations, by fast computing machines. *Chem Phys* **21**, 1087–1092.
32. S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi (1983). Optimization by simulated annealing. *Science* **220**, 671–680.
33. E. Aarts and H. Laarhoven *Simulated annealing: theory and applications* (Springer, New York, 1987).
34. M.J. Frisch, et al., Gaussian 09 Revision A.1, Gaussian Inc., Wallingford, CT, Gaussian, Inc. 2009.
35. A. Ünal, M. Şenyel, and Ş. Şentürk (2009). Conformational analysis and vibrational spectroscopic investigation of 3-phenylpropylamine. *Vib. Spectrosc.* **50**, 277–284.
36. A. Ünal and M. Okur (2018). Conformational analysis of N, N’-phenylenediylbis[3-(1-aminoethyl)-6-methyl-2H-pyran-2,4(3H)-dione]. *BSEU J. Sci.* **5**, 50–54.
37. T. B. Tai, P. V. Nhat, M. T. Nguyen, S. Li, and D. A. Dixon (2011). Electronic structure and thermochemical properties of small neutral and cationic lithium clusters and boron-doped lithium clusters: $Li_n^{0/+}$ and $Li_nB^{0/+}$ (n = 1–8). *J. Phys. Chem. A* **115**, 7673–7686.
38. B. G. A. Brito, L. Candido, J. N. Teixeria Rabelo, and G.-Q. Hai (2014). Binding energies of small lithium clusters: a comparison of different theoretical calculations. *Chem. Phys. Lett.* **616**, 212–216.
39. I. Boustani, W. Pewestorf, P. Fantucci, V. Bonaić-Koutecký, and J. Koutecký (1987). Systematic ab initio configuration-interaction study of alkali-metal clusters: relation between electronic structure and geometry of small Li clusters. *Phys. Rev. B* **35**, 9437–9450.
40. W. Klemperer, W. G. Norris, A. Buchler, and A. G. Emslie (1960). Infrared spectra of the lithium halide monomers. *J. Chem. Phys.* **33**, 1534–1540.
41. A. W. Potts and E. P. F. Lee (1979). Photoelectron spectra and electronic structure of lithium halide monomers and dimers. *J. Chem. Soc. Faraday Trans.* **2**, (75), 941–951.
42. G. Platel (1965). Measurement of the appearance potentials of the ions formed by electron impact in the vapor in the iodides of the alkali metals and of any mixture of lithium iodide/metal iodide. *J. Chim. Phys.* **62**, 1176–1180.
43. D. R. Lide *CRC Handbook of Chemistry and Physics*, 85th ed (CRC, Bosa Roca, 2004).
44. M. W. McGeoch and R. E. Schlier (1983). Autoionizing rydberg states of the Li_2 molecule: molecular constants for Li_2^+. *Chem. Phys. Lett.* **99**, 347–352.
45. K. P. Huber and G. Herzberg *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold Company, New York, 1979).
46. K. Hatua, A. Mondal, and P. K. Nandi (2017). Static second hyperpolarizability of diffuse electron compound M_2X (M = Li, na; X = H, F): Ab-initio study of basis set effect and electron correlation. *Chem. Phys. Lett.* **686**, 1–6.
47. R. Rousseau and D. Marx (2000). Exploring the electronic structure of elemental lithium: from small molecules to nanoclusters, bulk metal, and surfaces. *Chem. Eur. J.* **6**, 2982–2993.
48. E. Florez and P. Fuentealba (2009). A theoretical study of alkali metal atomic clusters: from Li_n to Cs_n (n = 2–8). *Int. J. Quantum Chem.* **109**, 1080–1093.
49. A. Ünal and B. Eren (2013). FT-IR, dispersive Raman, NMR, DFT and antimicrobial activity studies on 2-(Thiophen-2-yl)-1H-benzo[d]imidazole. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **114**, 129–136.
50. B. G. A. Brito, G.-Q. Hai, and L. Candido (2018). Analysis of the ionization potentials of small superalkali lithium clusters based on quantum Monte Carlo simulations. *Chem. Phys. Lett.* **708**, 54–60.
51. S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard (1988). Gas-phase ion and neutral thermochemistry. *J. Phys. Chem. Ref. Data* **17**, 1–861.
52. J. Ivanic, C. J. Marsden, and D. M. Hassett (1993). Novel structural principles in poly-lithium chemistry Predicted structures and stabilities of XLi3, XLi5 (X = F, Cl), YLi6 (Y = O, S), SLi8 and SLi10. *J. Chem. Soc. Chem.* **10**, 822–825.