Theoretical studies of the global minima and polarizabilities of small lithium clusters

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Abstract: Lithium clusters Li_n ($n=1-20$) have been investigated with density functional theory (DFT) and coupled-cluster (CC) methods. The global minima are located via an improved basin-hopping algorithm. Simulated polarizabilities are in good agreement with the measured data generally. The simulated polarizabilities for Li_6 , Li_{12} and Li_{19} are in reasonable agreement when thermal effects are included, except the Li_3 cluster. A linear correlation for the inverse relationship between the CCSD calculated polarizabilities and ionization potential (IP) has been reported to have the linear coefficient of 0.996, which further strengthens our simulations.

1. Introduction

Lithium, with only three electrons and one delocalized electron in the valence shell, is the lightest metallic element and is a good starting point for theoretical studies of light alkali metals and their spectroscopic properties [1]. Furthermore, there is continued interest in atomic clusters since they are the smallest condensed matter systems and their physical and chemical properties are known to be sensitive to system size [2]. Lithium clusters, Li_n , have been studied extensively both

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5 experimentally and theoretically in terms of their properties, making them ideal
6 systems for further investigations [3]. Experimental measurements for lithium
7 clusters include isotropic polarizability [4], ionization potentials (IPs) [5], electron
8 affinities (EAs) [6] and cohesive energies [7]. Meanwhile, theoretical investigations
9 have reported results using DFT and *ab initio* wave function approaches, including
10 geometrical and electronic structures [8], spectroscopic parameters [9], and
11 bonding analyses [6,10]. Despite these numerous theoretical studies, there are still
12 discrepancies, such as the geometrical structures of the reported global minima of
13 the various clusters [8]. For example, with the Li_{20} cluster, both structures with C_1
14 [11] and T_d [12] symmetries have been reported as stable structures and the
15 calculated polarizability for T_d structure is around 446.3 ± 120.0 a.u. higher than the
16 experimental result [12].
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29 One solution to this dilemma is to compare the computational results with
30 experimentally measured spectra [5,13] and assign the structures of the isomers
31 accordingly. This approach, although reasonable, has its limitations since it requires
32 highly accurate calculations [14]. Besides, both thermal and quantum fluctuations
33 [15] do play an important role in determining the properties of lithium clusters [9].
34 For the clusters with sufficiently flat potential landscapes, there are several local
35 minima that can co-exist on the time scale of experiment, which makes the
36 measured spectrum challenging to interpret [6]. In addition, with light mass nuclei,
37 quantum fluctuations such as zero-point motion and tunneling effects are also
38 non-negligible.
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47 In this paper, we report a systematic study of simulated polarizabilities of small
48 lithium clusters based on DFT and CC singles and doubles (CCSD) [16] levels of
49 theory, with global-minimum structures obtained using an improved basin-hopping
50 procedure. We compare our calculations with experimentally measured
51 polarizabilities [4] up to the Li_{20} cluster. We find that the CCSD results are closest to
52 the experimental ones, while the DFT results, with different exchange-correlation
53 functionals, are consistent with each other and in overall good agreement with CCSD.
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Energies of Li_n isomers are also compared at the CCSD(T) level of theory [17] to account for the triples contributions. . Thermal fluctuation effects are also discussed for the Li_6 , Li_{12} and Li_{19} clusters to understand the discrepancy between simulated polarizabilities and measured values. Li_3 is a particularly challenging case, where the calculated polarizability is 319.20 a.u., a lot higher compared with the measured value of 232.82 ± 23 a.u.. To further strengthen our calculated polarizability based on both DFT and CCSD levels of theory, we have also investigated the inverse relationship between the CCSD calculated polarizabilities and ionization potentials (IP) and find a linear correlation of 0.996 for all the clusters except for Li_3 . This suggests that the experimental measured polarizability for this system may need to be revisited.

2. Theory and Computational details

2.1 Theory

Over the years there have been investigations of the polarizabilities of small lithium clusters using DFT based linear response approaches [18]. Here, for the first time, we report extensive linear-response CCSD calculations for the Li_{10-20} clusters and CCSDT calculations for the Li_{1-4} clusters.

(1) Analytic Derivatives of the CC Energy

Within the framework of linear-response CC (LR-CC theory) [19], the modified energy functional that satisfies the generalized Hellmann-Feynman theorem is written as

$$E = \tilde{E} = \langle \Phi | (1 + \Lambda) e^{-T} H e^T | \Phi \rangle \quad (1)$$

$$\Lambda = \Lambda_1 + \Lambda_2 \quad (2)$$

$$\Lambda_m = \frac{1}{(m!)^2} \sum_{i_1, \dots, i_m} \sum_{a_1, \dots, a_m} \lambda_{i_1 \dots i_m}^{a_1 \dots a_m} X_{a_1} \dots X_{a_m} X_{i_1}^+ \dots X_{i_m}^+ \quad (m=1, 2) \quad (3)$$

where $\lambda_{i_1 \dots i_m}^{a_1 \dots a_m}$ are Lagrange multipliers that define de-excitation operator Λ . The second derivative of the energy, which corresponds to the polarizability, is represented as

$$\frac{d^2 \tilde{E}}{dx dy} =$$

$$\begin{aligned} & \left\langle \Phi \left| (1 + \Lambda) e^{-T} \frac{\partial^2 H}{\partial x \partial y} e^T \right| \Phi \right\rangle + \\ & \hat{P}(x, y) \left\langle \Phi \left| (1 + \Lambda) e^{-T} \left[\frac{\partial H}{\partial y}, \frac{\partial T}{\partial x} \right] e^T \right| \Phi \right\rangle + \left\langle \Phi \left| (1 + \Lambda) e^{-T} \left[\left[\frac{\partial H}{\partial y}, \frac{\partial T}{\partial y} \right], \frac{\partial T}{\partial x} \right] e^T \right| \Phi \right\rangle \quad (4) \end{aligned}$$

where $\hat{P}(x, y)$ is the symmetric permutation operator with $\hat{P}(x, y)f(x, y) = f(x, y) + f(y, x)$. The derivatives of cluster operator T are calculated from the first-order CC response equations

$$\left\langle \Phi_i^a \left| (e^{-T} \frac{\partial H}{\partial x} e^T + [e^{-T} H e^T, \frac{\partial T}{\partial x}]) \right| \Phi \right\rangle = 0 \quad (5)$$

$$\left\langle \Phi_{ij}^{ab} \left| (e^{-T} \frac{\partial H}{\partial x} e^T + [e^{-T} H e^T, \frac{\partial T}{\partial x}]) \right| \Phi \right\rangle = 0 \quad (6)$$

The above equations form a linear system of equations for derivatives of singly and doubly excited cluster amplitudes. We refer the reader to more comprehensive reviews for details [20].

(2) Global-Minimum Search Algorithm

In order to explore the impact of the cluster geometries on the calculated polarizabilities, we used an improved global minimum structure search approach based on the basin hopping algorithm [21] by local minimizations using DFT calculations as implemented in the TGmin program [22].

To improve the efficiency of the global minimum search, the approach also includes a comparison function for structure similarity based on the ultrafast shape recognition (USR) algorithm [23] to eliminate duplicate structures and to avoid local minima trapping during the global minimum search. A more controllable displacement function is implemented so under coordinated atoms have a higher probability to be displaced. The displaced structures are adjusted by a relaxation function based on the covalent radii of elements [24], so as to avoid atoms being too close to each other. By calling the batch system on the computing platform, numerous standalone local minimization calculations can be run simultaneously,

thereby improving the efficiency of the search and reducing the overall computational effort.

2.2 Computational Details

The initial global minimum structures searches were performed with the TGMIn program, described earlier, in conjunction with the PBE [25] exchange-correlation (XC) functional and the DZP [26] basis set (1s orbital being frozen). Structures from the global minimum search were further optimized using DFT with the B3LYP XC functional [27] and the cc-pVTZ [28] basis set. The local minimum structures are further confirmed by vibrational frequency calculations. These and all DFT and CC based polarizability [29] calculations were performed using all-electron Gaussian basis set calculations with the NWChem 6.5 program [30]. Polarizability calculations were performed at the CCSD level of theory and several DFT exchange-correlation functionals (BLYP [31], B3LYP, BHLYP [31,32], CAM-B3LYP [33]). The POL1 [34] basis set was used for all polarizability calculations except for cases where convergence issues were encountered and the cc-pVTZ basis was used. Several isomers were compared using the CCSD, DFT and CCSD(T)/POL1 single-point energies, respectively. Ionization potential (IP) calculations were also performed at the CCSD level of theory with the POL1 basis set. For the even, closed shell clusters, we have applied EOM-CCSD theory [35] to obtain the vertical IP energies (Table 6) for comparison.

3. Results and Discussion

As shown in Figs. 1&2, the geometries of Li_n clusters are found to be planar up to Li_5 (Li_1 and Li_2 are not shown). Several isomers are discussed where there is a debate in the literature. Furthermore, the global minima are further confirmed by their simulated polarizabilities and the results are listed in Fig. 3 and Table 1 for comparison. *All Li_n clusters have doublet multiplicity for n with odd values and singlet for n with even values unless mentioned specifically in Table S2.* Our results show that both DFT and CCSD give reasonably close polarizability values compared with experiment. All five DFT-based simulated results are very similar to each other with

standard deviations within 91-97 a. u., and CCSD gives the closest results to the measured one with a standard deviation of 74 a. u.. Simulated thermal effects at room temperature were also performed for Li₆, Li₁₂ and Li₁₉ clusters to shed light on polarizability discrepancies between calculations and experiment (Table 5).

3.1 Geometries and Polarizabilities of Li_n

Li₃ – There have already been many discussions about the Li₃ isomers including the pseudo-rotation barrier and dynamic effect for the Jahn-Teller distortion from D_{3h} to either *a* (vertex angle > 60°) or *b* (vertex angle < 60°) C_{2v} structures, vibronic energies, electron spin resonance, and electronic structures [36], etc. Fig. 4(a) shows its potential energy surface, where there are two local minima corresponding to *a* and *b* structures, respectively. The pseudo-rotation effect has not been considered in this report. Instead, the surface scan of CCSD calculated polarizability is shown in Fig. 4(b), which shows that most of the calculated values are well above 300.0 a.u., much higher than the measured result of 232.82±23 a.u. (Figs. 3(a) & 3(b)). This large discrepancy suggests that even considering the pseudo-rotation effect may not help resolve its problem. Therefore, we have tried other analyses to further understand the discrepancy. Firstly, we have investigated various basis sets for these two geometries of Li₃ as shown in Table 3. It shows that there are no significant basis-set effects that would narrow the CCSD and experimental gap. For example, the differences between aug-cc-pVDZ and aug-cc-pVQZ CCSD polarizabilities do not exceed 3 a.u.. Secondly, we have further performed the CCSDT/POL1 (Table 4) simulation on the polarizability of Li₃ and the result is almost the same as the CCSD one (Table 1). Consequently, this confirms that high-order correlation effects does not account for the polarizability discrepancy of Li₃. Thirdly, we have also investigated the inverse relationship (equation (7)) [37], where *I* represents ionization potential, *N* for number of electrons, *Z* for nuclear charge between the CCSD calculated polarizability and ionization potential (IP) of the lithium cluster Li_n. Its corresponding linear correlation coefficient is 0.996 as shown in Fig. 4(c) [38]. The measured one, on the other hand, as represented by the red spot in Fig. 4(c), is below the linear fitted line. This again helps confirm, to some extent, our calculated results.

$$\alpha(N, Z) = (Z - N + 1)^3 I^{-3}(N, Z) f(N, Z) \quad (7)$$

(7)

Furthermore, we have investigated the impact of spin multiplicity on Li_3 and its cation Li_3^+ as well, since it is said that the multiplicity has effects for the polarizations of molecules (Table S2) [39]. As shown in Table S2, both molecules prefer the lower multiplicity states energetically. The Li_3 isomer with $^4A'_2$ state has a larger polarizability (>60.0 a.u.) than the other two isomers with 2A_1 and 2B_2 states respectively. Same trend for Li_3^+ , higher multiplicity states of 3A_1 and $^3\Sigma_u^+$ have larger polarizabilities than that of $^1A'_1$. This phenomenon is due to the more dispersive of the higher orbitals occupied in the higher-multiplicity state $^4A'_2$ for Li_3 and 3A_1 , $^3\Sigma_u^+$ for Li_3^+ .

Li₄, Li₅ – The global-minima structures of Li_4 and Li_5 as shown in Fig. 1, are planar lithium clusters. All larger lithium clusters (Li_n , $n \geq 6$) are non-planar ones. On the other hand, there is a fairly stable no-pair bonding state for the T_d symmetrized Li_4 with electronic state of 5A_2 and having all the four valence electrons unpaired [39].

Li₆ – There is ample literature discussing the isomers of Li_6 cluster and having different conclusions for the most stable one [40]. For example, the C_{5v} isomer, which is considered as the lowest isomer in a very recent work [41], is less energetically favorable than the D_{4h} one based on our calculations with B3LYP, CCSD, and CCSD(T) methods. The CCSD(T) energy of the C_{5v} cluster is located 6.56 kcal/mol above the D_{4h} one which includes four twisted tetrahedral building blocks (Table 2 & Fig. 1). The C_{2v} structure has also been investigated and its optimized geometry changes to D_{4h} symmetry, which is the most stable one in this report. Meanwhile, it shows that CCSD(T) results change the order of C_{5v} and D_{3h} compared with the CCSD ones, consistent with several previously reported data [42], which illustrates the importance of correlation effects due to the triple excitations in determining the relative energies of the Li_6 clusters. Herein the D_{3h} planar structure

is the same as that found for Au₆ [43]. Furthermore, the CCSD simulated polarizability of the most stable D_{4h} isomer is also closest to the measured value among the three isomers (Table 2) [42]. However, even for the D_{4h} isomer one can observe a significant difference between the CCSD and experimental polarizabilities (amounting to 94 a.u.). Table 1 also demonstrates a general trend in the calculated BLYP, B3LYP, BHLYP, CAM-B3LYP, and CCSD polarizabilities, which are significantly above the experimental data, as shown in Fig. 1 too. The zero-point corrected free energies based on B3LYP are further investigated and the free-energy gap ΔG_{zero} does not change the energetic order of these three isomers, but make them closer to each other as shown in Table 2.

Li₇ – Its global-minimum structure has a pentagonal bipyramid structure with D_{5h} symmetry, which is the same as former reports [41]. It is interesting to note that this structure becomes the basic building blocks for larger lithium clusters (Fig. 1).

Li₈ – The two isomers of Li₈ shown in Fig. 1 are relatively close in energy. Although the C₁ isomer has closer polarizability to the experimental result, the T_d isomer is 0.45 kcal/mol more stable based on the CCSD(T) energies. The latter contains four tetrahedral building blocks while the C₁ isomer can be viewed as combinations of two planar rhomboidal subgroups (Table 2). It is interesting to note that CCSD(T) decreases the energy gap between these two isomers. Besides, the result of ΔG_{zero} changes the order of these two isomers. Comparing all the methods here, the CAM-B3LYP calculated polarizability yields the best agreement with the experimental data (Table 1).

Li₉ – The lowest energy isomer of Li₉ has C₁ symmetry, which is close to the C_{4v} one, as shown in Fig. 1. This structure includes eight tetrahedral subgroups, which is around 3.16 kcal/mol more stable than the C_{2v} one according to the CCSD(T) energies. The result of ΔG_{zero} gives the same order. Furthermore, the polarizability of C₁ (close to C_{4v}) isomer is almost 85 a.u. closer to the experimental result than that of C_{2v} (Table 2), which further confirms the global minimum of Li₉ cluster.

Li₁₀ – Here two isomers of Li₁₀ are lower in energy, with the D_{2d} structure being the lowest energy one, as confirmed by both B3LYP and CCSD(T) energies (Table 2). Although the C_{4v} isomer has a closer polarizability to the measured one, both of them are close to each other with a small gap of around 10 a.u. (Table 2). The result of ΔG_{zero} gives the same order showing that the D_{2d} structure is more stable.

Li₁₁₋₂₀ – The geometries of the local-minima structures of lithium clusters Li₁₁₋₂₀ are shown in Fig. 2 and their simulated polarizabilities are listed in Table 1, accompanied by the experimental results for comparison. The match is quite good, except for two clusters Li₁₂ and Li₁₉, where the measured polarizabilities are more than one (Li₁₂) or two (Li₁₉) hundred higher than the calculated results (Table 1 and Fig. 3). For the Li₁₉ cluster, the discrepancy is 245.51 a.u. without the inclusion of experimental errors that are in the range of ~10% mainly caused by the velocity measurement. On the other hand, for Li₂₀ cluster, our calculated value is very close to the measured one with a gap of only 40 a.u., while previously published works have found either one hundred lower [44] or four hundred higher [12] than the measured data.

Furthermore, for Li₂₀, previously published work [12] report a simulated polarizability of 1667.3 a.u. and our calculated result is 1241.7 a.u., much closer to the measured result of 1201.2 a.u. These results show the accuracy of our algorithm for locating the global-minimum structure of the Li₂₀ cluster. Unlike the Au₂₀ cluster [45], with a global-minimum structure of T_d symmetry, the global-minimum structure of Li₂₀ is of C₁ symmetry. It is worth noting that the Li_n clusters prefer 3D structures instead of planar geometries, very different from Au_n clusters. Clearly, even though the valence electrons of Li and Au are both s-shell electrons, the crucial difference is in the s-d hybridization, due to direct and indirect relativistic effects, in the latter.

3.2 Thermal Effects

To investigate the thermal fluctuation effects on the structures of the Li_6 , Li_{12} and Li_{19} clusters, Gaussian basis set *ab initio* molecular dynamics (AIMD) simulations were performed on the optimum Li_6 , Li_{12} and Li_{19} clusters to sample the minima, respectively. These simulations were performed with the 6-31G* basis [46] and B3LYP exchange-correlation functional at 300K. The velocity-Verlet algorithm [47] was used to propagate nuclei and the temperature was controlled via the stochastic velocity-rescaling thermostat of Bussi, Donadio, and Parrinello [48] which correctly samples the canonical ensemble and minimally impacts dynamic properties. Structures were collected from short (1 ps) and long trajectories (~ 10 ps), from which 50 random snapshots were extracted for the subsequent polarizability calculations. The AIMD calculations were performed with a development version of NWChem [49].

Statistical analyses of these calculations are given in Table 5. The averaged polarizabilities $\langle\alpha\rangle$ of these randomly selected structures of Li_{12} and Li_{19} are about 15-30 a.u. higher above the polarizabilities (α_0) obtained in the gas-phase calculations for optimized structures based on all the five simulation methods including CCSD theory. The corresponding standard deviation δ is around 30 a.u. for each DFT method, and around 20 a. u. for the CCSD level of theory. For Li_6 , the averaged simulated value is about 30 a.u. higher and the standard deviation is less than 20 a.u. for all these five levels of theories. For Li_{12} , the CCSD simulated polarizability is within the range of experimental value. For Li_{19} , the gap between the averaged polarizability and experimental error is within ~ 50 a.u. of threshold. All the coordinates for the GM clusters Li_n , with $n = 2 - 20$ and the correspondingly bond-length distributions for $n = 11 - 20$ are provided in the supplementary material [28]. Statistical analyses based on the data sets from the longer trajectories (~ 10 ps) shows no improvement compared with the shorter trajectories, which is presented in the supplementary material [50]. This is not surprising as these clusters are small.

4. Conclusions

In this work, we have systematically studied the global minima and polarizabilities of lithium clusters Li_n ($n=1-20$) with DFT and CC methods. We have used an improved basis-hopping based search algorithm to locate the global minima. Our calculations show that the CCSD results are closest to the experimental ones, the DFT results based on different exchange-correlation functional are consistent with each other and in overall good agreement with the measured data too. We have also studied the thermal fluctuation effects on the simulated polarizabilities via AIMD sampling at 300 K for the Li_6 , Li_{12} and Li_{19} clusters. As has been discussed above, thermal effects cannot account for the significant discrepancies between calculated and measured data for these clusters. For the largest cluster considered here (Li_{20}), we have demonstrated that proper determination of the cluster geometry plays a pivotal role in obtaining quantitative agreement with the experimental data. We also report a linear correlation (coefficient 0.996) for the inverse relationship between the CCSD calculated polarizability and IP for the Li_n clusters, which further strengthens our simulations. The measured polarizabilities of Li_3 at various levels of theories including CCSDT, is still below the linear fitted line, which calls into question about the discrepancy of the polarizability for Li_3 .

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Li₃-C_{2v} (a)

Li₃-C_{2v} (b)

Li₄-D_{4h}

Li₅-C_{2v}

Li₆-D_{4h}

Li₆-C_{5v}

Li₆-C_{5v}

Li₇-D_{5h}

Li₈-T_d

Li₈-C₁

Li₉-C₁

Li₉-C_{2v}

Li₁₀-D_{2d}

Li₁₀-C_{4v}

Fig. 1. The geometries of Li_{3-10} clusters including the global minima and isomers

Fig. 2. The geometries of Li_{11-20} clusters (the schematic connection for Li-Li bond length $> 3.0 \text{ \AA}$ are omitted)

Fig. 3. The comparison of CCSD and DFT simulated and experimental polarizabilities for Li_1 - Li_{10} clusters. Color codes: black (experimental), red (CCSD), blue (BLYP), light blue (B3LYP), light green (BHLYP), dark green (CAM-B3LYP).

Fig. 4. The potential energy and polarizability surfaces of Li₃ performed via CCSD/POL1 calculations: (a) the potential energy scan surface; (b) the polarizability scan surface. R here represents the equal length of Li-Li bond length of the isosceles triangle Li₃. Angle here is the one formed between these two equal Li-Li bonds. (c) The relationship between the polarizability (α) and ionization potential (IP) of the lithium cluster Li_n. There are two dots corresponding to Li₃: the black dot represents the calculated α while the red dot represents measured α . All IP values are calculated at CCSD/POL1 level of theory. α and IP values are in atomic units and the factor “n” refers to the number of

atoms presents in the cluster. The linear fitting parameter is 0.99596.

Table 1. The comparison between the experimental and calculated CCSD & DFT isotropic polarizabilities (in a.u.) of Li_n clusters ($n = 1-20$).

$^a\text{Li}_n$	BLYP	B3LYP	BHLYP	CAM-B3LYP	CCSD	Expt. ^c
Li_1	135.19	138.60	143.26	142.31	167.71	163.87 ± 16
Li_2	196.31	194.15	190.82	188.12	216.00	221.35 ± 22
Li_3	313.98	317.38	325.54	322.70	315.15	232.82 ± 23
Li_4	358.98	347.39	335.49	327.65	338.00	326.62 ± 33
Li_5	454.92	443.52	431.46	423.98	435.71	428.52 ± 43
Li_6	456.96	445.62	435.06	426.72	453.67	360.36 ± 36
Li_7	523.73	523.74	536.65	535.50	562.85	538.52 ± 54
Li_8	600.26	590.09	578.37	569.34	611.83	561.47 ± 56
Li_9	615.60	603.62	588.20	591.01	633.81	601.28 ± 60
Li_{10}	723.72*	710.21*	695.58*	683.77*	740.50	701.83 ± 70
Li_{11}	781.27	774.88	772.61	763.48	821.06	801.70 ± 80
Li_{12}	818.33*	806.42*	795.73*	784.35*	843.16	955.57 ± 96
Li_{13}	858.20	844.73	833.63	822.15	887.59	929.92 ± 93
Li_{14}	896.07*	881.01*	869.30*	858.44*	931.52	925.87 ± 93
Li_{15}	937.73	919.34	903.36	890.30	968.51	992.01 ± 99
Li_{16}	958.09*	947.07*	939.03*	927.53*	1001.71	939.37 ± 94
Li_{17}	1126.64	1098.31	1071.09	1052.30	1146.56	1170.16 ± 117
Li_{18}	1037.64*	1023.51*	1158.48*	1000.06*	1089.41	1166.11 ± 117
Li_{19}	1120.07	1115.36	1119.58	1168.96	1190.54	1436.05 ± 144
Li_{20}	1189.02*	1173.80*	1158.42*	1144.05*	1241.74	1201.21 ± 120
$^b\delta$	91.79	95.98	93.46	96.97	74.05	/

^a All calculated isotropic polarizabilities (except the ones marked by “*”) are obtained by POL1 basis set at the B3LYP/cc-pVTZ optimized geometries on the basis of global-minimum searched structures.

^b The δ is the standard deviation of isotropic polarizabilities between the simulated value and the measured one.

^c Ref. 11

* cc-pVTZ basis set is used due to convergence problem in calculating the isotropic polarizability.

Table 2. The optimized B3LYP energy, single point CCSD(T) energy, and CCSD simulated isotropic polarizabilities of Li₆, Li₈, Li₉ and Li₁₀ isomers.

Isomers	Relative Energy (kcal/mol)				Isotropic	Expt.
					Polarizability (a.u.)	Polarizability (a.u.)
	B3LYP	ΔG_{zero}	CCSD	CCSD(T)	CCSD	Expt.
Li ₆						
D _{4h}	0.00	0.00	0.00	0.00	453.86	
C _{5v}	3.28	0.27	6.36	6.56	524.87	360.36±36
D _{3h}	5.14	2.77	5.24	7.88	513.78	
Li ₈						
T _d	0.00	2.84	0.00	0.00	611.83	
C ₁	2.30	0.00	2.90	0.45	597.30	561.47±56
Li ₉						
C ₁	0.00	0.00	0.00	0.00	636.58	
C _{2v}	1.73	1.95	2.10	3.16	721.84	601.28±60
Li ₁₀						
D _{2d}	0.00	0.00	0.00	0.00	740.50	
C _{4v}	9.56	8.08	9.63	10.53	730.02	701.83±70

Table 3. CCSD simulated polarizabilities (in a.u.) of two Li_3 isomers based on different basis sets of the a and b geometries obtained from CCSDT/POL1 optimization

	POL1	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	cc-pV5Z
$\text{Li}_3 (a)$	323.70	323.86	326.76	325.88	323.36
$\text{Li}_3 (b)$	315.15	314.59	318.02	317.04	314.17
Num. Basis	72	69	138	240	273

($R_a=2.736 \text{ \AA}$, $\theta_a=71.23^\circ$; $R_b=2.983 \text{ \AA}$, $\theta_b=52.49^\circ$)

Table 4. CCSDT/POL1 simulated polarizabilities (in a.u.) of small clusters Li_{1-4} and the a and b geometries of Li_3 are obtained from CCSDT/POL1 optimization

	Li_1	Li_2	$\text{Li}_3 (a)$	$\text{Li}_3 (b)$	Li_4
α	167.72	214.92	315.85	315.27	344.94
Expt. α	163.87 ± 16	221.35 ± 22	232.82 ± 23		326.62 ± 33

Table 5. The statistical analysis of the isotropic polarizabilities computed from 50 randomly selected geometries of Li₆, Li₁₂, and Li₁₉ at both DFT and CCSD levels of theory.

	BLYP	B3LYP	BHLYP	CAM1	^d CCSD	Expt.
Li ₆						
^a α ₀	456.96	445.62	435.06	426.72	453.67	
^b ⟨α⟩	486.92	476.24	465.96	456.75	485.86	360.36±36
^c δ	16.09	16.21	16.14	18.25	17.17	
Li ₁₂						
^a α ₀	818.33*	806.42*	795.73*	784.35*	843.16	
^b ⟨α⟩	844.75*	831.65*	819.60*	807.70*	860.98	955.57±96
^c δ	30.32*	29.22*	27.94*	27.54*	23.26	
Li ₁₉						
^a α ₀	1120.07	1115.36	1119.58	1168.96	1190.54	
^b ⟨α⟩	1152.15	1147.62	1147.85	1202.82	1224.36	1436.05±144
^c δ	31.89	31.51	32.05	32.84	23.34	

^a α₀ is the computed isotropic polarizability of Li₆, Li₁₂ and Li₁₉ at the B3LYP/cc-pVTZ optimized geometries using DFT and CCSD levels of theory, respectively.

^b ⟨α⟩ is the mean value of isotropic polarizability on the basis of 50 randomly selected geometries

(α_{*i*, *i*=1-50}) generated from AIMD: $\langle \alpha \rangle = \frac{1}{50} \sum_{i=1}^{50} \alpha_i$

^c δ is the standard deviation: $\delta = \sqrt{\frac{1}{50} \sum_{i=1}^{50} (\alpha_i - \langle \alpha \rangle)^2}$

^d Here 18 (for Li₁₂) and 14 (for Li₁₉) randomly selected geometries were used for expensive CCSD calculations.

* cc-pVTZ basis set is used here instead of POL1 due to convergence issue.

Table 6. The computed IP of lithium clusters based on two types of methods. IP-DD-CCSD represents the vertical IP from the direct differences between CCSD calculated energies for neutral and cation lithium clusters. IP-EOM-CCSD represents the vertical IP from EOM-CCSD calculation.

Clusters	IP-DD-CCSD (eV)	IP-EOM-CCSD (eV)
Li ₁	5.35	/
Li ₂	5.19	5.2
Li ₃	4.12	/
Li ₄	4.67	4.72
Li ₅	4.42	/
Li ₆	4.56	4.66
Li ₇	3.92	/
Li ₈	4.67	4.75
Li ₉	3.44	/
Li ₁₀	4.16	4.24
Li ₁₁	3.93	/
Li ₁₂	4.12	4.2
Li ₁₃	3.8	/
Li ₁₄	4.15	4.21
Li ₁₅	3.58	/
Li ₁₆	3.69	3.77
Li ₁₇	3.71	/
Li ₁₈	4.08	4.16
Li ₁₉	3.73	/
Li ₂₀	4.1	4.18

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[50] See supplemental material at [URL will be inserted by AIP] for statistical analysis of the isotropic polarizabilities (Table S1), optimized geometry coordinates of Li_n ($n=2-20$) clusters (Section 2), bond length distributions for the Li_n ($n=11-20$) clusters (Figure S1-S10). [Supplementary Material]

Figure
1

Figure
2

Figure
3

Figure
4