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Equilibrium geometries and electronic properties of Be_nLi (n=2–15) clusters from first principles*

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This paper studies the equilibrium geometries and electronic properties of Be_n and Be_nLi clusters, up to n=15, by using density-functional theory(DFT) at B3LYP/6–31G(d) level. The lowest-energy structures of Be_n and Be_nLi clusters were determined. The results indicate that a single lithium impurity enhances the stability and chemical reactivity of the beryllium clusters. It finds that the geometries of the host clusters change significantly after the addition of the lithium atom for $n \geq 8$. The lithium impurity prefers to be on the periphery of beryllium clusters, and occupies vertex sites. Both Be_4Li, Be_9Li, and $Be_{13}Li$ were found to be particularly stable with higher average binding energy, local peaks of second-order energy difference and fragmentation energies. For all the Be_nLi clusters studied, we found charge transfers from the Li to Be site and co-existence of covalent and metallic bonding characteristics.

Keywords: Be_nLi clusters, DFT, lowest-energy structure, electronic property
PACC: 3640, 3640B, 7115M

1. Introduction

In recent years, atomic clusters have drawn more and more attention[1−4] owing to their fundamental interest in basic research and the possibility of constructing nanostructured materials. Their properties are known to evolve nonmonotonically with size. Many of these properties can be changed by doping the clusters or mixing the clusters with other species. The rich diversity of mixed alloys, especially in extended systems, has led to their widespread application in electronics and electrocatalytic processes.[5] The alkaline-earth-metal element Be is interesting species in that its simplest cluster, dimer exists as van der walls cluster bound by weak dispersion forces. This implies that the bonding character of the clusters must change as the cluster size increases, eventually exhibiting the metallic property of bulk system. As a result, there have been numerous studies in recent years.[6−13] Kolchin *et al* [6] found that small beryllium clusters have characteristics typical of a shell model. Wang *et al* [7] have studied the structural and electronic properties of beryllium clusters up to 21 atoms by using density-functional theory (DFT), they predict that the transition from van der Walls to covalent bonding occurs at about the size n=7 and to metallic bonding at around $n \geq 13$. Srinivas *et al* [9] studied the lowest-energy structure of Be_n ($2 \leq n \leq 9$) clusters considering all possible spin-multiplicity, they found a predominance of higher multiplicity states among the low-energy isomers of the larger clusters. Kawai and Weare[11] studied from van der Waals to metallic bonding: the growth of Be clusters, they predicted that the strong hybridization between s state and d state occurs at n=6. Cerowski and co-workers[13] studied the evolution of the electronic structure of Be clusters, they found that size n=4, 10, 17, 20 are magic numbers of the Be_n clusters. More and more researches indicate beryllium clusters possess much novel and unique properties due to its special electronic configuration.

As far as X-doped beryllium clusters are concerned, there are more investigations reported.[14−17] Ge and co-workers[14] reported the lowest energy structures and electronic properties of $NaBe_n$ (n=1–12) clusters by using DFT. The results show that

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the atomic structures of $NaBe_n$ clusters are significantly different from the host geometries. Wei and co-workers[15] reported the ground structures and electronic properties of Li_2Be_N (N=1–10) clusters by using DFT. The results indicate that the symmetry of Li_2Be_N clusters are lower than that of Be_N clusters. Also, they found that charge transfers from Li to Be site for all clusters and coexistence of van der Waals-like and covalent bonding characteristics for smaller clusters. Thus, it is necessary to study X-doped clusters' properties. Although a number of investigations have been carried out on X-doped beryllium clusters, however, relatively few reports are available on Be_nLi systems. In addition, pure lithium clusters are different in structure from beryllium clusters, then, what will happen when adding one Li atom to beryllium clusters? Much insight can be gained by examining the effect of a monovalent impurity which is doped in a divalent host clusters. So, stimulated by this interesting question and to understand the influence of the alkaline–metal of the impurity atom on the atomic and electronic structures of a Be host cluster, we have carried out a systematic study of Li-doped beryllium clusters Be_nLi (n=2–15) from first-principles. Some of the important properties of these clusters reported in this paper are the geometry, energetics and electronic properties.

This paper is organized as follows. In Section 2, we briefly describe the computational methods employed in this work. The results and discussion are presented in Section 3. Finally, we conclude with a brief summary in Section 4.

2. Computational details

The geometry optimizations of the Be_nLi (n=2–15) clusters are performed by using DFT at the B3LYP/6–31G(d) level. In order to test the reliability of our calculation, the Be_2 dimer is calculated. The theoretical results that Be–Be bond length (2.51Å) (1Å=0.1 nm), binding energy (0.105 eV/atom) and vibrational frequency (278cm^{-1}) are in good agreement with the experimental value of 2.47Å, 0.11 eV and 276 cm^{-1}[18,19] respectively.

All theoretical calculations are performed with GAUSSIAN 03 program package.[20] In order to examine the doping effect, geometry optimizations of the pure beryllium clusters are also calculated by using identical methods and basis sets. For each initial structure, previous studies of the beryllium, lithium, and Be-Li mixed clusters are seen as a guide. The stabilities of Be_n and Be_nLi clusters were examined by the calculation of harmonic frequencies. For each of these clusters, all computed frequencies were confirmed as real. In this paper, spin unrestricted calculations were performed for all allowable spin multiplicities.

3. Results and discussion

3.1. Growth behaviour of different sized Li-doped beryllium clusters

Using the computation details described in Section 2, we obtain some low-lying isomers and determine the lowest-energy structures for Be_nLi clusters up to n=15 (in Fig.1). For comparison, we also use the same method reoptimized the pure Be_n clusters, only the lowest -energy structures are shown in Fig.1. The results of Be_n clusters with $n < 13$ are in good agreement with previous conclusions[6,7,9,12]. For $n \leq 7$, the lowest-energy structures of Be_nLi clusters can be obtained by directly adding one Li atom to the pure Be_n clusters.

For the Be_2Li cluster, the lowest-energy structure is a quasi-linear molecule with Be-Be-Li separation angle 179.3° and binding energy of 0.48 eV/atom (2a). The isosceles triangle with doublet and vertex angle 53.0° (2b), the linear chain Li-centre (Be–Li–Be) (2c) and the isosceles triangle with quartet and vertex angle 47.0° (2d) are higher in energy than the lowest-energy structure at 0.232 eV, 0.538 eV and 0.646 eV, respectively.

In the case of n=3, the most stable geometry of Be_3 is a closed equilateral triangular structure with bond lengths of 2.17Å and binding energy of 0.472 eV/atom ($3a_0$). The value of the bond length is in good agreement with the B3LYP estimate[12] of 2.16Å, the BLYP estimate[7] of 2.18Å. The binding energy is in reasonable agreement with the B3LYP value of 0.47 eV/atom,[12] the BLYP value of 0.48 eV/atom.[7] Adding one Li atom directly to the Be_3, we find that the lowest-energy structure of Be_3Li is a trigonal pyramid with Li atom at apex (3a), similar to Be_4. While the planar rhombus is a metastable isomer (3b) (ΔE=0.704 eV). The other low-lying isomer for Be_3Li is a trigonal pyramid with C_s symmetry (3c), 0.865eV higher than the lowest-energy structure.

The lowest-energy structure found for Be_4 is a

regular tetrahedron with bond lengths of 2.04Å and the T_d symmetry, which can be generated by capping the Be atom on the top site of the stable Be_3 frame, and this is consistent with the previous theoretical[12,7] results. Adding one Li atom on the apex of the stable Be_4 and having a little distortion, we obtain that the lowest-energy structure of Be_4Li is a trigonal bipyramid with Li atom at apex (4a), similar to Be_5. The other three low-lying isomers are the sailing boat-like structure(4b), the quartet pyramid (4c) and the planar structure (4d), respectively. They are higher in total energy by 0.763 eV, 1.548 eV and 2.690 eV than the lowest-energy structure.

For Be_5, its most favourable structure is a trigonal bipyramid with a 1.99Å short bond and a 2.05Å long bond, in agreement with the results obtained by Beyer *et al*[12] and Wang *et al.*[7] Obviously, the configuration of Be_5 can be easily understood as growth on the basis of Be_4 and Be_5Li can be easily understood as growth on the basis of Be_4Li (5a). There are other isomers for Be_5Li (5b)–(5e) (in Fig.1). For example, the slightly distorted square bipyramid with Li at apex structural isomer is higher in energy by 0.141 eV (5b).

In the case of Be_6, its most stable structure is an octahedron with average bond lengths 2.04 Å and is in agreement with the results obtained by Refs.[6, 7]. For Be_6Li, the lowest-energy structure can be obtained by adding one Li atom on the peripheral site of the stable Be_6 and also having a little distortion (6a). It should be pointed out that the Be_6Li (6a) is spin quartet. There are other isomers for Be_6Li (6b)–(6f) (in Fig.1). Such as, when one Be atom in the Be_7 ($7a_0$ in Fig.1) is substituted by Li, a new structure (6d) is formed, but 0.197 eV higher than the lowest-energy structure.

For Be_7, its most favourable structure is a distorted pentagonal bipyramid and is in agreement with the results obtained by Refs.[7, 12]. For Be_7Li, there are two stable structures with little difference in total energy: one is a capped pentagonal bipyramid with Li atom at the capped site (7a), another can be understood as the immediate consequence of nestification during which Be_4Li and Be_4 share a common Be atom (7b) (ΔE=0.003 eV). Their energy difference is so small that both (7a) and (7b) structures being defined as the lowest-energy structures are appropriate. The (7c) structure with C_s symmetry is 0.892 eV higher in energy than the lowest-energy structure.

As far as n=8, the lowest-energy structure Be_8 is a distorted bicapped octahedron structure. Our result is in agreement with the theoretical predictions of Ref.[9]. For Be_8Li, the lowest-energy structure (8a)can be taken as a Li atom which substitutes a Be atom in the most stable Be_9 structure with slight distortion. The (8b) structure is higher in energy by 0.080 eV. It is noteworthy that the (8c) structure which can be viewed as being simply stacked by Be_4Li and Be_4 is only a metastable isomer, whose energy is higher by 0.619 eV. The other isomers (8d) and (8e) are higher in energy by 1.195 eV and 1.426 eV, respectively, and they are all spin sextet.

In the case of Be_9, its most favourable structure is squirrel-cage structure Be_{10} with a missing apex atom. Our result is in agreement with the theoretical predictions by of Ref.[9]. For Be_9Li, the lowest- energy structure (9a) is obtained by a Li atom which substitutes a Be atom in the most stable Be_{10} structure with slight distortion, it also can be taken as growth on the basis of Be_8Li by adding a Be atom. The metastable structure (9b) is higher in energy by 0.140 eV.

The most stable geometry for Be_{10}appears as squirrel-cage structure with high symmetry (S_8). For $Be_{10}Li$, the most stable structure is a distorted icosahedrons with a missing Be atom, it also can be understood as growth on the basis of Be_9Li. The metastable structure (10b) with C_s symmetry and spin sextet is higher in energy by 2.055 eV.

For Be_{11}, the lowest-energy structure can be taken as a cage-like distorted icosahedron structure with a missing Be atom. Our result agrees with the theoretical predictions of Ref.[7]. For $Be_{11}Li$, the most stable structure is a strongly distorted icosahedrons (11a). It is noteworthy that a slightly distorted icosahedron is a metastable isomer of $Be_{11}Li$ (11b) (ΔE=1.550 eV).

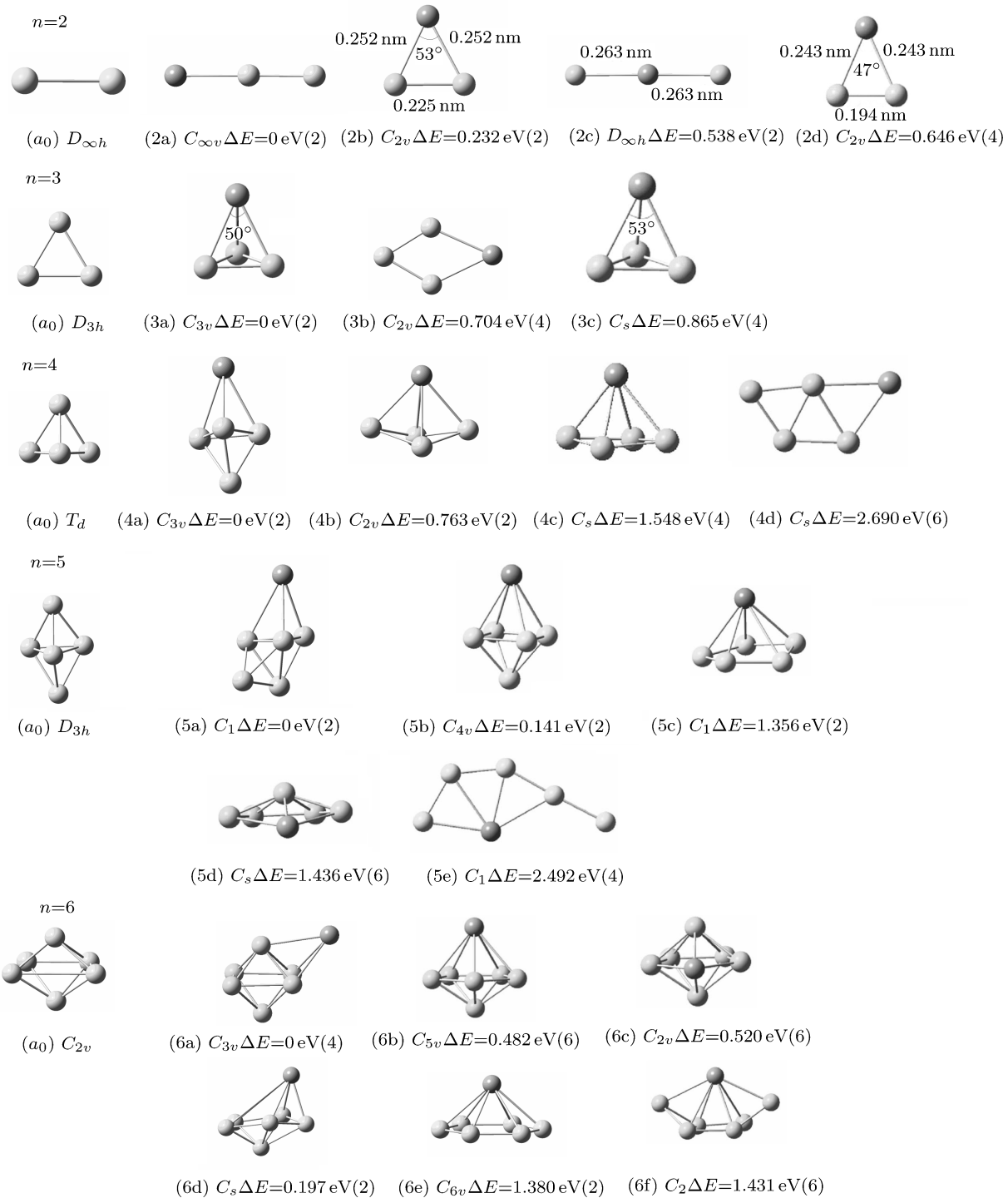
The configuration of Be_{12} is a slightly distorted icosahedron. This structure agrees with the theoretical predictions of Ref.[7]. For $Be_{12}Li$, following the same trend as that of $Be_{11}Li$, we find that its most stable structure is a capped icosahedron with Be atom at the capped site (12a). The (12b) structure with C_1 symmetry and spin sextet is 0.096 eV higher in energy than (12a).

This trend of forming icosahedron structure does not appears at n=13. The most stable structure found for Be_{13} is not an icosahedron but a prolate cage. For the Be_nLi clusters with $n > 12$, the lowest-energy structures follow a prolate pattern with stacks of small unit. For example, the lowest-energy structure of

$Be_{13}Li$ is a stacked structure with 1-4-5-4 layers.

Similar to Be_{13}, the most stable structures for Be_{14} and Be_{15} are also prolate cage which mostly consist of four or five member rings. Similar stacked structure is obtained for $Be_{14}Li$ and $Be_{15}Li$. These equilibrium structures for Be_nLi (n=2–15) imply that formation of layers with four or five member rings is the dominant growth pattern of these larger-sized clusters. Our present results suggest a structural transition from spherical configuration to prolate layered structures around n=13. This must be related to the further hybridization of atomic orbitals and the resulting transition from covalent bonding to metallic bonding at around $n \geq 13$.

According to the above discussion, it is concluded that the lowest-energy structures of all Be_nLi clusters, but n=6, are spin doublet. The lowest-energy structure of Be_6Li is spin quartet. The lithium impurity prefers to be on the periphery of beryllium clusters, and occupies vertex sites.



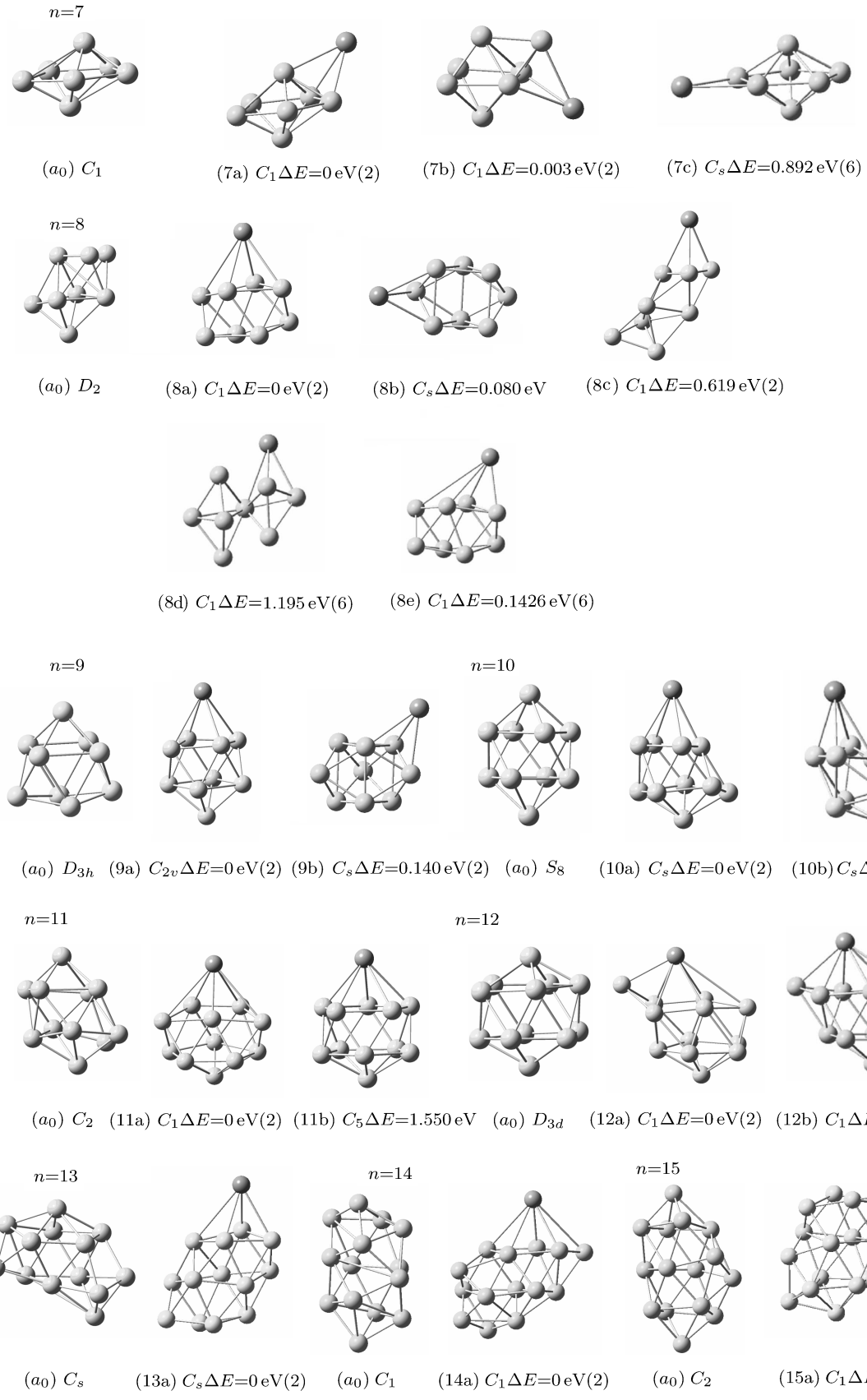


Fig.1. Lowest-energy and low-lying structures of Be_nLi (n=2–15) clusters and lowest-energy structures of pure Be_n (n=2–15) clusters.

3.2. Relative stability and electronic properties of Be_nLi clusters

3.2.1. Relative stability

The relative stability of the different sized clusters can be predicted by calculating the average binding energy and the second-order difference of total energy. The average binding energy for the Be_n and Be_nLi clusters can be defined by the following formula:

$$E'_{\rm b}(n) = \frac{(nE({\rm Be}) - E({\rm Be}_n))}{n}, \quad (1)$$

$$E_{\rm b}(n) = \frac{(nE({\rm Be}) + E\,({\rm Li}) - E({\rm Be}_n{\rm Li}))}{n+1}, \quad (2)$$

where E (Be) and E (Li) represent the energies of free atom Be and Li respectively, E (Be_nLi) and E (Be_n) represent the total energies of the most stable Be_nLi and Be_n clusters, respectively. From Fig.2, it can be seen that the average binding energy generally increases with cluster size. Thus, the clusters can continue to gain energy during the growth process. Moreover, this clearly indicates that the Li doped clusters enhances the binding energy of the host cluster up to n=9. After $n > 9$, the binding energies are close to each other. Furthermore, the star symbol line reveals that the local peaks appears at n=4 and 10. This indicates that Be_4 and Be_{10} are more stable than their neighbours, this observation is consistent with previous studies.[13] However, when Li is doped in the Be_n clusters, as can be seen from Fig.2, the local maxima of $E_b(n)$ appear at the sizes of 4, 9, and 13.

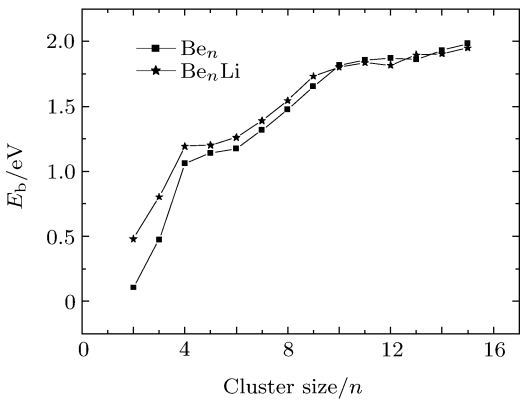


Fig.2. Size dependence of the binding energy per atom of Be_nLi and Be_n clusters.

In Fig.3, we present the second-order difference of total energy for the Be_n and Be_nLi clusters, which are defined by

$$\Delta_2 E'\,[{\rm Be}_n] = -2E\,[{\rm Be}_n] + E\,[{\rm Be}_{n+1}] + E\,[{\rm Be}_{n-1}]\,, \quad (3)$$

$$\Delta_2 E\,[{\rm Be}_n{\rm Li}] = -\,2E\,[{\rm Be}_n{\rm Li}] + E\,[{\rm Be}_{n+1}{\rm Li}] + E\,[{\rm Be}_{n-1}{\rm Li}]\,, \quad (4)$$

where E is the total energy of the system. In cluster physics, the second-order difference of cluster energies is a sensitive quantity that characterizes relative stability of atomic clusters as a function of cluster size.[21] For Be_n clusters, noticeable local peaks were found at n=4, 7, 10 and 13, especially at n=4 and 10, indicating that both Be_4 and Be_{10} clusters should be more stable than the neighbouring clusters, this is consistent with the trend of average binding energies shown in Fig.2. The particularly high stability of Be_4, Be_{10} can be understood in view of the magic numbers of total valence electrons of 8, 20 predicted by the electronic shell model.[22,23] For Be_nLi system, noticeable local peaks were found at n=4, 7, 9, 11 and 13, indicating that these clusters possess higher stability.

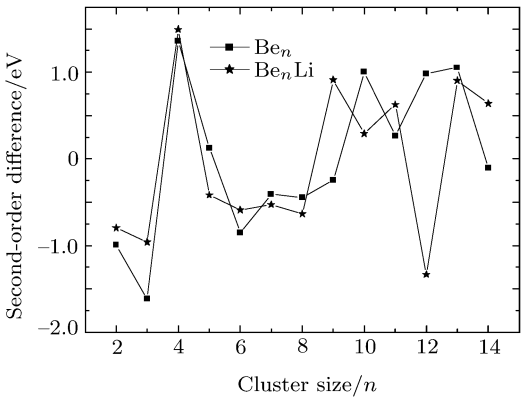


Fig.3. Second-order difference of total energy of Be_nLi and Be_n clusters.

The stability of these clusters is also analysed by examining the fragmentation energies. The calculated fragmentation energies for Be_n and Be_nLi clusters are respectively

$$\Delta' E\,[{\rm Be}_n] = -E\,[{\rm Be}_n] + E\,[{\rm Be}_{n-1}] + E\,[{\rm Be}]\,, \quad (5)$$

$$\Delta E\,[{\rm Be}_n{\rm Li}] = -E\,[{\rm Be}_n{\rm Li}] + E\,[{\rm Be}_{n-1}{\rm Li}] + E\,[{\rm Be}]\,, \quad (6)$$

where E is the total energy of the system. Figure 4 shows the fragmentation energies for the Be_n and Be_nLi clusters. As shown in Fig.4, the local peaks of $\Delta' E$ appear at the size of 4, 10 and 14. However, when Li is doped in the Be_n clusters, this dope is obvious, the local maxima of ΔE appear at the size of 4, 9, and 13, implying that these clusters possess relatively

higher stability, which can also be obtained from Fig.2 and Fig.3.

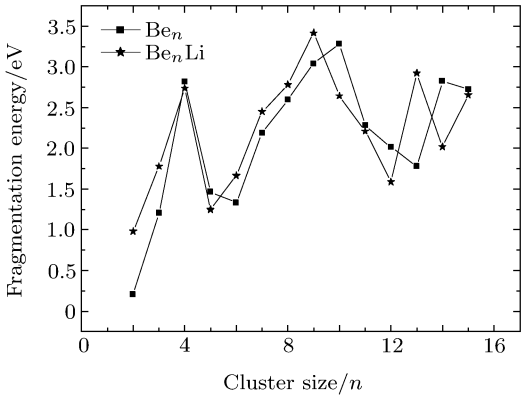


Fig.4. Size dependence of the fragmentation energy of Be_nLi and Be_n clusters.

3.2.2. Electronic properties

In Fig.5, we present the HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gaps for the Be_n and Be_nLi clusters with n=2–15. The energy difference between the HOMO and LUMO is generally considered as an important parameter of the electronic stability of a small cluster.[24] A smaller energy gap indicates larger chemical reactivity. As shown in Fig.5, Be_nLi are usually smaller than those of Be_n clusters except at n=9. This indicates that the Li doped clusters enhance the chemical reactivity of the host cluster.

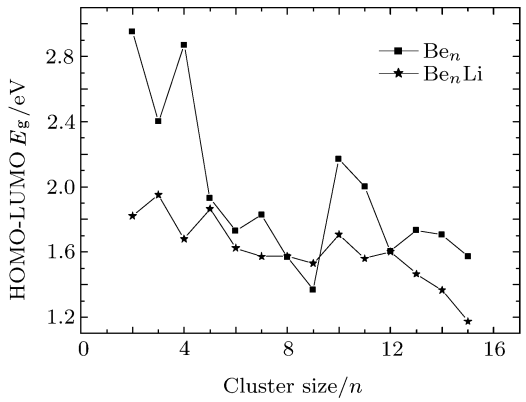


Fig.5. Size dependence of HOMO-LUMO Be_nLi and Be_n clusters.

To gain more information of electronic properties, we consider the natural electronic charges for the lowest-energy structures of the Li atom of the Be_nLi clusters, which are plotted in Fig.6. Since Be is more electronegative than Li atom, the atomic charges on the Li atom is expected to be more positive than the charge on the Be atoms. The calculations confirmed this expectation. Charge always transfers from the Li to the Be atom with the increase of size and indicates that Li acts as an electron donor in all Be_nLi clusters. It can be seen from Fig.6, from n=1 to n=2, there is about 0.027e charge transfer. From n=2 to n=3, there is an abrupt increase. From n=5 to n=13, the charge transfer from the Li atom to the Be atom displays an odd-even oscillation feature and generally increases. The local minima for the different sized Be_nLi clusters can be found at 6, 8, 10, and 12, the local maxima for the different sized Be_nLi clusters can be found at 4, 7, 9, and 11, this finding provides support of our calculated relative stability by aid of the calculated second-order difference of cluster energies. A small amount charge transfers from the Li to the Be site, this fact also implies that Be_nLi clusters may simultaneously possess the covalent and metallic bonding characteristics as the cluster size increases.

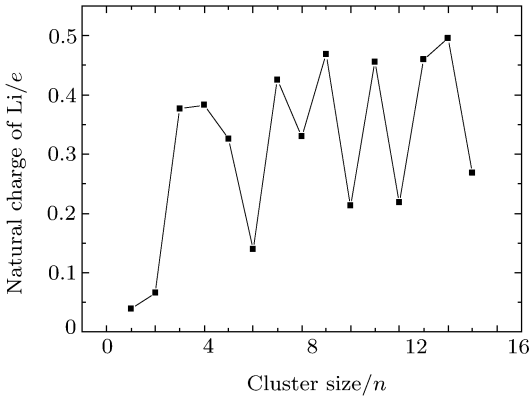


Fig.6. Size dependence of natural charges of Li atom of Be_nLi clusters.

The electronic properties of these clusters is also analysed by examining the results of natural bond orbital analysis (NBO),[25] which is based on the use of localized orbitals constructed from the occupancy-weighted symmetric orthogonalized natural atomic orbitals and provides effective electronic configurations for each atom in a cluster.[26] For examples, in the lowest-energy structures of Be_8Li (8a in Fig.1), Be_9Li (9a in Fig.1), and $Be_{10}Li$ (10a in Fig.1), the natural electron configurations of Li are (core)($2s^{0.64}2p^{0.03}$), (core)(2s$^{0.51}$2p0.02), and (core) ($2s^{0.54}2p^{0.02}$), respectively. It can be easily seen that the Li atom in the Be_9Li cluster offers more electrons to share with Be atoms than that in the Be_8Li and $Be_{10}Li$ clusters. Therefore, the electrostatic interaction between the Li atom and the Be atoms of the Be_9Li cluster is stronger than that for the Be_8Li and $Be_{10}Li$ clusters. This conclusion can further illuminate that the Be_9Li cluster is more stable than the Be_8Li and $Be_{10}Li$ clusters.

Table 1. The geometry, symmetry (Sym), spin multiplicity ($2S+1$), total energy (E_t), average binding energy (E_b), and lowest frequency of Be_nLi (n=2–15) clusters.

n	Geometry	Sym.	$2S+1$	E_t/a.u.	E_b/eV	ω_L/cm^{-1}
2	Linear	$C_{\infty v}$	2	–36.8808202	0.48	139.48
3	Triangular pyramid	C_{3v}	2	–51.6146199	0.80	214.92
4	Trigonal bipyramid	C_{3v}	2	–66.3838034	1.19	209.83
5	Capped trigonal bipyramid	C_1	2	–81.0980567	1.20	135.18
6	Capped square bipyramid	C_{3v}	4	–95.8276344	1.26	190.36
7	Capped pentagonal bipyramid	C_1	2	–110.5789127	1.39	119.26
8	Capped square antiprism	C_1	2	–125.3496211	1.55	74.75
9	Bicapped square antiprism	C_{2v}	2	–140.1436769	1.73	118.17
10	Disorder	C_s	2	–154.9042042	1.80	108.41
11	Distorted icosahedral	C_1	2	–169.6540170	1.84	71.48
12	Distorted capped icosahedral	C_1	2	–184.3808283	1.82	74.09
13	prolate cage	C_s	2	–199.1566968	1.90	132.50
14	prolate cage	C_1	2	–213.8992761	1.90	51.50
15	prolate cage	C_1	2	–228.6653613	1.95	43.01

Finally, as can be seen from Table 1, the harmonic vibrational frequency of all the lowest-energy structures of Be_nLi (n=2–15) clusters are real, this reassured accurately their stabilities.

4. Conclusion

In summary, we have systematically studied the Be_nLi (n=2–15) clusters at the B3LYP level by employing 6–31G(d) basis sets, including their growth behaviours, stabilities and electronic properties. Average binding energies, second-order energy difference, and fragmentation energies are calculated and discussed. From the analysis of second-order energy difference, we know that Be_nLi clusters at n=4, 9, 13 possess relatively higher stability. The results of HOMO-LUMO gaps indicate that the Li doped clusters enhance the chemical reactivity of the host cluster. The natural charges of the Li atom of Be_nLi clusters show that a small amount charge transfers from the Li to the Be site, this fact implies that Be_nLi clusters may simultaneously possess the covalent and metallic bonding characteristics as the cluster size increases.

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