Electronic Supplementary Information (ESI)

Structures and ionization energies of small lithium doped germanium clusters

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The Electronic Supplementary Information contains:

Part A: Experimental supplementary information

- Deconvolution scheme used to analyse the Ge_nLi_m mass spectra
- Additional photo-ionization efficiency curves (Fig. S1 and Table SI)

Part B: Computational supplementary information

- Structures and relative energies of low-energetic cationic and neutral $Ge_nLi_m^{0,+}$ (n = 5−10; m = 1−4) at the B3LYP/6-311+G(d) level of theory (Figs. S2−S7)
- Total and partial density of states of Ge_nLi_m (n = 5−10, m = 0−4) (Fig. S8).
- Shapes of the molecular orbitals of Ge_5Li_m (m = 0−4) (Fig. S9).
- Average lithium adsorption energies of the Ge_nLi_m (n = 5−10, m = 1−4) (Table SII)

Part A

Deconvolution scheme used to analyse the Ge_nLi_m mass spectra

Due to the natural isotope distribution of lithium and germanium, the mass spectra (see Fig. 1) are dominated by broad peaks, which reflect the coexistence of Ge_nLi_m clusters with different amounts of lithium (for a given n). The isotope patterns of different Ge_nLi_m clusters overlap with each other and cannot readily be resolved with our current instrumentation except for the smallest sizes ($n < 5$). To extract information on the intensities of the individual clusters, a deconvolution scheme is applied. A single stoichiometry (Ge_nLi_m) has an isotope pattern, which can be approximated by a Gaussian function for sizes with $n > 5$. Therefore, the convoluted spectrum is modeled as a sum of Gaussian functions, corresponding to the different stoichiometries, superposed on a fixed baseline. The full-width-at-half-max' (*FWHM*) of the Gaussian peaks are known from the natural isotope distribution and the amplitudes are fitting parameters. The integrals I^d from the deconvoluted spectrum can then be derived from the integrals I of the convoluted spectrum by:

$$I_j^d = C_{jj} \sum_i I_i C_{ij}^{'} \qquad (1)$$

The matrix elements are given by:

$$C_{ij} = FWHM_i \left[erf\left(2\sqrt{\ln 2}\, \frac{t_j - t_i + \Delta t}{FWHM_i} \right) - erf\left(2\sqrt{\ln 2}\, \frac{t_j - t_i - \Delta t}{FWHM_i} \right) \right] \qquad (2)$$

The integration interval Δt, the distance between the peaks t_j-t_i and the $FWHM_i$ are known parameters.

Additional photo-ionization efficiency (PIE) curves

Besides those shown in Fig. 2, PIE curves could also be measured for certain clusters that are not treated computationally in the present work. The PIE curves of these Ge_nLi_m clusters are shown in Fig. S1 and the derived ionization energies are listed in Table SI.

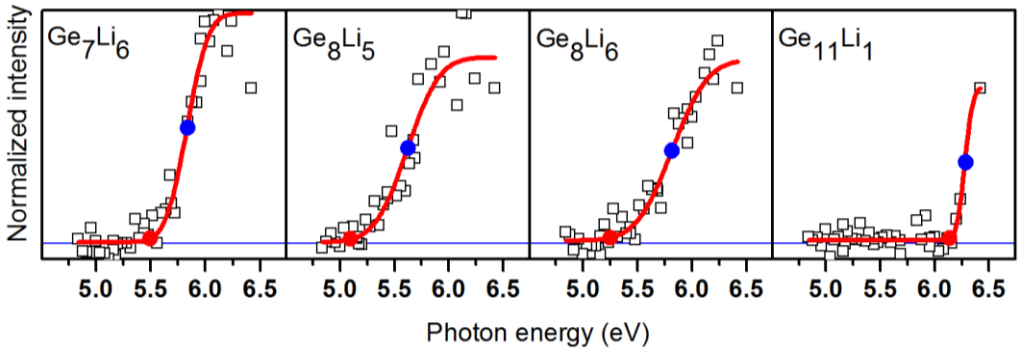


Fig. S1. PIE curves of Ge_7Li_6, Ge_8Li_5, Ge_8Li_6 , and $Ge_{11}Li_1$ clusters. The open squares represent the experimental data, while the solid (red) lines represent smeared-out step functions fitted to the data. The experimental VIE and the ionization threshold are indicated by a blue and a red dot, respectively.

Table SI. Experimentally determined vertical ionization energies (VIE) and ionization thresholds as derived from the PIE curves in Fig. S1 following the produce detailed in the article. The standard error from the fitting procedure is given between brackets.

Cluster	VIE (eV)	Ionization threshold (eV)
Ge_7Li_6	5.83 (0.03)	5.49 (0.12)
Ge_8Li_5	5.62 (0.07)	5.10 (0.38)
Ge_8Li_6	5.82 (0.03)	5.24 (0.15)
$Ge_{11}Li_1$	6.28 (0.03)	6.14 (0.12)

Part B

Structures and relative energies of low-energetic cationic and neutral $Ge_nLi_m^{0,+}$ (n = 5−10; m = 1−4) clusters

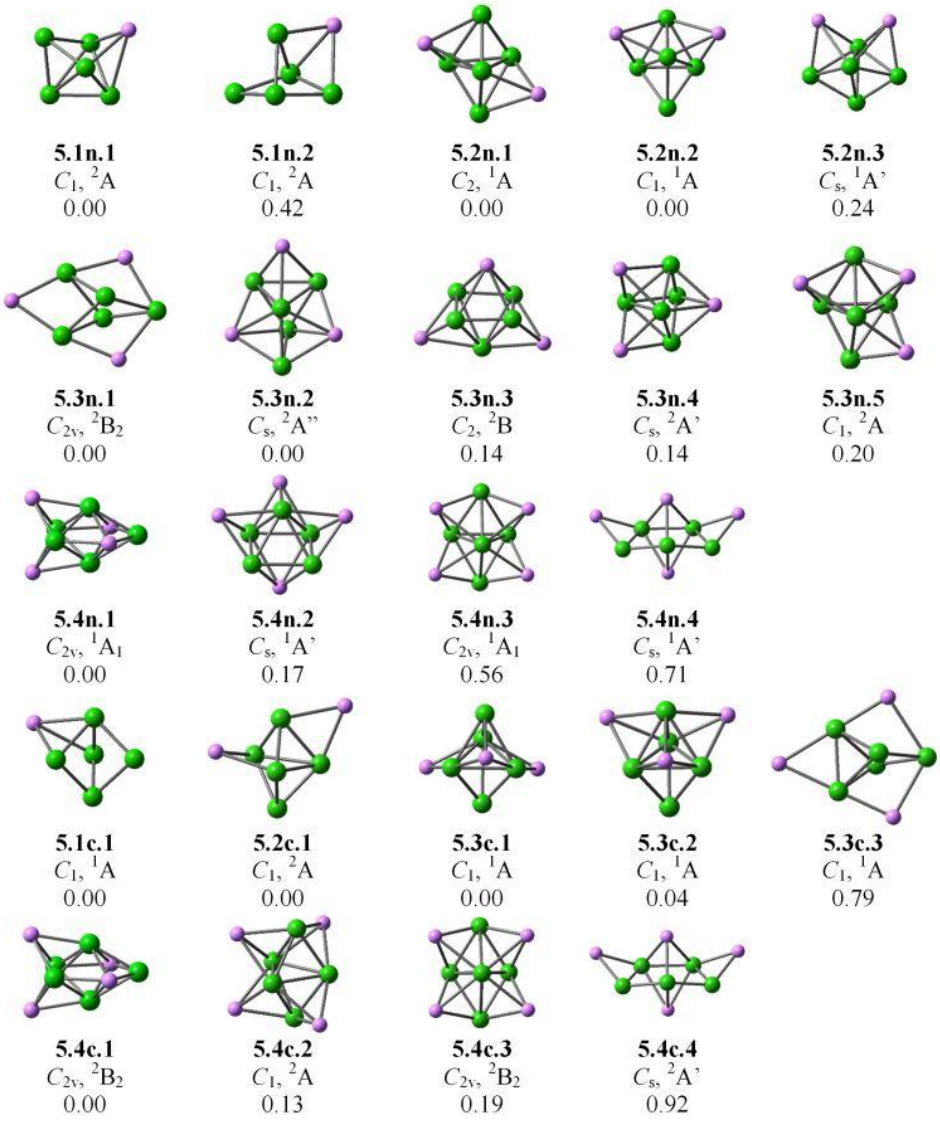


Fig. S2. The shape, relative energy (in eV), and point group of low energetic isomers of $Ge_5Li_m^{0,+}$ (m = 1−4) at the B3LYP/6-311+G(d,p) level.

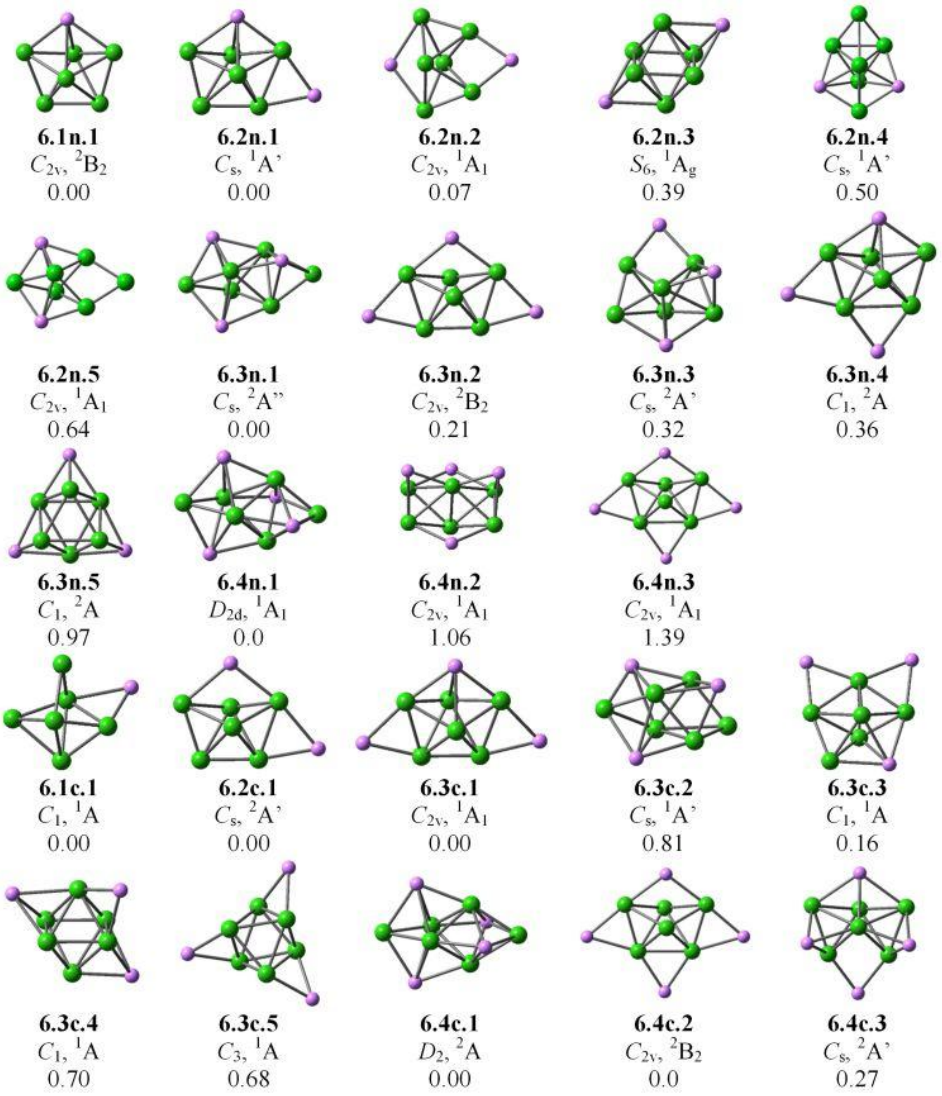
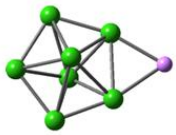


Fig. S3. The shape, relative energy (in eV), and point group of low energetic isomers of $Ge_6Li_m^{0,+}$ (m = 1−4) at the B3LYP/6-311+G(d,p) level.



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C_{2v}, $^2B_2$
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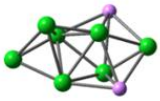

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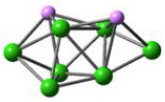

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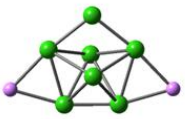

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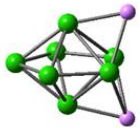

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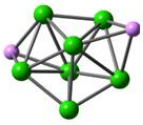

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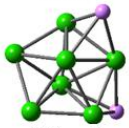

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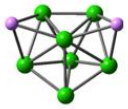

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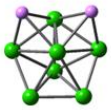

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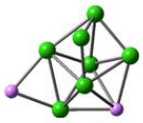

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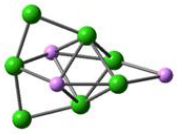

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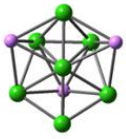

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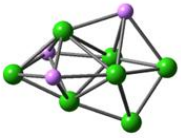

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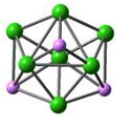

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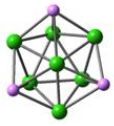

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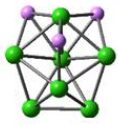

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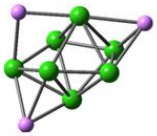

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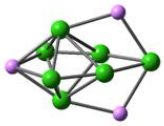

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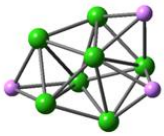

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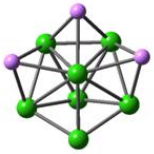

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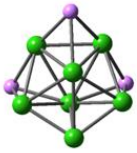

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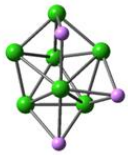

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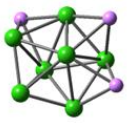

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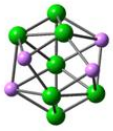

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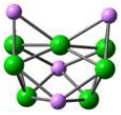

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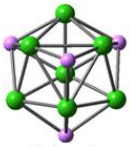

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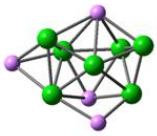

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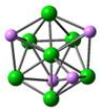

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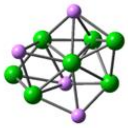

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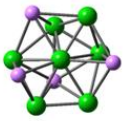

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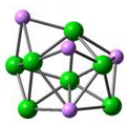

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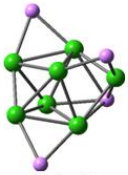

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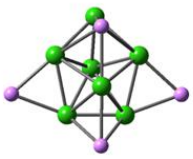

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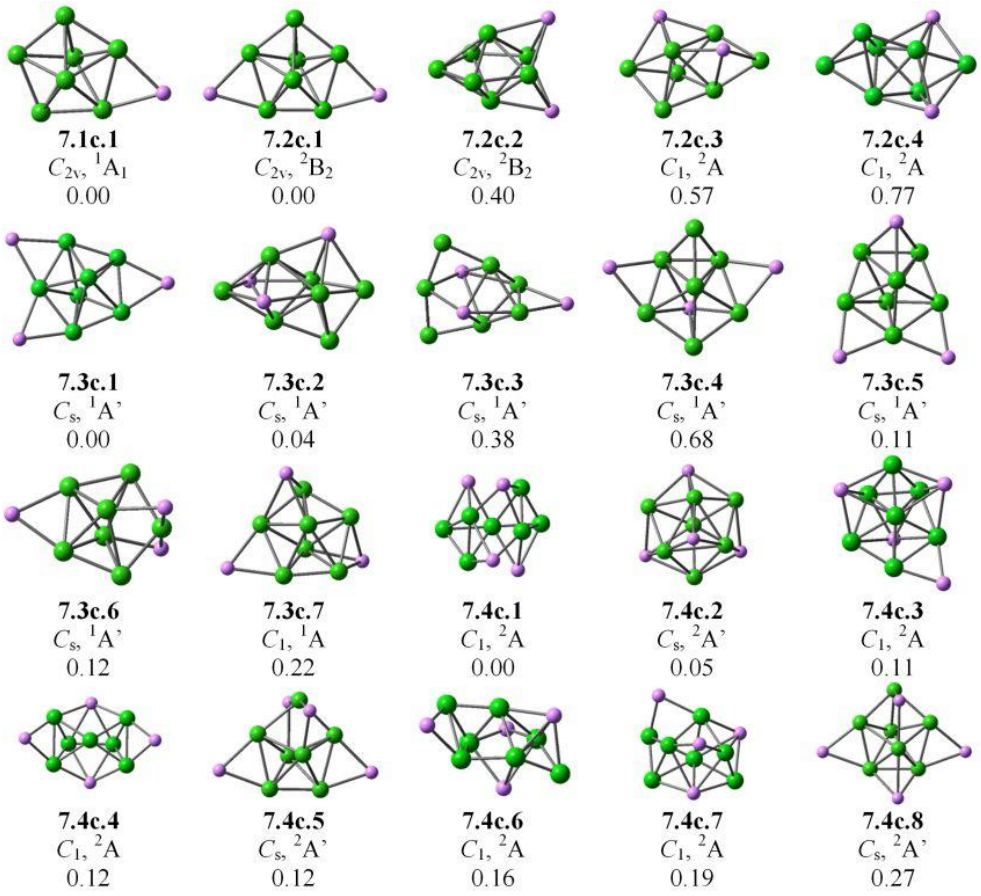
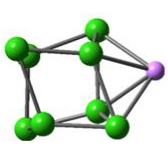


Fig. S4. The shape, relative energy (in eV), and point group of low energetic isomers of $Ge_7Li_m^{0,+}$ (m = 1−4) at the B3LYP/6-311+G(d,p) level.



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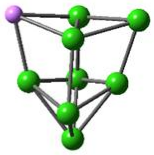

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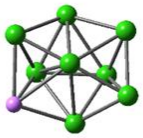

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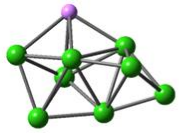

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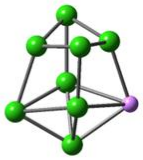

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8.1n.6
C_s, ^{2}A'
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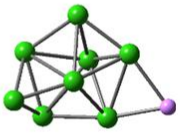

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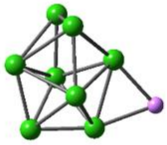

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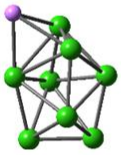
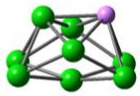
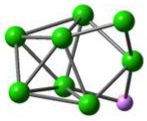
C_1, ^{2}A
0.28



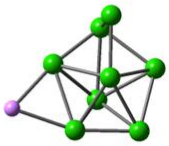
8.1n.9
C_1, ^{2}A
0.35



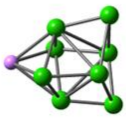
8.1n.10
C_s, ^{2}A'
0.45



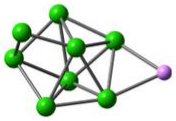
8.1c.1
C_1, ^{1}A
0.00



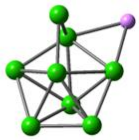
8.1c.2
C_1, ^{1}A
0.04



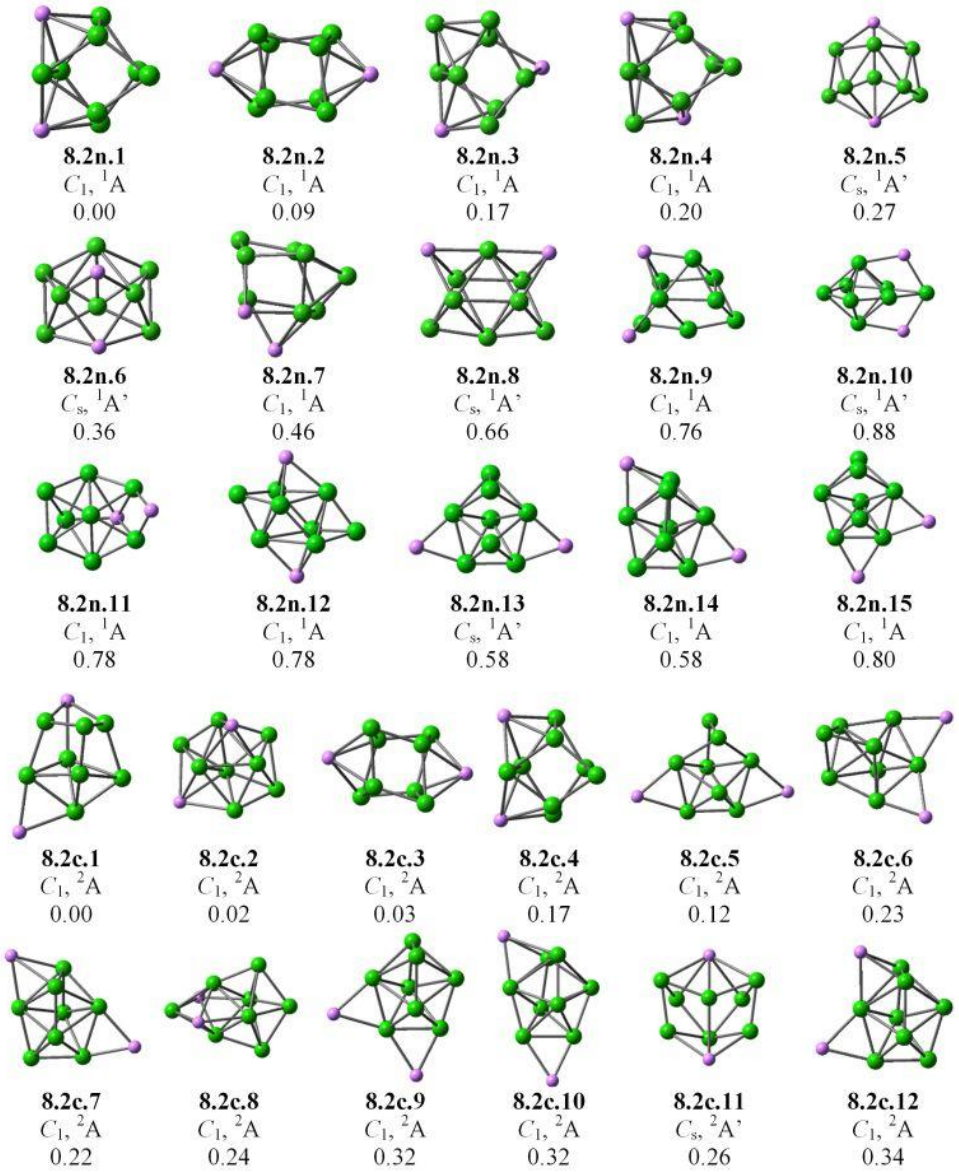
8.1c.3
C_1, ^{1}A
0.38



8.1c.4
C_1, ^{1}A
0.10



8.1c.5
C_1, ^{1}A
0.10



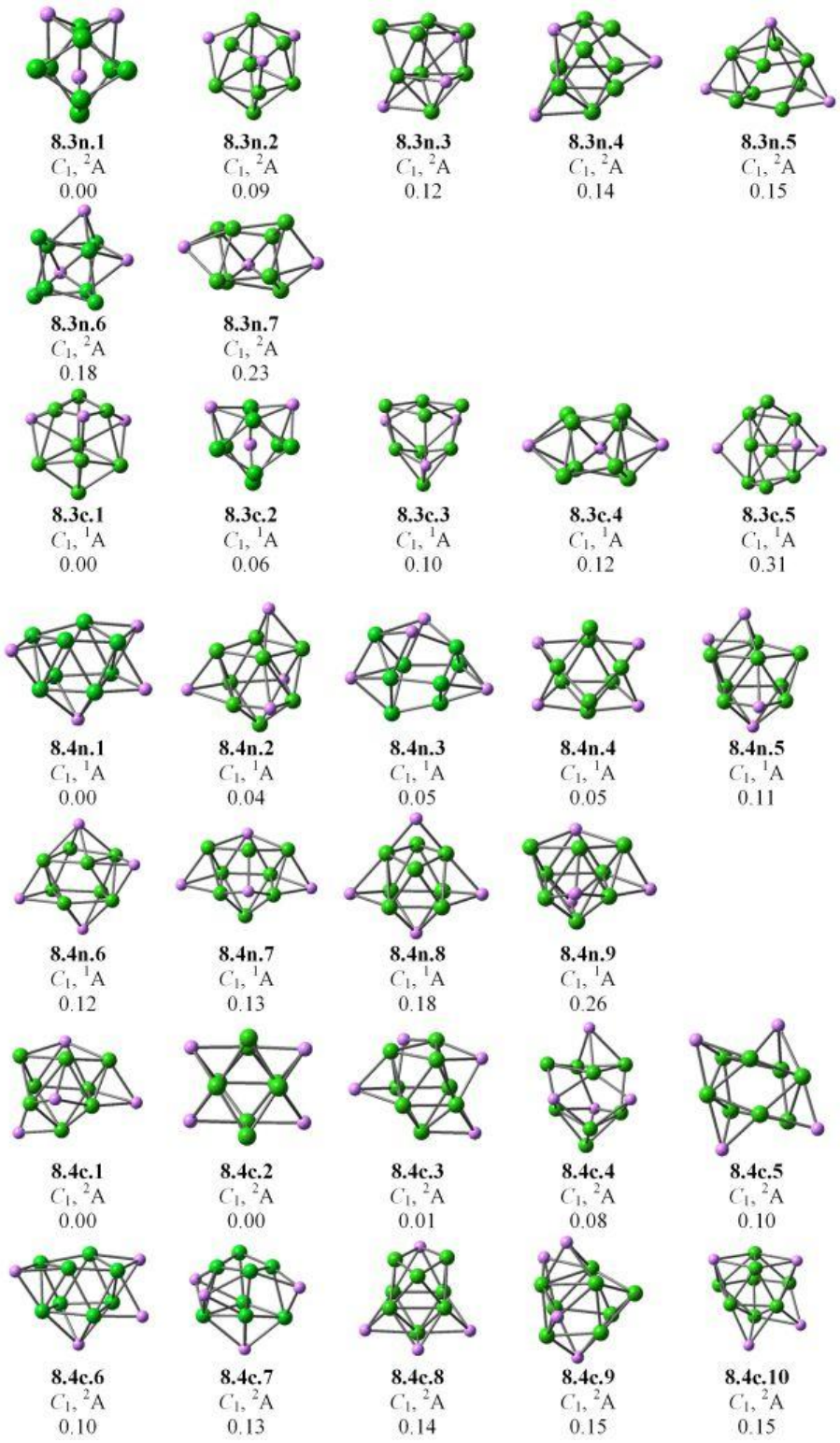
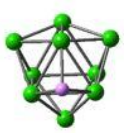
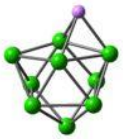


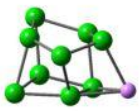
Fig. S5. The shape, relative energy (in eV), and point group of low energetic isomers of $Ge_8Li_m^{0,+}$ (m = 1−4) at the B3LYP/6-311+G(d,p) level.



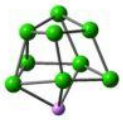
9.1n.1
C_{3v}, $^2A_1$
0.00



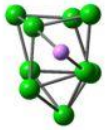
9.1n.2
C_1, ^2A
0.08



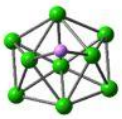
9.1n.3
C_1, ^2A
0.09



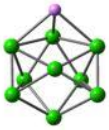
9.1n.4
C_1, ^2A
0.19



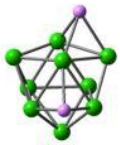
9.1c.1
C_1, ^1A
0.00



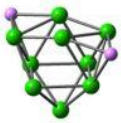
9.1c.3
C_{2v}, $^1A_1$
0.07



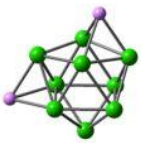
9.1c.4
C_s, $^1A'$
0.14



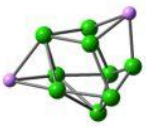
9.2n.1
C_1, ^1A
0.00



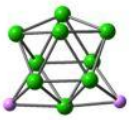
9.2n.2
C_1, ^1A
0.05



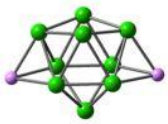
9.2n.3
C_s, $^1A'$
0.03



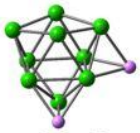
9.2n.4
C_1, ^1A
0.03



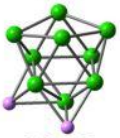
9.2n.5
C_{2v}, $^1A_1$
0.04



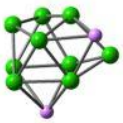
9.2n.6
C_{2v}, $^1A_1$
0.05



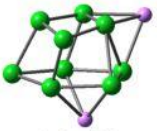
9.2n.7
C_1, ^1A
0.07



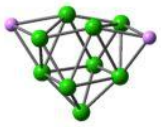
9.2n.8
C_1, ^1A
0.12



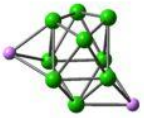
9.2n.9
C_1, ^1A
0.14



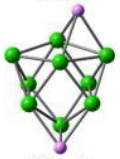
9.2n.10
C_1, ^1A
0.15



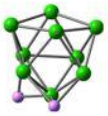
9.2c.1
C_2, ^2B
0.00



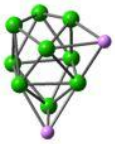
9.2c.3
C_1, ^2A
0.03



9.2c.2
C_1, ^2A
0.08



9.2c.4
C_1, ^2A
0.16



9.2c.5
C_1, ^2A
0.16

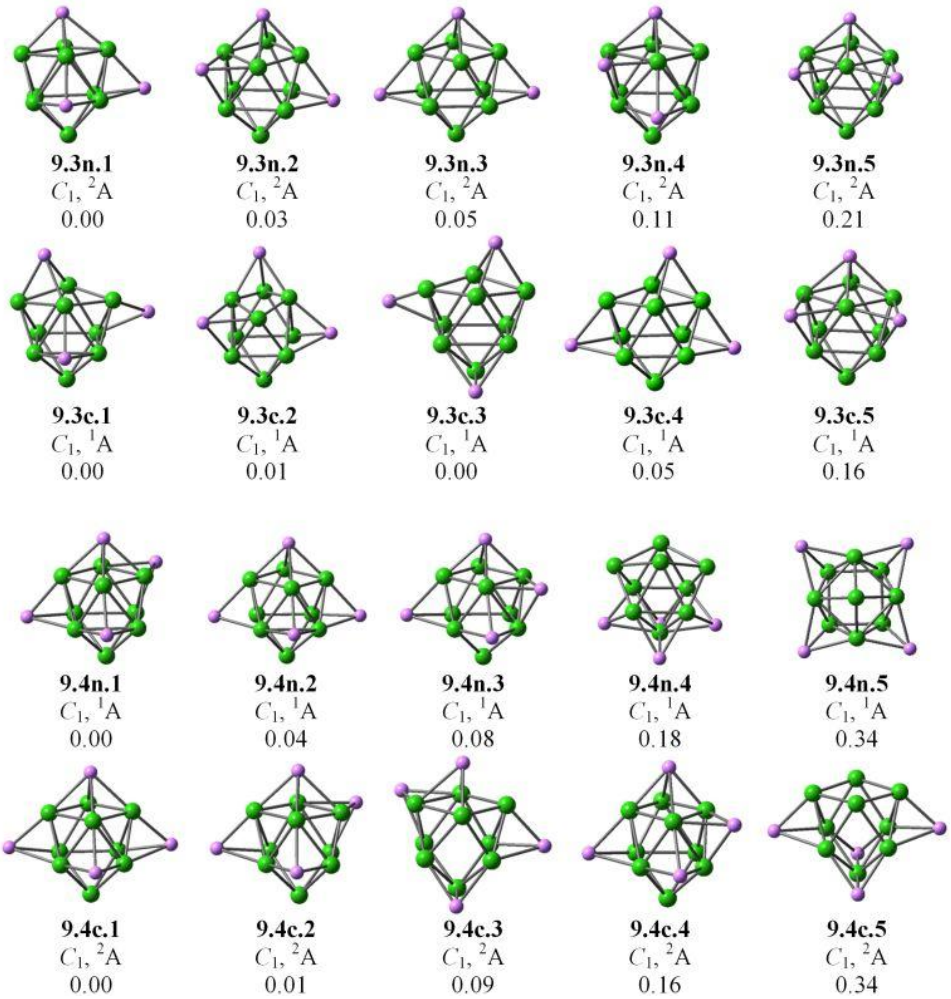
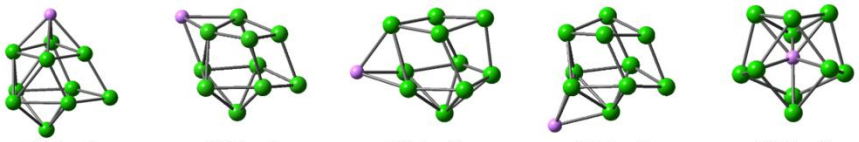


Fig. S6. The shape, relative energy (in eV), and point group of low energetic isomers of $Ge_9Li_m^{0,+}$ (m = 1−4) at the B3LYP/6-311+G(d,p) level.



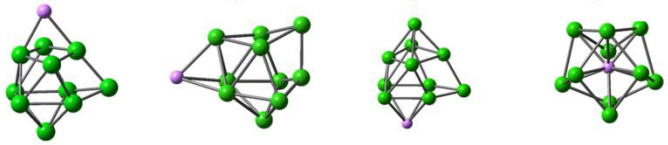
10.1n.1
0.0
C_s, ^{2}A'

10.1n.2
0.03
C_1, ^{2}A

10.1n.3
0.03
C_s, ^{2}A'

10.1n.4
0.05
C_s, ^{2}A'

10.1n.5
0.57
D_{4d}, ^{2}A$_1$

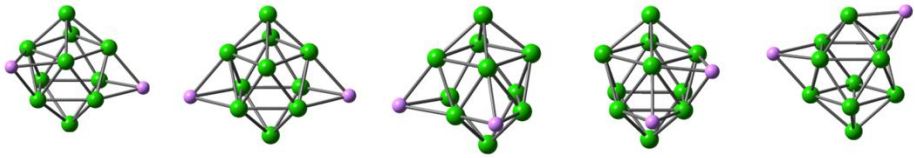


10.1c.1
0.00
C_1, ^{1}A

10.1c.2
0.00
C_1, ^{1}A

10.1c.3
0.53
C_1, ^{1}A

10.1c.4
1.67
D_{4d}, ^{1}A$_1$



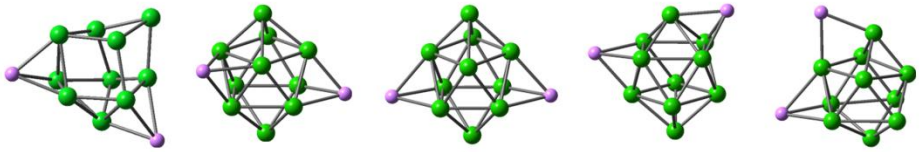
10.2n.1
C_2, ^{1}A
0.00

10.2n.2
C_{2v}, ^{1}A$_1$
0.05

10.2n.3
C_1, ^{1}A
0.05

10.2n.4
C_1, ^{1}A
0.10

10.2n.5
C_s, ^{1}A'
0.11



10.2c.1
C_1, ^{2}A
0.00

10.2c.2
C_2, ^{2}A
0.10

10.2c.3
C_{2v}, ^{2}A$_1$
0.14

10.2c.4
C_s, ^{2}A
0.15

10.2c.5
C_1, ^{2}A
0.18

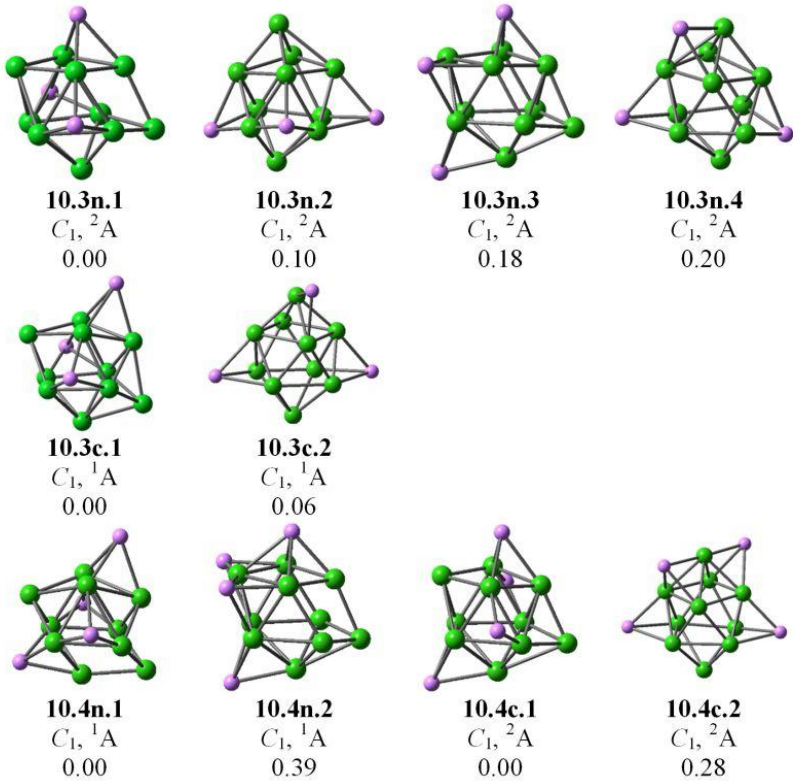


Fig. S7. The shape, relative energy (in eV), and point group of low energetic isomers of $Ge_{10}Li_m^{0,+}$ (m = 1−4) at the B3LYP/6-311+G(d,p) level.

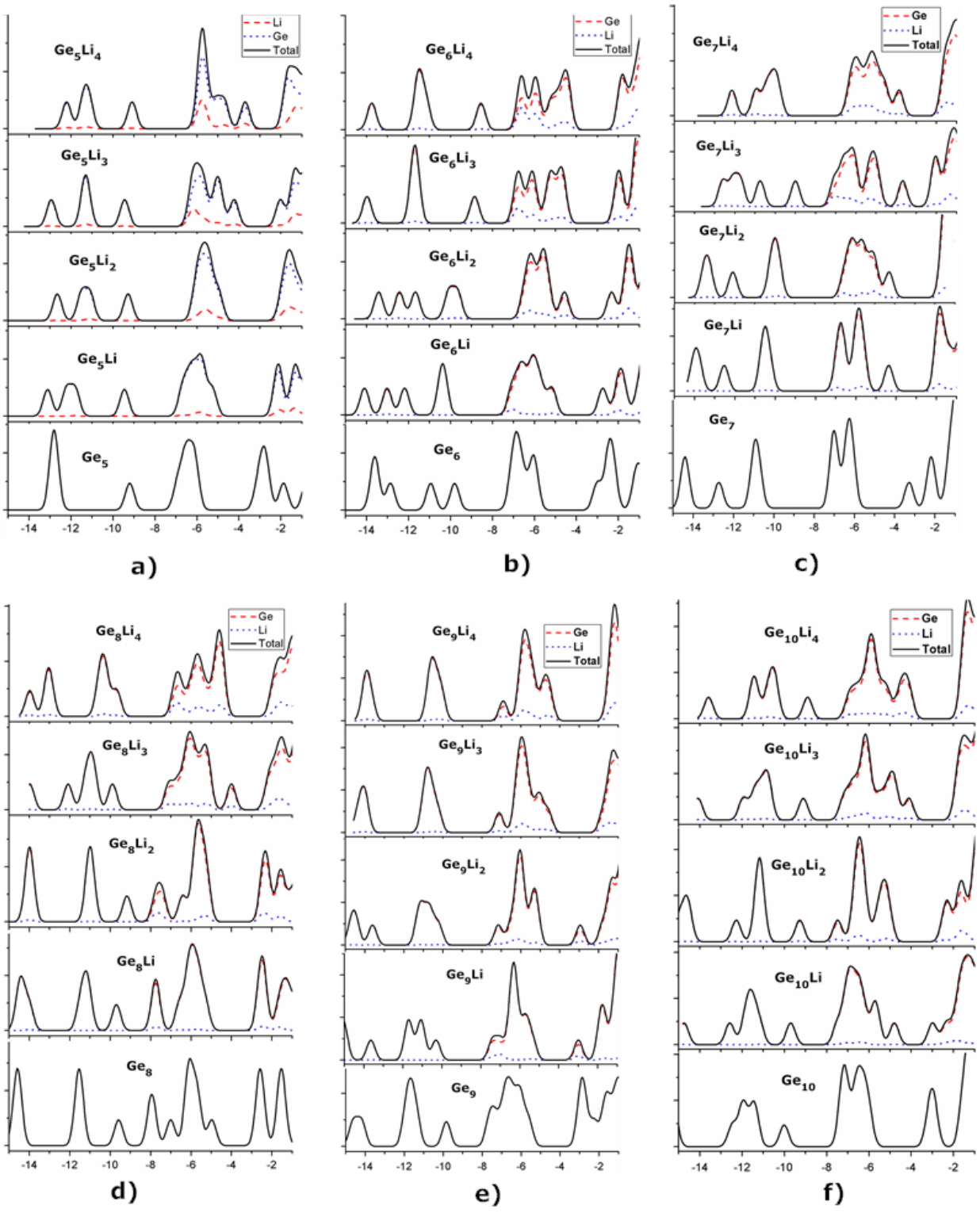


Fig. S8. Total and partial density of states of Ge_nLi_m clusters (n = 5−8, m = 0−4).

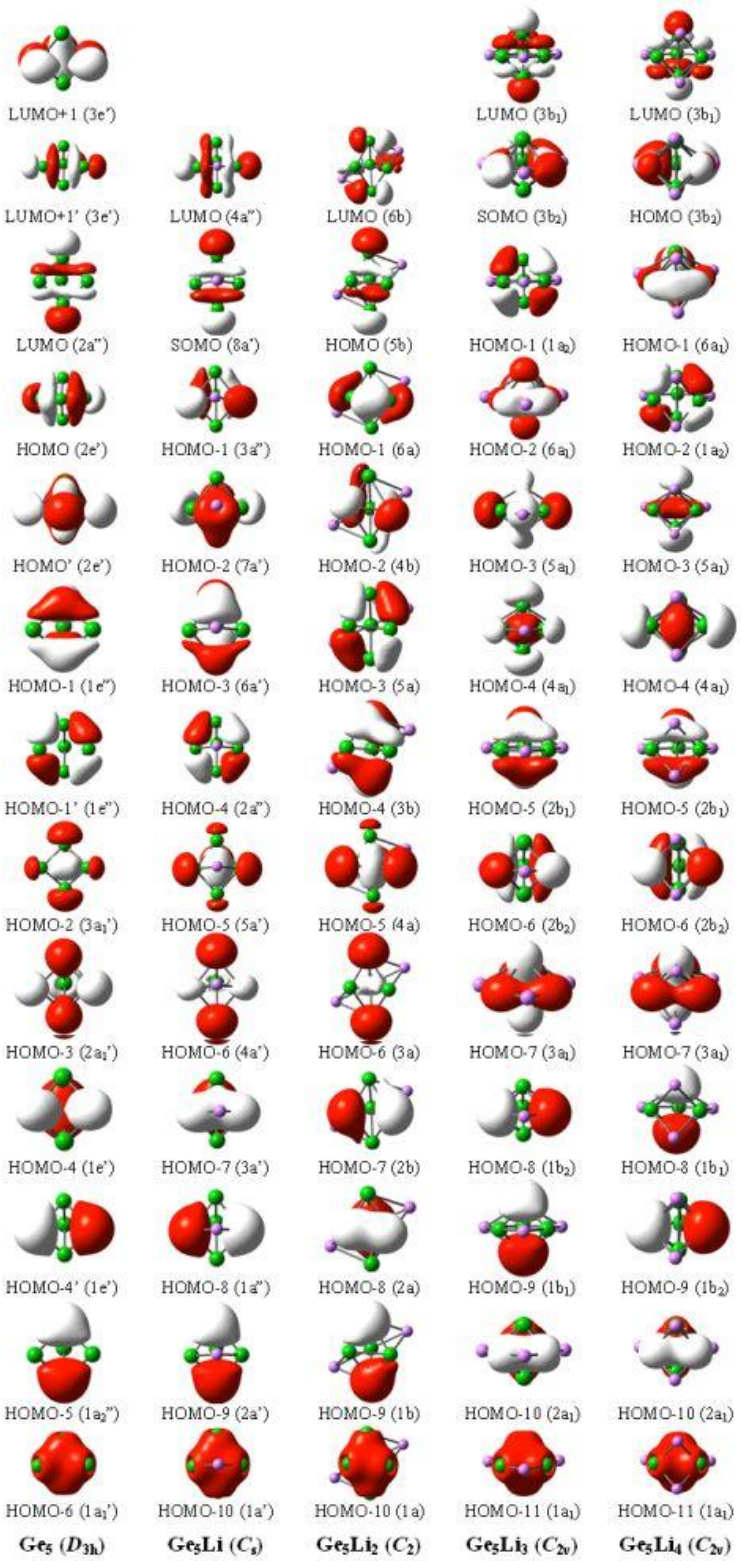


Fig. S9. Shapes of the molecular orbitals of Ge_5Li_m (m = 0−4).

Table SII. Average lithium adsorption energies (E_d, eV) of the Ge_nLi_m (n = 5−10, m = 1−4) clusters at the B3LYP/6-311+G(d) level.

n	E_d **(eV)**			
	Ge_nLi	Ge_nLi_2	Ge_nLi_3	Ge_nLi_4
5	1.95	2.16	1.88	1.84
6	1.71	1.89	1.74	1.89
7	1.44	1.60	1.57	1.74
8	1.82	2.12	1.90	1.93
9	1.8	2.09	1.99	2.09
10	1.42	1.86	1.65	1.67