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A Gaussian-3 Theoretical Study of Small Silicon−Lithium Clusters: Electronic Structures and Electron Affinities of Si_nLi^- ($n = 2-8$)

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The molecular structures of neutral Si_nLi ($n = 2-8$) species and their anions have been studied by means of the higher level of the Gaussian-3 (G3) techniques. The lowest energy structures of these clusters have been reported. The ground-state structures of neutral clusters are "attaching structures", in which the Li atom is bound to Si_n clusters. The ground-state geometries of anions, however, are "substitutional structures", which is derived from Si_{n+1} by replacing a Si atom with a Li^-. The electron affinities of Si_nLi and Si_n have been presented. The theoretical electron affinities of Si_n are in good agreement with the experiment data. The reliable electron affinities of Si_nLi are predicted to be 1.87 eV for Si_2Li, 2.06 eV for Si_3Li, 2.01 eV for Si_4Li, 2.61 eV for Si_5Li, 2.36 eV for Si_6Li, 2.21 eV for Si_7Li, and 3.18 eV for Si_8Li. The dissociation energies of Li atom from the lowest energy structures of Si_nLi and Si atom from Si_n clusters have also been estimated respectively to examine relative stabilities.

1. Introduction

Small silicon clusters have been studied both experimentally and theoretically because of their intrinsic interest from the point of view of chemical structure and bonding.[1] For Si_n clusters, the ground-state structures confirmed by theoretical methods[2−6] and experimental schemes, such as anion photoelectron spectroscopy[7−11] or Raman[1] and infrared measurements,[12] are *line* for Si_2, *isosceles triangle* for Si_3, *rhombus* geometry for Si_4, *trigonal bipyramid* for Si_5, *tetragonal bipyramid* for Si_6, and *pentagonal bipyramid* for Si_7. Although the predicted lowest-energy ground states for larger cluster were found to be dependent on the type of the calculation and also on the optimization technique,[13] many calculations[14−16] showed that the lowest-energy geometries of Si_8 and Si_9 are *distorted bicapped octahedron* and *bicapped pentagonal bipyramid*, respectively. At the MP2(full)/6-31G(*d*) level of theory, the geometries of Si_n ($n = 2-9$) clusters are shown in Figure 1.

Metal−silicon clusters have also attracted a lot of attention in the past decade. Specially, alkali-silicon clusters possess scientific value since it has been known that they serve as promoters in catalysts and can be used as power source material for spaceflight aero-crafts, emitters, and many other products.[17,18] Extensive experimental and theoretical studies on alkali metal−silicon clusters have recently been reported in the literature. For example, the ionization potentials and electron affinities of sodium-doped silicon clusters have been explored by experimental methods and various theoretical schemes.[19,20]

For silicon−lithium clusters, Wang et al.[21] explored the structures of Si_nLi ($n = 2-7$) clusters with the QCISD/6-311+G(*d,p*)//MP2/6-31G(*d*) method. Rabilloud and co-workers[13,22,23] reported the equilibrium geometries and properties of neutral and charged $Si_nLi_p^{(+)}$ ($n \leq 6$, $p \leq 2$) species by means of MP2 and density functional theory (DFT) methodologies. These theoretical studies focused on Si_nLi clusters with ($n \leq 7$) and reported their ionization potentials and equilibrium geometries without electronic state. In principle, structure optimization with electronic state is more rational. As we know, the final structures are decided by electronic state, especially for open-shell species. For anion Si_nLi^-, only the structures and their vertical electron detachment energies have been presented by Li et al.[24] Recently, we have performed DFT calculations and found that some ground-state structures of Si_nLi^- are different from those reported previously.[25]

In this study, we have performed a higher level of *ab initio* calculations in order to investigate the reliable electronic structures and properties, such as electron affinities and dissociation energies, of small silicon−lithium clusters. We have also calculated the electron affinities and dissociation energies of Si_n clusters and compared them with the available experimental values in order to check the reliability of the predicting results.

2. Computational Methods

All of calculations at the Gaussian-3 (G3) theory[26] have been performed using the Gaussian 03 package.[27] The G3 theory is a composite technique in which the geometry optimization is carried out at the MP2(full)/6-31G(*d*) level. The energy, a series of single-point energy calculation at the levels of QCISD(T)/6-31G(*d*), MP4/6-31G(*d*), MP4/6-31+G(*d*), MP4/6-31G(2 *df,p*), and MP2(full)/G3large, is carried out. And then, this energy is modified by a series of corrections. Finally, the HF/6-31G(*d*) vibrational frequencies, scaled by 0.8929, are applied for the zero-point vibrational energy (ZPVE) correction at 0 K. The combined G3 methods are the higher level of *ab initio* calculations of molecular energies of compounds containing first and second row atoms. The average absolute deviation from experiment for the 299 energies including enthalpies of formation, ionization potential, electron affinities, and proton affinities are 1.02 kcal/mol.[26]

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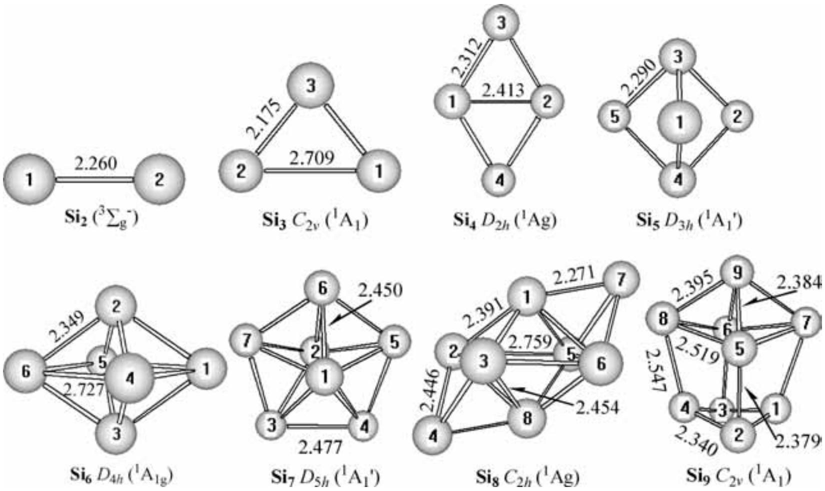


Figure 1. The ground-state geometries for Si_n ($n = 2-9$) obtained at the MP2(full)/6−31G(d) level.

3. Results and Discussion

A. Lowest-Energy Structures and Isomers of Anion Si_nLi^-.

The geometries optimized with the MP2(full)/6-31G(d) method for Si_nLi^- ($n = 2-8$) clusters are displayed in Figure 2, where the relative energies from the lowest-energy isomers calculated with the G3 scheme are also given. The ground-state of all the Si_nLi^- clusters examined is a singlet. Two types of geometric structures are taken into account. One is the "substitutional structure", which can be regarded as being derived from Si_{n+1} by replacing a Si atom with a Li atom (to be more exact, with a negatively charged ion Li^-). And the other is the "attaching structure" in which the Li atom is bound to Si_n geometry. For the "attaching structure", two types of structures are also taken in account. One is the bridge-site type and the other is the apex-site type, in which the lithium atom is bound to one of the silicon atoms. However, it is found that the apex-site type is either a saddle point or a local minimal point on the potential surface. An important fact is that the lowest-energy structures of Si_nLi^- can be regarded as being derived from $Si_{(n+1)}$ by replacing a Si atom with a Li atom, namely the "substitutional structure".

The lowest-energy structure of the Si_2Li^- anion, **2a**, displays C_{2v} symmetry with $^1A_1$ state. For the negatively charged ion Si_3Li^-, there are three isomers. As can be seen from Figure 2, the bridge-site type structure **3a** with C_{2v} symmetry and $^1A_1$ state is more stable in energy than that of the apex-site type structure **3b** by 18.4 kcal/mol. Another isomer, **3c**, with $^1A'$ state, is a saddle point on the potential surface due to having an imaginary 168 i frequency with a″ mode at the MP2(full)/6-31G(d) level of theory. The $^1A'$ state isomer undergoes Jahn−Teller distortion to give a geometry with C_1 symmetry. However, the C_1 isomer is essentially the same as the **3a** structure. It is obvious that both **2a** and **3a** belong to "substitutional structures".

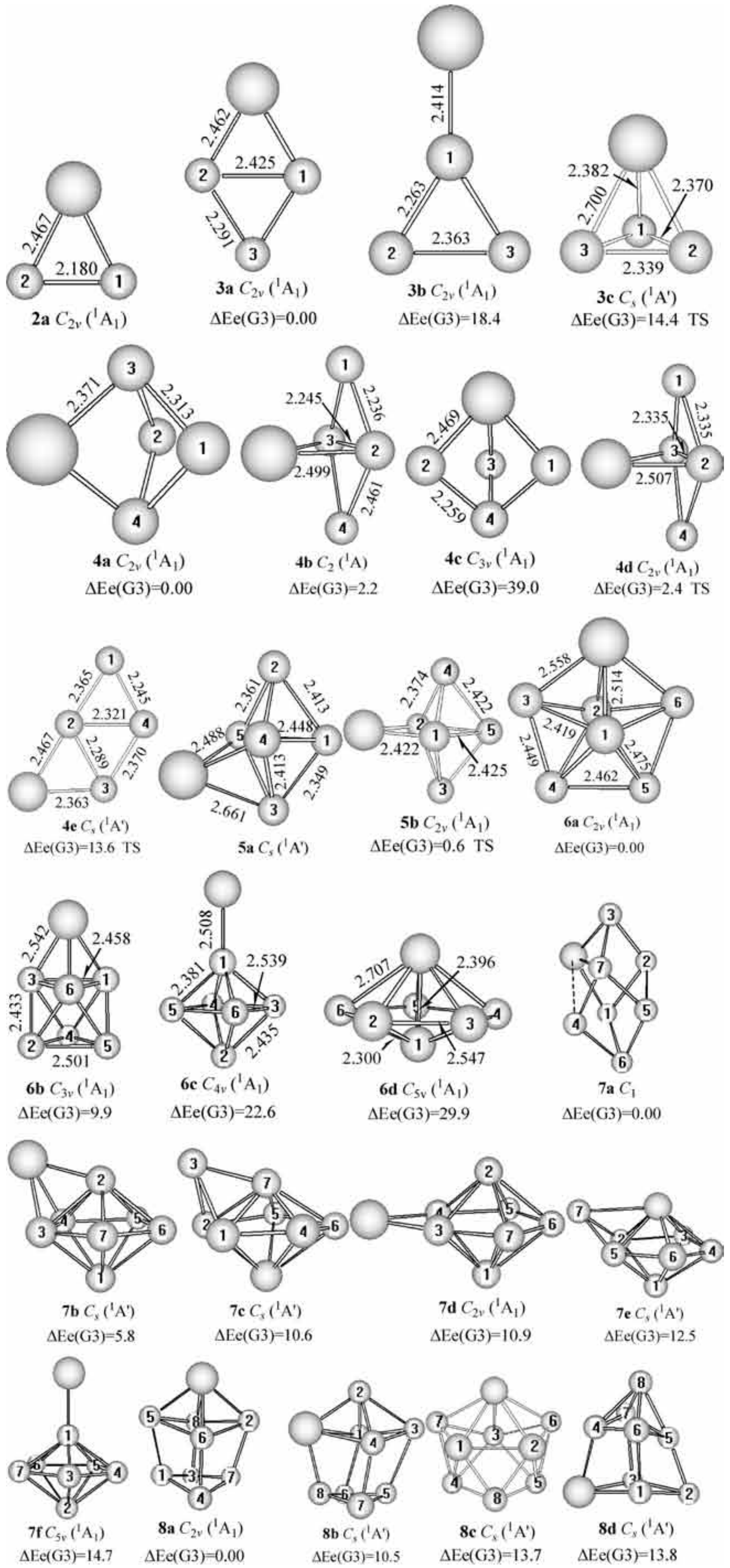
For Si_4Li^-, five isomers are reported in this paper. Both isomers **4a** and **4c** are "substitutional structures", and the remaining isomers, **4b**, **4d**, and **4e**, are "attaching structures". The **4d** isomer with C_{2v} symmetry and $^1A_1$ state is a saddle point on the potential surface due to having an imaginary 286 i cm^{-1} frequency with a_2 mode at the MP2(full)/6-31G(d) level of theory. It undergoes Jahn−Teller distortion to give the C_2-symmetry of ^1A state **4b** isomer. However, the **4b** isomer is higher in energy than the C_{2v}-symmetry of $^1A_1$ state **4a** by 2.2 kcal/mol at the G3 level. The **4e** isomer with C_s symmetry and $^1A'$ state is also a saddle point due to having an imaginary 27i frequency with a'' mode at MP2(full)/6-31G(d) level of theory. It undergoes Jahn−Teller distortion to give a geometry with C_1 symmetry. However, the C_1 isomer is essentially the same as the **4b** structure. The **4c** isomer with C_{3v} symmetry and $^1A_1$ state is a local minimum at the MP2(full)/6−31G(d) level. Energetically, it is higher than the ground-state structure **4a** by 39.0 kcal/mol at the G3 level of theory.

For Si_5Li^-, when a Si atom in Si_6 frame is replaced by negatively charged ion Li−, an isomer with C_{2v} and $^1A_1$ state, **5b**, is obtained. However, vibrational analysis at the MP2(full)/6-31G(d) level yields one imaginary b_1 (70 i cm^{-1}) frequency, indicating distortion to lower symmetry. Following the mode b_1, **5b** collapses to C_s-symmetry of $^1A'$ state **5a**, which is the ground state.

For Si_6Li^-, four isomers are shown in Figure 2. Both isomers **6a** and **6d** are "substitutional structures". Both isomers **6b** and **6c** are "attaching structures". Li et al.[24] reported that the C_{3v} symmetry of $^1A_1$ state isomer **6b**, face-capped Si_6 with Li atom, was the ground-state structure. However, the **6b** isomer is higher in energy than the **6a** with C_{2v} symmetry and $^1A_1$ state by 9.9 kcal/mol, as can be seen from Figure 2. The apex-site-type structure **6c** with C_{4v} symmetry and $^1A_1$ state is a local minimum. Energetically, it is higher than **6a** by 22.6 kcal/mol. The **6d** isomer with C_{5v} symmetry and $^1A_1$ is higher in energy than **6a** by 29.9 kcal/mol.

For Si_7Li^-, six isomers are shown in Figure 2. Three isomers, **7b**, **7d**, and **7f**, are "attaching structures", and the remaining isomers are "substitutional structures". The **7b** isomer with C_s symmetry and $^1A'$ state was thought to be the ground-state in a previous study.[24] However, the **7b** isomer is higher in energy than **7a** with C_1 symmetry by 5.8 kcal/mol. The apex-site-type geometry of **7f** with C_{5v} symmetry and $^1A_1$ state and the bridge-site-type geometry of **7d** with C_{2v} symmetry and $^1A_1$ state are also higher in energy than **7a** by 14.7 and 10.9 kcal/mol, respectively. The C_s symmetry of the $^1A'$ **7c** isomer is less stable than **7a**, namely, "substitutional structure", by 10.6 kcal/mol, and the C_s symmetry of the $^1A'$ **7e** isomer is higher in energy than the ground-state structure **7a** by 12.5 kcal/mol.

For Si_8Li^-, four isomers are shown in Figure 2. Three isomers, **8a**, **8b**, and **8d**, are "substitutional structures". Energetically, the lowest-energy structure, **8a** with C_{2v} symmetry and $^1A_1$ state, is more stable than the C_s symmetry of $^1A'$ state **8b** and **8d** isomers by 10.5 and 13.8 kcal/mol, respectively. The remaining **8c** isomer with C_s symmetry and $^1A'$ state is similar



2a C_{2v} ($^1A_1$)

3a C_{2v} ($^1A_1$) ΔEe(G3)=0.00

3b C_{2v} ($^1A_1$) ΔEe(G3)=18.4

3c C_s ($^1A'$) ΔEe(G3)=14.4 TS

4a C_{2v} ($^1A_1$) ΔEe(G3)=0.00

4b C_2 (^1A) ΔEe(G3)=2.2

4c C_{3v} ($^1A_1$) ΔEe(G3)=39.0

4d C_{2v} ($^1A_1$) ΔEe(G3)=2.4 TS

4e C_s ($^1A'$) ΔEe(G3)=13.6 TS

5a C_s ($^1A'$)

5b C_{2v} ($^1A_1$) ΔEe(G3)=0.6 TS

6a C_{2v} ($^1A_1$) ΔEe(G3)=0.00

6b C_{3v} ($^1A_1$) ΔEe(G3)=9.9

6c C_{4v} ($^1A_1$) ΔEe(G3)=22.6

6d C_{5v} ($^1A_1$) ΔEe(G3)=29.9

7a C_1 ΔEe(G3)=0.00

7b C_s ($^1A'$) ΔEe(G3)=5.8

7c C_s ($^1A'$) ΔEe(G3)=10.6

7d C_{2v} ($^1A_1$) ΔEe(G3)=10.9

7e C_s ($^1A'$) ΔEe(G3)=12.5

7f C_{5v} ($^1A_1$) ΔEe(G3)=14.7

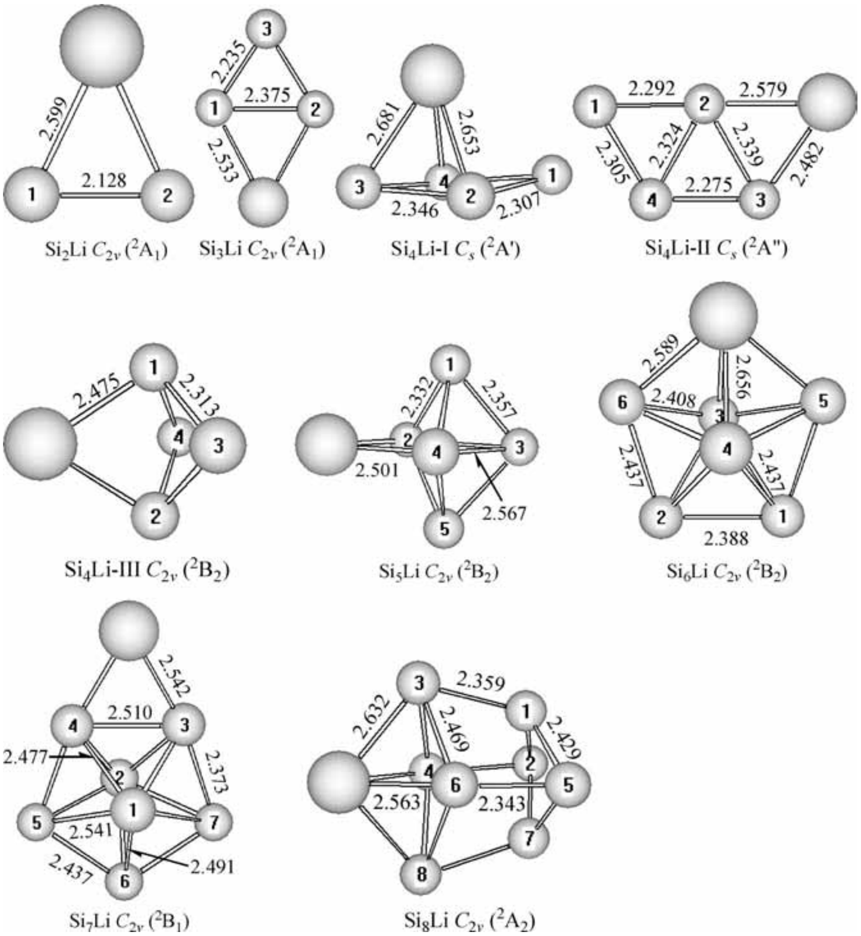
8a C_{2v} ($^1A_1$) ΔEe(G3)=0.00

8b C_s ($^1A'$) ΔEe(G3)=10.5

8c C_s ($^1A'$) ΔEe(G3)=13.7

8d C_s ($^1A'$) ΔEe(G3)=13.8

Figure 2. The anion Si_nLi^- geometries optimized with the MP2(full)/6-31G(*d*) scheme. Only silicon atoms are numbered. The relative energies Δ*Ee*(G3) are obtained at the G3 level without ZPVE correction and in kcal/mol. The structures denoted as "TS" are ones in a transition state. The bond distances for Si_nLi^- ($n = 2-6$) are shown in Angstrom. The Si_7Li^- and Si_8Li^- bond lengths are listed in Tables 1 and 2, respectively.



Si_2Li C_{2v} ($^2A_1$) Si_3Li C_{2v} ($^2A_1$) Si_4Li-I C_s ($^2A'$) Si_4Li-II C_s ($^2A''$)

Si_4Li-III C_{2v} ($^2B_2$) Si_5Li C_{2v} ($^2B_2$) Si_6Li C_{2v} ($^2B_2$)

Si_7Li C_{2v} ($^2B_1$) Si_8Li C_{2v} ($^2A_2$)

Figure 3. Neutral Si_nLi geometries optimized with the MP2(full)/6-31G(*d*) scheme. Only silicon atoms are numbered. Bond lengths are in angstroms.

to the C_1 structure reported by Li et al.[24] However, the **8c** isomer is higher in energy than **8a** by 13.7 kcal/mol.

As discussed above, we concluded that the lowest-energy structures of Si_nLi^- can be regarded as being derived from $Si_{(n+1)}$ by replacing a Si atom with a negatively charged ion Li^-, that is, "substitutional structure". We also pointed out that the ground-state of Si_nBe is same as that of Si_nLi^- because the electronic structure of the anion Li^- is close to that of the Be atom. Of course, further work on Si_nBe is needed to confirm this point of view.

Additionally, the ground-state structures of Si_nLi^- (n = 2,3,5,6,8), **2a**, **3a**, **5a**, **6a**, and **8a**, can also be regarded as being derived from Si_n by attaching to a Li atom. For example, **5a** can be regarded as being derived from Si_5 by face-capping with a Li atom, and the **6a** is derived from Si_6 by edge-capping with a Li atom. The ground-state structures of Si_4Li^- and Si_7Li^- are conclusive evidence that the lowest-energy structures are "substitutional structures".

B. Lowest-Energy Structures and Isomers of Neutral Si_nLi. The geometries optimized with MP2(full)/6-31G(*d*) method for Si_nLi ($n = 2-8$) clusters are displayed in Figure 3. The ground-state of all the Si_nLi clusters examined is a doublet. The geometry of the lowest-energy structure is an "attaching structure" in which the Li atom is bound to at least two silicon atoms. This result is the same as that in previous studies.[13,21-23,25]

At the G3 level, The results for ground-state structures of Si_nLi ($n = 2-6$) with the exception of Si_4Li are the same as those reported previously.[13,21-23,25] The C_{2v}-symmetry Si_2Li has a $^2A_1$ ground-state with a low-lying $^2B_1$ excited state. This latter state is only 4.6 kcal/mol higher in energy at the G3 level of theory. The C_{2v}-symmetry Si_3Li has a $^2A_1$ ground-state with a low-lying $^2B_2$ excited state. Again, the latter state is higher in energy by 16.9 kcal/mol at the G3 level of theory. The ground-state geometry of Si_5Li and Si_6Li displays C_{2v} symmetry with $^2B_2$ state.

Three minima for Si_4Li are shown in Figure 3. Both Si_4Li-I and Si_4Li-II display C_s symmetry, whereas the former is $^2A'$ state, and the later is $^2A''$ state. The $^2A''$ state is higher in energy than the $^2A'$ state by 1.0 kcal/mol (or 1.2 kcal/mol including ZPVE correction) at the G3 level of theory. This result is different from those reported previously.[13,21-23,25] We have also performed DFT calculations. At the B3LYP level with G3 large basis set, the planar structure of $^2A''$ state is lower in energy than that of the $^2A'$ state by 0.8 kcal/mol. All of these show that the potential energy surfaces of Si_4Li are very flat, and many isomeric arrangements are possible. The C_{2v} symmetry of the $^2B_2$ Si_4Li-III isomer with its corresponding anion is higher in energy than the Si_4Li-I geometry by 10.56 kcal/mol at the G3 level of theory.

For Si_7Li, the lowest energy structure displays C_{2v} symmetry with $^2B_1$ state. The C_1 geometry (resembling **7a**) is higher in energy than that of the ground-state structure by 11.5 kcal/mol (or 11.2 kcal/mol including ZPVE correction) at the G3 level. For Si_8Li, the lowest energy structure has C_{2v} symmetry with $^2A_2$ state.

The distances between Li and Si atoms in neutral geometries are longer than in anion geometries. For example, the Li−Si bond lengths of Si_2Li and Si_3Li are longer than the correspond-

TABLE 1: Bond Lengths in Angstroms for Si_7Li^- Isomers Calculated at the MP2(full)/6-31G(d) Level

isomers	bond	bond length	isomers	bond	bond length
7a (C_1)	1Si−2Si	2.497	**7c** (C_s)	3Si−7Si	1.380
	1Si−4Si	2.460		4Si−6Si	2.473
	1Si−6Si	2.319		4Si−7Si	2.432
	1Si−Li	2.480		4Si−Li	2.660
	2Si−3Si	2.364		6Si−7Si	2.479
	2Si−5Si	2.501		6Si−Li	2.552
	3Si−7Si	2.272	**7d** (C_{2v})	1Si−3Si	2.561
	3Si−Li	2.615		1Si−6Si	2.577
	4Si−6Si	2.470		1Si−7Si	2.638
	4Si−7Si	2.368		3Si−4Si	2.433
	4Si−Li	3.447		3Si−7Si	2.328
	5Si−6Si	2.361		6Si−7Si	2.366
	5Si−7Si	2.422		3Si−Li	2.460
	7Si−Li	2.536	**7e** (C_s)	1Si−2Si	2.419
7b (C_s)	1Si−3Si	2.560		1Si−3Si	2.648
	1Si−6Si	2.595		1Si−4Si	2.470
	1Si−7Si	2.643		2Si−3Si	2.343
	2Si−3Si	2.564		2Si−5Si	2.583
	2Si−6Si	2.527		2Si−7Si	2.306
	2Si−7Si	2.539		2Si−Li	2.503
	2Si−Li	2.461		3Si−4Si	2.378
	3Si−4Si	2.437		3Si−Li	2.603
	3Si−7Si	2.369		4Si−Li	2.583
	6Si−7Si	2.394		7Si−Li	2.907
7c (C_s)	1Si−2Si	2.427	**7f** (C_{5v})	1Si−3Si	2.470
	1Si−3Si	2.449		2Si−3Si	2.580
	1Si−4Si	2.419		3Si−4Si	2.412
	1Si−7Si	2.429		1Si−Li	2.573
	1Si−Li	2.489			

TABLE 2: Bond Lengths in Angstroms for Si_8Li^- Isomers Calculated at the MP2(full)/6-31G(d) Level

isomers	bond	bond length	isomers	bond	bond length
8a	1Si−3Si	2.389	**8c**	1Si−8Si	2.452
	1Si−5Si	2.395		1Si−Li	2.729
	2Si−6Si	2.435		3Si−4Si	2.543
	2Si−Li	2.540		3Si−6Si	2.393
	8Si−Li	2.494		3Si−Li	2.594
	3Si−8Si	2.364		4Si−7Si	2.393
8b	1Si−2Si	2.361		4Si−8Si	2.509
	1Si−3Si	2.379		6Si−Li	2.700
	1Si−6Si	2.421	**8d**	1Si−2Si	2.397
	1Si−Li	2.782		1Si−6Si	2.551
	2Si−3Si	2.555		1Si−Li	2.547
	2Si−Li	2.465		2Si−5Si	2.270
	3Si−5Si	2.671		4Si−6Si	2.413
	5Si−7Si	2.348		4Si−8Si	2.412
	7Si−8Si	2.314		4Si−Li	2.532
	8Si−Li	2.541		5Si−6Si	2.505
8c	1Si−2Si	2.821		5Si−8Si	2.375
	1Si−4Si	2.453		6Si−8Si	2.487
	1Si−7Si	2.330			

ing anion by 0.13 and 0.07 Å, respectively. The reason (based on the reported Si_nNa system described by Kishi et al.[20]) is that the additional electron going into the singly occupied molecular orbital (SOMO) of the neutral Si_nLi becomes doubly occupied in the anion, which localizes mainly on the Si_n framework. However, the electron back-donation from the Si_n framework to the Li atom is induced and makes the bond between the Si_n and Li atoms strong.

C. Electron Affinities. The adiabatic electron affinities (EA) (defined as the difference of total energies in the manner EA = E(optimized neutral) − E(optimized anion)) of Si_n and Si_nLi clusters are calculated and filled in Tables 3 and 4, respectively, at the G3 level of theory.

TABLE 3: Adiabatic Electron Affinities for Si_n Clusters[a]

species	EA_0	EA_n	EA_0(MP2)	exp.
Si_2 ($^3\Sigma_g^- \leftarrow {}^2\Pi_u$)	2.20(50.8)	2.21(50.9)	2.20	2.20 ± 0.01[b]
Si_3 ($^1A_1 \leftarrow {}^2A_1$)	2.30(52.5)	2.29(52.2)	2.29	2.29 ± 0.002[c]
Si_4 ($^1A_g \leftarrow {}^2B_{2g}$)	2.18(50.4)	2.18(50.2)	2.18	2.13 ± 0.001[c]
Si_5 ($^1A_1' \leftarrow {}^2A_2''$)	2.47(57.0)	2.48(57.2)		2.59 ± 0.02[c]
Si_6 ($^1A_{1g} \leftarrow {}^2A_{2u}$)	2.08(48.0)	2.09(48.3)		2.00 ± 0.02[d]
Si_7 ($^1A_1' \leftarrow {}^2A_2''$)	1.87(43.0)	1.87(43.0)		1.85 ± 0.02[c]
Si_8 ($^1A_g \leftarrow {}^2A_2$)	2.44(56.4)	2.45(56.6)		2.36 ± 0.1[e]

[a] Presented in eV (kcal/mol in parentheses). EA_0 is electron affinity with ZPVE correction at the HF level, and EA_n is without. EA_0(MP2) is electron affinity with ZPVE correction at the MP2(full)/6-31G(d) level. At the MP2(full)/6-31G(d) level, the geometries of the ground state of the anion Si_n^- (n = 2−7) are similar to those of the corresponding neutral. For anion Si_8^-, the geometries are C_{3v} symmetry. Also refer to refs 1, 4, 6, and 9. [b] Reference 7. [c] Reference 9. [d] Reference 20. [e] Reference 10.

TABLE 4: Adiabatic Electron Affinities for Si_nLi Clusters[a]

species	EA_0	EA_n	EA_0 (MP2)	EA_0 (B3LYP)[b]	EA_n (B3LYP)[b]	ΔEA_0
Si_2Li	1.87(43.2)	1.87(43.2)	1.88	1.79	1.79	−0.33
Si_3Li	2.06(47.5)	2.08(48.0)	2.06	1.97	1.99	−0.21
Si_4Li	2.01(46.4)	2.03(46.8)	2.02	1.78	1.79	−0.17
Si_5Li	2.61(60.3)	2.62(60.5)		2.46	2.47	0.14
Si_6Li	2.36(54.4)	2.38(54.8)		2.24	2.25	0.28
Si_7Li	2.21(51.0)	2.21(50.9)		2.23	2.23	0.34
Si_8Li	3.18(73.3)	3.21(74.0)		2.98	3.01	0.74

[a] Presented in eV (kcal/mol in parentheses). EA_0 is electron affinity with ZPVE correction, and EA_n is without. EA_0(MP2) is electron affinity with ZPVE correction calculated at the MP2(full)/6-31G(d) level. $\Delta EA_0 = EA_0(Si_nLi) - EA_0(Si_n)$. [b] The EA is calculated with the B3LYP/DZP++ scheme. EA_0 is reported in ref 25. EA_n is first presented in this work.

As can be seen from Table 3, the energy differences between EA with ZPVE correction and EA without are within 0.01 eV, and the theoretically predicted EAs are in good agreement with the experimental values (taken from refs 7, 9, 10, and 20). The average absolute deviations from experiment for EA of Si_n (n = 2−8) are 0.05 eV. The largest deviations by 0.11−0.12 eV are Si_5 clusters. For Si_8, we have performed previously calculations at various DFT levels of theory with DZP++ basis sets. The deviations from experiment for EA are more than 0.50 eV.[6] However, the deviations are only 0.08−0.09 eV at the higher level of the G3 calculation. Hence, poor DFT results are obtained for Si_8.

For Si_nLi (n = 2−8) clusters, the EA_0 (including ZPVE correction) is predicted to be 1.87 eV for Si_2Li, 2.06 eV for Si_3Li, 2.01 eV for Si_4Li, 2.61 eV for Si_5Li, 2.36 eV for Si_6Li, 2.21 eV for Si_7Li, and 3.18 eV for Si_8Li, as can seen from Table 4. The average value difference between the G3 EA_0 and the B3LYP/DZP++ EA_0 (listed in Table 4) is 0.11 eV, and the average value difference between the G3 EA_0 and the B3LYP EA_n (excluding ZPVE correction) is 0.098 eV for Si_nLi with the exception of Si_4Li (At the B3LYP level, the ground-state structure of Si_4Li is a planar structure of $^2A''$ state, which differs from $^2A'$ state predicted with the G3 scheme, as discussed above). This indicates that the EA without ZPVE correction predicted by the B3LYP method is more consistent with the G3 result with ZPVE correction. There are no experimental values for comparison.

It is interesting to note that (i) the EA of Si_nLi clusters is lower than that of the corresponding Si_n at the cluster size $n \leq 4$, whereas it is higher at $n \geq 5$, and (ii) the EA differences between Si_nLi and Si_n increase with increasing cluster size (see the last column in Table 4).

TABLE 5: Dissociation Energies (D_e) for the Neutral Si_n and Si_nLi Species[a]

dissociation	D_e	D_e(MP2)	exp.	dissociation	D_e	D_e(MP2)
$Si_2 \rightarrow Si + Si$	3.29(75.9)	3.29	3.21[b]	$Si_2Li \rightarrow Si_2 + Li$	2.75(63.5)	2.73
$Si_3 \rightarrow Si_2 + Si$	4.21(97.1)	4.20	4.09[c]	$Si_3Li \rightarrow Si_3 + Li$	2.41(55.7)	2.41
$Si_4 \rightarrow Si_3 + Si$	4.55(104.9)	4.54	4.60 ± 0.15[d]	$Si_4Li \rightarrow Si_4 + Li$	1.99(45.8)	1.97
$Si_5 \rightarrow Si_4 + Si$	4.28(98.6)			$Si_5Li \rightarrow Si_5 + Li$	2.50(57.6)	
$Si_6 \rightarrow Si_5 + Si$	4.62(106.6)			$Si_6Li \rightarrow Si_6 + Li$	2.07(47.8)	
$Si_7 \rightarrow Si_6 + Si$	4.40(101.5)			$Si_7Li \rightarrow Si_7 + Li$	1.43(33.0)	
$Si_8 \rightarrow Si_7 + Si$	2.96(68.3)			$Si_8Li \rightarrow Si_8 + Li$	2.10(48.5)	

[a] Presented in eV (kcal/mol in parentheses) with ZPVE correction. D_e with ZPVE is calculated at the HF level, and D_e(MP2) with ZPVE is calculated at the MP2(full) level. [b] Reference 28. [c] Reference 29. [d] Reference 30.

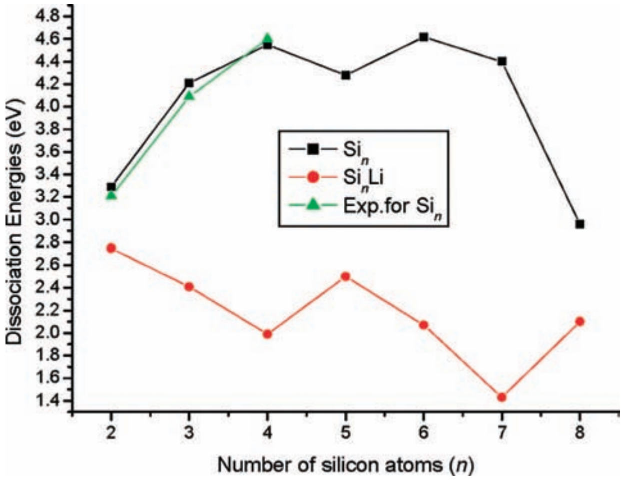


Figure 4. Dissociation energies (eV) with ZPVE corrections for the reaction $Si_nLi \rightarrow Si_n + Li$ and $Si_n \rightarrow Si_{n-1} + Si$ versus the number of atoms n for Si_nLi and Si_n clusters.

D. Dissociation Energies. The dissociation energies (D_e) (defined as the energy required in the reaction $Si_nLi \rightarrow Si_n$ + Li for Si_nLi and $Si_n \rightarrow Si_{n-1}$ + Si for Si_n) of Si_n and Si_nLi clusters are evaluated and exhibited in Table 5. Theoretical D_e values predicted with the G3 scheme are, again, in good agreement with experimental values (taken from refs 28−30) for Si_2, Si_3, and Si_4 clusters. The deviations from experiment are respectively −0.08, −0.12, and 0.05 eV. The reliable D_e values are predicted with the G3 method to be 2.47 eV for Si_5, 2.08 eV for Si_6, 1.87 eV for Si_7, and 2.44 eV for Si_8. For Si_nLi, there are no experimental values for comparison. The theoretical values are predicted to be 2.75 eV for Si_2Li, 2.41 eV for Si_3Li, 1.99 eV for Si_4Li, 2.50 eV for Si_5Li, 2.07 eV for Si_6Li, 1.43 eV for Si_7Li, and 2.10 eV for Si_8Li.

From the D_e, the stability of bonding a Li atom to silicon clusters can be found. The higher values of these dissociation energies indicate that the cluster bonding of a Li atom is stable. A better way of comparing the local relative stabilities of different size clusters is by means of the incremental binding energies.[3,14] Figure 4 sketched the dissociation energies of the Si_n and Si_nLi species with respect to the size of the clusters. As can be seen from Figure 4, the two converse oscillating curves, the top curve for Si_n and the lower curve for Si_nLi, show that (i) the Si_nLi for $n = 4$ and 7 are less stable than for $n = 2$ and 5 because the dissociation energies are local minima for $n = 4$ and 7 and local maxima for $n = 2$ and 5. Conversely, the Si_n clusters for $n = 4$ and 7 (and 6) are more stable than for $n =$ 2 and 5. (ii) The Si_n cluster bonding of a Si atom is more stable than the bonding of a Li atom, since the dissociation energy of Si_{n+1} is always larger than that of Si_nLi.

TABLE 6: Bond Lengths (in Å) and Energy Differences (in kcal/mol) for Si_3, Si_2Li, and Their Anions

		bond lengths		energy differences	
species	bond	CCSD/aug-cc-pVTZ	MP2(full)/6−31G(d)	ΔE 1[a]	ΔE 2[b]
Si_3 (C_{2v},$^1A_1$)	Si−Si	2.185	2.175	−0.04	−0.006
	Si−Si	2.185	2.175		
	Si−Si	2.728	2.709		
Si_3^- (C_{2v},$^2A_1$)	Si−Si	2.260	2.235	−0.17	−0.36
	Si−Si	2.260	2.235		
	Si−Si	2.426	2.422		
Si_2Li (C_{2v},$^2A_1$)	Si−Si	2.122	2.128	−0.008	0.008
	Si−Li	2.596	2.599		
	Si−Li	2.596	2.599		
Si_2Li^- (C_{2v},$^1A_1$)	Si−Si	2.163	2.180	−0.13	−0.35
	Si−Li	2.496	2.467		
	Si−Li	2.496	2.467		

[a] $\Delta E_1 = E$(CCSD/aug-cc-pVTZ) − E(CCSD/aug-cc-pVTZ//MP2-(full)/6-31G(d)). [b] $\Delta E_2 = E$(G3) − E(G3//CCSD/aug-cc-pVTZ.

TABLE 7: Adiabatic Electron Affinity and Dissociation Energy for Si_3 and Si_2Li[a]

	Si_3		Si_2Li	
methods	EA	D_e	EA	D_e
CCSD/aug-cc-pVTZ	2.26	3.55	1.64	2.41
CCSD/aug-cc-pVTZ// MP2(full)/6-31G(d)	2.26	3.55	1.64	2.41
G3	2.29	4.25	1.87	2.79
G3// CCSD/aug-cc-pVTZ	2.28	4.25	1.86	2.79

[a] Presented in eV without ZPVE correction.

E. Comparison with CCSD/aug-cc-pVTZ Results. In order to validate the G3 results, the CCSD/aug-cc-pVTZ, CCSD/aug-cc-pVTZ//MP2(full)/6-31G(d), and G3//CCSD/aug-cc-pVTZ calculations for Si_3, Si_2Li, and their anions are performed. Their structural parameters and energy differences are shown in Table 6, and EA and D_e are displayed in Table 7. As can been seen from Table 6, the MP2(full)/6-31G(d) geometries of neutral Si_3 and Si_2Li are in good agreement with those of CCSD/aug-cc-pVTZ, because their energy differences are small (within 0.04 kcal/mol). For anions, their geometric change between the MP2(full) and the CCSD are obvious, since the energy differences are large (0.17 and 0.36 kcal/mol for Si_3^-, and 0.13 and 0.35 kcal/mol for Si_2Li^-).

As can be seen from Table 7, the CCSD/aug-cc-pVTZ EA and D_e are the same as the results of CCSD/aug-cc-pVTZ//MP2(full). For Si_3, the CCSD EA agrees with experimental value. It is less than the experimental value (and/or the G3 result) by 0.03 eV. However, the CCSD D_e is less than the experimental value by 0.5 eV. For Si_2Li, the CCSD EA and D_e are less than the G3 results by 0.23 and 0.38 eV, respectively. Although there is no experimental value for comparison, the trend of Si_2Li that the CCSD results are less than the G3 calculations is the same as that of Si_3.

In a word, the agreement between the G3 results and experimental values would make the present calculations suitable as a benchmark for calibration of lower-level approaches to be employed for larger clusters.

F. Comparison ZPVE Correction at the HF Level with That at the MP2(full)/6-31G(d) Level. In order to validate the ZPVE correction of the HF calculation, the electron affinities and dissociation energies with MP2(full)/6-31G(*d*) ZPVE correction for Si$_n$ and Si$_n$Li ($n = 2-4$) are performed and listed in Tables 3, 4, and 5. As can be seen from these tables, the result of MP2(full) ZPVE correction is close to that of the HF ZPVE correction, and both of them are in good agreement with experimental results. However, the ZPVE calculation at the HF level compared to calculation at the MP2(full) level provides significant savings in computational time and disk storage.

4. Conclusions

The structures and energies of small Si$_n$Li clusters ($n = 2-8$) and their anion have been systematically investigated by means of the higher level of the G3 techniques. The lowest energy structures of these clusters have been reported. The ground-state geometries of neutral Si$_n$Li are "attaching structures" in which the Li atom is bound to Si$_n$ clusters. The ground-state geometries of anion Si$_n$Li$^-$, however, are "substitutional structures", which are derived from Si$_{n+1}$ by replacing a Si atom with a Li$^-$. The adiabatic electron affinities for Si$_n$ and Si$_n$Li have been estimated. The results of Si$_n$ are in good agreement with experimental values. The average absolute deviations from experiment for Si$_n$ ($n = 2-8$) are 0.05 eV. For Si$_n$Li ($n = 2-8$) clusters, the reliable adiabatic electron affinities are predicted to be 1.87 eV for Si$_2$Li, 2.06 eV for Si$_3$Li, 2.01 eV for Si$_4$Li, 2.61 eV for Si$_5$Li, 2.36 eV for Si$_6$Li, 2.21 eV for Si$_7$Li, and 3.18 eV for Si$_8$Li. The dissociation energies of Li from the lowest energy structure of Si$_n$Li and Si from Si$_n$ clusters have been calculated and used to reveal relative stability. The theoretical dissociation energies of Si from Si$_n$ ($n = 2-4$) are also in good agreement with the limited experiment values. The dissociation energies of Li atom from Si$_n$Li are predicted to be 2.75 eV for Si$_2$Li, 2.41 eV for Si$_3$Li, 1.99 eV for Si$_4$Li, 2.50 eV for Si$_5$Li, 2.07 eV for Si$_6$Li, 1.43 eV for Si$_7$Li, and 2.10 eV for Si$_8$Li. To the best of our knowledge, there are no experimental data regarding the electron affinity and dissociation energy for Si$_n$Li systems. Our results may thus provide a reference for further investigations.

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References and Notes

(1) Honea, E. C.; Oġura, A.; Murray, A. C.; Raghavachari, K.; Sprenġer, W. O.; Jarrold, M. F.; Brown, W. L. *Nature (London)* **1993**, *366*, 42.

(2) Raghavachari, K. *J. Chem. Phys.* **1985**, *83*, 3520.

(3) Raghavachari, K. *J. Chem. Phys.* **1986**, *84*, 5672.

(4) Raghavachari, K.; Rohlfing, C. M. *J. Chem. Phys.* **1991**, *94*, 3670.

(5) Curtiss, L. A.; Deutsch, P. W.; Raghavachari, K. *J. Chem. Phys.* **1992**, *96*, 6868.

(6) Yang, J. C.; Xu, W. G.; Xiao, W. S. *J. Mol. Struct. (THEOCHEM)* **2005**, *719*, 89.

(7) Arnold, C. C.; Kitsopoulos, T. N.; Neumark, D. M. *J. Chem. Phys.* **1993**, *99*, 766.

(8) Rohlfing, C. M.; Raghavachari, K. *J. Chem. Phys.* **1992**, *96*, 2114.

(9) Xu, C.; Taylor, T. R.; Burton, G. R.; Neumark, D. M. *J. Chem. Phys.* **1998**, *108*, 1395.

(10) Kawamata, H.; Negishi, Y.; Kishi, R.; Iwata, S.; Nakajima, A.; Kaya, K. *J. Chem. Phys.* **1996**, *105*, 5369.

(11) Arnold, C. C.; Neumark, D. M. J. *Chem. Phys.* **1993**, *99*, 3353.

(12) Li, S.; Van Zee, R. J.; Weltner, W. *J. Chem. Phys.* **1994**, *100*, 7079.

(13) Sporea, C.; Rabilloud, F.; Cosson, X.; Allouche, A. R.; Aubert-Frécon, M. *J. Phys. Chem. A* **2006**, *110*, 6032.

(14) Raghavachari, K.; Rohlfing, C. M. *J. Chem. Phys.* **1988**, *89*, 2219.

(15) Sieck, A.; Porezag, D.; Frauenheim, T.; Pederson, M. R.; Jackson, K. *Phys. Rev. A* **1997**, *56*, 4890.

(16) Zhu, X.; Zeng, X. C. *J. Chem. Phys.* **2003**, *118*, 3558.

(17) Koyasu, K.; Akutsu, M.; Mitsui, M.; Nakajima, A. *J. Am. Chem. Soc.* **2005**, *127*, 4998.

(18) Jaeger, J. B.; Jaeger, T. D.; Duncan, M. A. *J. Phys. Chem. A* **2006**, *110*, 9310.

(19) Kishi, R.; Iwata, S.; Nakajima, A.; Kaya, K. *J. Chem. Phys.* **1997**, *107*, 3056.

(20) Kishi, R.; Kawamata, H.; Negishi, Y.; Iwata, S.; Nakajima, A.; Kaya, K. *J. Chem. Phys.* **1997**, *107*, 10029.

(21) Wang, H.; Lu, W. C.; Li, Z. S.; Sun, C. C. *J. Mol. Struct. (THEOCHEM)* **2005**, *730*, 263.

(22) Sporea, C.; Rabilloud, F.; Allouche, A. R.; Frécon, M. *J. Phys. Chem. A* **2006**, *110*, 1046.

(23) Sporea, C.; Rabilloud, F.; Aubert-Frécon, M. *J. Mol. Struct. (THEOCHEM)* **2007**, *802*, 85.

(24) Li, S. D.; Ren, G. M.; Jin, Z. H. *J. Chem. Phys.* **2003**, *119*, 10063.

(25) Yang, J. C.; Lin, L. H.; Zhang, Y. S. *Theor. Chem. Acc.* **2008**, *121*, 83.

(26) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(28) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979; Vol *IV*.

(29) Stull, D. R.; Prophet, H. *JANAF Thermochemical Tables*; National Standard Reference Data Series (NSRDS-NBS 37); U.S. GPO: Washington, DC, 1971.

(30) Hoops, A. A.; Bise, R. T.; Choi, H.; Neumark, D. M. *Chem. Phys. Lett.* **2001**, *346*, 89.

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