Heats of formation and thermochemical parameters of small silicon clusters and their ions, Si$_n^{+/0/-}$ with n = 2–13

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ABSTRACT

Total atomization energies and heats of formation of small silicon clusters Si$_n$ and their ions are calculated using G4 (n = 2–13) and CCSD(T)/CBS (aug-cc-pV(n+d)Z for n = 2–6) methods. Experimental data for Si$_n$ were available with large uncertainties. A new ground state structure for Si$_{11}^-$ was located. Using $\Delta_f H°$(Si,298 K) = 451.5 kJ/mol, $\Delta_f H°$(Si$_n$, 298 K) are computed as: Si$_2$: 588/588 kJ/mol (G4/CBS), Si$_3$: 625/632, Si$_4$: 633/639, Si$_5$: 669/692, Si$_6$: 675/701, Si$_7$: 698, Si$_8$: 866, Si$_9$: 872, Si$_{10}$: 833, Si$_{11}$: 996, Si$_{12}$: 1051 and Si$_{13}$: 1158. Adiabatic electron affinities, ionization, binding and dissociation energies of Si$_n$ are determined.

1. Introduction

Silicon is heavily used in the semiconductor and optoelectronic industries [1]. In these important applications, silicon is often used in its bulk solid state. However bulk silicon cannot satisfy the current needs of miniaturization of electronic devices. The demand for smaller and smaller devices has thus been stimulating a wealth of studies of silicon clusters, as they open up new avenues for development of nanoscaled materials [2].

Defined as entities built up from a few to hundreds of atoms, clusters are intermediates between free molecules and bulk materials. In terms of dimension, the cluster size is in fact reaching the nanoscale range. Attempts to make silicon nanowires as assemblies of small silicon clusters have been reported [3].

Extensive investigations have been performed on Si clusters using various experimental methods [4–18], and quantum chemical computations [19–25]. The molecular structure and some spectroscopic signatures [7,8], as well as the energetic parameters such as ionization energies (IE) and electron affinities (EA), of the small silicon clusters Si$_n$ with n ⩽ 20 have been relatively well determined [6,9]. On the contrary, their standard heats of formation ($\Delta_f H$), the key thermochemical parameters, are not established yet, even though total atomization energies (TAE) were determined for some small Si$_n$ species (n up to 8) [11–17], because the heat of formation of the silicon element was not well determined [17].

For the silicon element, an earlier value of $\Delta_f H_{298.15}$(Si,g) = 455.6 ± 4.2 kJ/mol was tabulated in 1973 by Hultgren et al. [26]. In their 1995 papers, Rocabois et al. [11,12] reviewed the values of $\Delta_f H$(Si) reported from 1954 and according to their list,

there have been not less than twelve different values determined using the second law of thermodynamics, and twenty one values from the third law, and these values range from 412.6 ± 5.9 to 468.6 ± 12.6 kJ/mol. These authors [11] proposed after careful evaluation a value of 445.3 ± 5 kJ/mol. In the 1998 JANAF database [27], a value of $\Delta_f H_{298.15}$(Si) = 450 ± 8 kJ/mol was selected, and the latter value, which is apparently the average of the two values given above, was chosen in the NIST Chemistry Web Book [28]. Other theoretical values for the atomic heat of formation (0 K) include 452.3 ± 2.1 kJ/mol [29] and 449.3 ± 2.5 kJ/mol [30].

When determining the heats of formation of Si$_7$ and Si$_8$ from their experimental TAEs, Meloni and Gingerich [17] pointed out the large difference (up to 73–83 kJ/mol) derived from two different values for $\Delta_f H$(Si), and summarized quite well the acute problem encountered: 'Evidently, the choice of the enthalpy of sublimation of silicon makes a significant difference on the $\Delta_f H_{298.15}$(Si$_n$,g) values' (Ref. [17], p. 5474).

More recently, Karton and Martin [31] carefully reexamined the heat of formation of the Si element by means of high accuracy quantum chemical computations on a few selected Si-compounds whose experimental data were well established, and accordingly proposed the value of 448.5 ± 0.8 kJ/mol (107.2 ± 0.2 kcal/mol). This value appeared fortuitously to be an average between the values of Rocabois et al. [11] and JANAF/CODATA [27] mentioned above.

In this work, we set out to determine first the TAEs of a set of small Si clusters using quantum chemical computations. Together with the atomic heat of formation, the values of the Si$_n$ molecules, with n = 2–13, can subsequently be derived. We consider not only the neutral clusters but also their positive (Si$_n^+$) and negative (Si$_n^-$) ions. A consistent set of thermochemical parameters are thus determined using the composite G4 method, and for the smaller

systems, a further calibration is also done using the coupled-cluster theory with complete basis set CCSD(T)/CBS protocol.

2. Computational methods

All electronic structure calculations are carried out using the GAUSSIAN 09 [32] and MOLPRO 2008 [33]] suites of programs. Geometries of the small Si_n, $n = 2$–13, clusters have been well established in the literature. However, we carry out additional searches for possible lower-lying isomers of each of the Si_n size considered, in particular for the ions, using a stochastic search algorithm [34]. Geometry optimizations and vibrational calculations of the structures located are performed using the popular hybrid B3LYP functional in conjugation with the 6-311+G(d) basis set. B3LYP geometries and vibrational frequencies are also parts of the original composite G4 approach [35] but with the 6-31G(2df,p) basis set.

In order to obtain more accurate TAE values, the electronic energies of the global minima for the small sizes of $n = 2$–6, are also calculated using the coupled-cluster CCSD(T) theory [36]. CCSD(T)/CBS computations are restricted to these smaller clusters simply due to the computational expenses that go beyond our computational resources. For CCSD(T) computations, geometries are reoptimized at the CCSD(T)/aug-cc-pVTZ level. Single-point electronic energies are subsequently calculated using the restricted/unrestricted coupled-cluster R/UCCSD(T) formalism with the correlation-consistent aug-cc-pVnZ (aVnZ, $n = Q$ and 5) basis sets [37]. The CCSD(T) total energies are then extrapolated to the complete basis set limit (CBS) energies using expression (1) [38]:

$$E(x) = E_{CBS} + B/x^3 \qquad (1)$$

where $x = 4$ and 5 for the aVnZ basis, $n = Q$ and 5, respectively.

Zero-point energies (ZPE) are calculated from CCSD(T)/aug-cc-pVTZ harmonic vibrational frequencies at corresponding equilibrium geometries. Additional smaller corrections are included in the TAE calculations. Core-valence corrections (ΔE_{CV}) are obtained at the CCSD(T)/cc-pwCVTZ level [39] from the differences of total energies with full and frozen core electrons. Douglas–Kroll–Hess (DKH) scalar relativistic corrections (ΔE_{DKH-SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, are calculated using the spin-free, one-electron DKH Hamiltonian [40]. ΔE_{DKH-SR} is defined as the difference in the atomization energy between the results obtained from basis sets re-contracted for DKH calculations and the atomization energy obtained with the normal valence basis set of the same quality. The DKH calculations are obtained as the differences of the results from the CCSD(T)/aug-cc-pVTZ and the CCSD(T)/aug-cc-pVTZ-DK levels of theory. Finally, a spin–orbit (SO) correction of 1.8 kJ/mol (0.43 kcal/mol) for the Si atom obtained from the excitation energies of Moore [41] is used. The total atomization energy (ΣD_0 or TAE) of a compound is given by (2):

$$\Sigma D_0 = \Delta E_{elec}(CBS) + \Delta E_{CV} + \Delta E_{DHK-SR} + \Delta E_{SO} - \Delta E_{ZPE} \qquad (2)$$

By combining our computed ΣD_0 values from either the G4 and CCSD(T)/CBS calculations, with the heat of formation at 0 K for the element Si, we can derive the enthalpy of formation $\Delta_f H°$ values at 0 K for the molecules in the gas phase. Similar to arguments previously used for the case of the boron element [42], we thus adopt the latest value $\Delta_f H°(Si,g) = 448.5$ kJ/mol at 0 K for the Si element [31] as mentioned above, and the rationale for this selection was discussed in our previous work [43,44]. We obtain the heats of formation at 298 K by following the usual thermochemical proce-

dures. The value $\Delta_f H°(Si,g) = 451.5$ kJ/mol is this obtained at 298 K. We use the calculated heats of formation at 0 K to evaluate the IEs, EAs and other energetic quantities.

It has been established that tight d functions can be necessary for calculating accurate atomization energies for second-row elements (cf. [45] and references therein). Thus, we include a set of tight d functions for Si in the correlation consistent basis sets denoted as aug-cc-pV($n + d$)Z, or in a simpler notation as aV($n + d$)Z. Single-point CCSD(T) electronic energy calculations are carried out using the aV($n + d$)Z basis sets, with $n = 4$ and 5, at CCSD(T)/aVTZ geometries. The final total valence electronic energies are again extrapolated to the complete basis set using Eq. (1).

3. Results and discussion

3.1. Shape of the lowest-lying isomers of Si_n clusters and their ions

Geometries of the small Si_n clusters considered and their positive and negative ions were well determined and abundantly discussed in the relevant literature [19–25], and thus do not warrant additional description. In order to specify the structures actually computed in the present work, we display in Figure 1 the shapes of the equilibrium structures of the lowest-lying isomers of each size in the neutral, cationic and anionic states, together with their symmetry point group and electronic state. The B3LYP/6-311+G(d) optimized geometries of the lowest-lying isomers are listed in the Table S1 of the Supplementary Information. As for a convention, each structure is labeled by x.n where x = a (anion), n (neutral) or c (cation) and n = the actual size of the cluster ranging from 2 to 13 (cf. Figure 1).

It is confirmed that no low energy structure with endohedrally located Si atom within a Si cage is located. The neutral geometry is distorted, as expected, following electron attachment and detachment, in particular in the larger sizes. However, no structural rearrangement or disruption really occurs. Each of the ionic structures is characterized by a low spin (doublet) ground state.

The main difference with respect to previous results concerns the size 11. In fact, our results disagree with those reported by Li et al. [46] on the ground state of Si_{11}^-. These authors [46] used full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) calculations based on single-parent evolution algorithm and found that **a.11.3** is the global minimum (see structures given below).

a.11(^{2}A', C_s)   a.11.2 (^{2}A, C_1)   a.11.3 (^{2}A$_2$, C_{2v})
0.00 eV   0.07   0.12
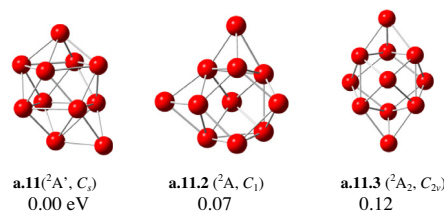
We now find that the two isomers **a.11** and **a.11.2** are even more stable than **a.11.3** by about 0.1 eV (G4). The existence of two new and low symmetry isomers was not mentioned in Ref. [46]. Although they are nearly degenerate, we select **a.11** formed by capping a Si atom on a face of a bicapped squared anti-prism cage of the pure Si_{10}^{-2} dianion [24] as the lowest-lying structure of the anion Si_{11}^-, and it is shown in Figure 1.

The shape of the neutral remains unchanged following electron removal giving the cation **c.13**, but a strong geometrical relaxation however occurs upon electron attachment yielding the anion **a.13** (Figure 1). The anion shape in fact differs significantly from that of the neutral and cationic counterparts.
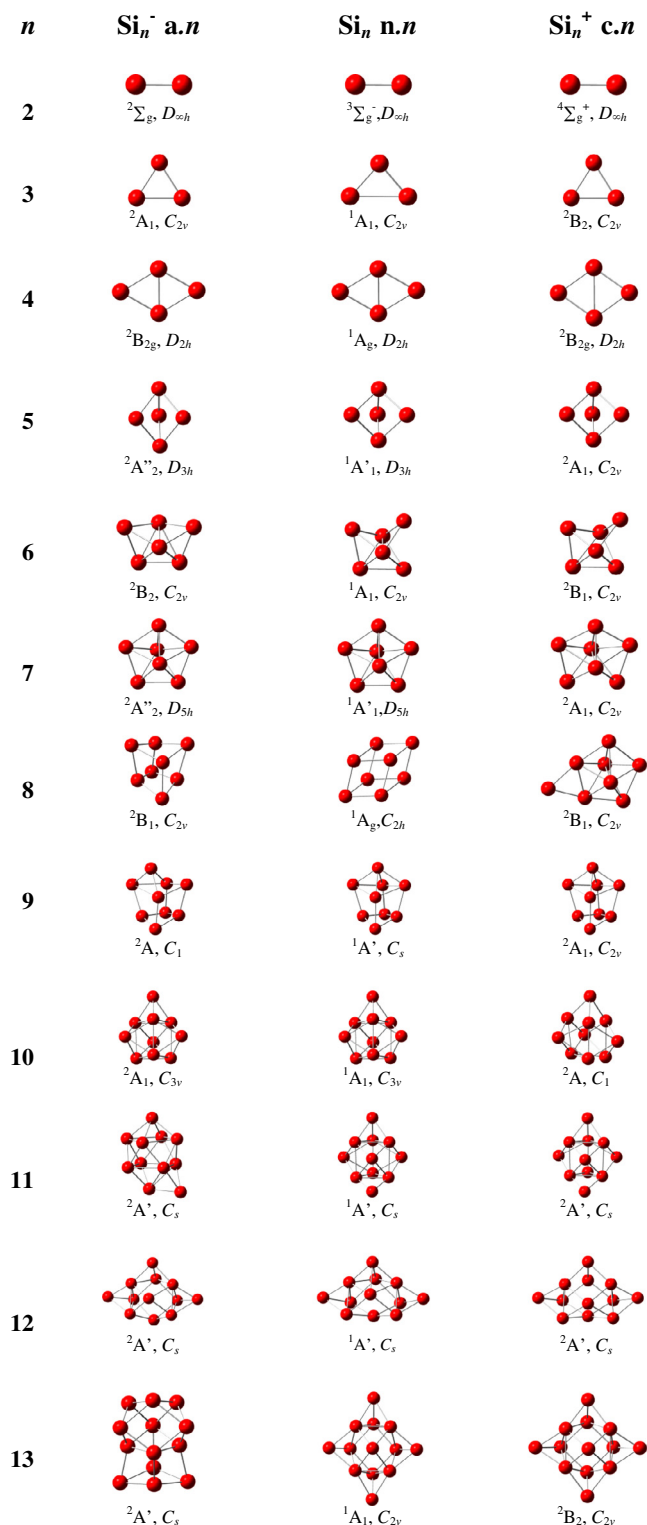
Figure 1. Shapes of the lowest-lying isomers of Si_n in the neutral (**n.n**, middle), cationic (**c.n**, right) and anionic (**a.n**, left) states.

3.2. Total atomization energies (TAE)

Table 1 lists the different components obtained in the CCSD(T)/CBS protocol (referred hereafter as CBS) to predict the total atomization energies (ΣD_0, TAE) of the Si_n clusters and ions, for $n = 2–6$, using the aVnZ (denoted as CBS(1)) and aV($n + d$)Z (CBS(2)) basis sets. Table 2 summarizes the calculated TAE's whereas Table 3 lists the heats of formation ($\Delta_f H°$) at both 0 and 298 K derived from

TAE's calculated using both G4 and CBS protocols. For the purpose of comparison, available experimental values [11–17] for both quantities of the neutrals Si_n with $n = 2–8$ are also given in Tables 2 and 3.

The inclusion of the tight d functions causes some small reductions of the TAEs. The calculated CBS(1) TAEs without tight d polarization function differ up to 6 kJ/mol from the CBS(2) values including these functions (Table 1). This significant deviation demonstrates again the importance of tight polarization functions in treatment of systems having multiple second-row atoms.

Of the G4 and CBS TAE values, the CBS(2) is the smaller one, except for Si_2 (Table 2). The G4 and CBS(1) TAE values for the neutral species differ by 5, 6 and 4 kJ/mol for Si_2, Si_3 and Si_4, respectively. The deviations are getting larger for Si_5 (20 kJ/mol) and Si_6 (22 kJ/mol) (Table 2). The deviations between G4 and CBS(2) TAEs are even larger. Such a difference can in part be attributed to the inherent treatment of the Si atom in each protocol and the one-electron functions used. All calculated TAEs compare only fairly with experimental data [11–17]. We should first stress over the large error bars of the reported experimental data (Table 2). For small species where a comparison is possible, some relevant points can be presented as follows:

n.2: Computed values are apparently underestimated, but the G4 and CBS(2) values of TAE(Si_2) = 312 kJ/mol is closer to the experimental one of 319 ± 7 kJ/mol [11,13] than the CBS(1) counterpart of 307 kJ/mol. The non-corrected (electronic) CBS(2) value of 318 kJ/mol for Si_2 listed in Table 1 is nearly identical with that reported earlier by Feller et al. [47] also using CCSD(T)/CBS but with basis set up to aug-cc-pV(6+d)Z. These authors derived a value of 314 kJ/mol for TAE(Si_2) including in fact a correction of 2 kJ/mol for the higher-order correlation. If the latter correction is included, we thus obtain the same value as in Ref. [47] for TAE(Si_2).

n.3: both values TAE(Si_3) = 724 (G4) and 718 (CBS(1)) and 717 kJ/mol (CBS(2)) are overestimated with respect to the experimental result of 705 ± 16 kJ/mol [11,13], even though they are close to the upper limit of the error margin. Let us mention that for the triatomic neutral Si_3, our CBS results point out that both singlet and triplet states are energetically degenerate. Previous studies [18] found a singlet ground state with a small singlet–triplet separation of about 4 kJ/mol.

n.4: both computed values of 1165 (G4) and 1161 (CBS(1)) and 1159 kJ/mol (CBS(2)) for TAE(Si_4) are again overestimated but still within the upper error margin of the experimental of 1151 ± 22 kJ/mol [11,14].

n.5: the good agreement for TAE(Si_5), between 1557 kJ/mol by CBS(1) and 1559 ± 24 kJ/mol by experiment [11,15] appears to be fortuitous, in view of the fact that the values of 1577 (G4) and 1554 kJ/mol (CBS(2)) are further deviated, even though they still within the error bar of the experimental result.

n.6: the TAE(Si_6) = 1995 kJ/mol derived by CBS(2) appears to be closer to the experimental data of 1981 ± 32 kJ/mol [11] than the G4 counterpart of 2022 kJ/mol.

n.7 and **n.8**. A disparate behavior of G4 values emerges. While the TAE(Si_7) = 2446 kJ/mol is not consistent with experiment, being 2381 ± 36 kJ/mol [17], the TAE(Si_8) = 2729 kJ/mol compares better with the experimental result of 2735 ± 65 kJ/mol [17]. Note that both experimental values were determined using the same Knudsen cell mass spectrometric techniques. In view of the large error margin, the agreement for Si_8 is again fortuitous.

For the larger Si_n with $n = 9–13$, along with their cations and anions, the corresponding TAEs can now only be predicted by G4 results as summarized in Table 2. Overall, the CBS(2) results (Table 2) represent the best values we have obtained so far for this series. The large difference between G4 and CBS TAE values is disappointing. As the deviation tends to increase with increasing cluster size, a difference of at least 40 kJ/mol can be expected for the sizes

Table 1
Total atomic energy (TAE) (kJ/mol) for the anionic Si_n^-, neutral Si_n and cationic Si_n^+ ($n = 2$–6) and different components of the CCSD(T)/CBS protocols.

Structure	State	CBS(1)[a]	CBS(2)[b]	E_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	TAE(1)	TAE(2)
a.2	$^2\Sigma_g^+$	529.9	529.6	3.48	0.63	−1.40	−3.60	522.0	521.8
n.2	$^3\Sigma_g^-$	312.6	318.3	3.24	1.17	−0.39	−3.60	306.5	312.2
c.2	$^4\Sigma_g^+$	−446.0	−446.3	2.64	1.17	0.61	−3.60	−450.5	−450.7
a.3	$^2A_1$	952.7	951.5	6.58	2.10	−2.50	−5.40	940.4	939.1
n.3	$^1A_1$	729.2	727.9	7.41	2.83	−1.35	−5.40	717.8	716.5
c.3	$^2B_2$	−56.7	−58.1	5.41	2.60	−0.66	−5.40	−65.5	−67.0
a.4	$^2B_{2g}$	1385.7	1383.5	11.67	4.06	−3.39	−7.20	1367.5	1365.3
n.4	^1A_g	1177.7	1175.6	12.22	5.01	−2.22	−7.20	1161.1	1159.0
c.4	$^2B_{2g}$	409.9	408.0	11.77	4.39	−1.26	-7.20	394.1	392.1
a.5	$^2A''_2$	1819.2	1815.8	17.53	7.07	−4.09	−9.00	1795.6	1792.3
n.5	$^1A'_1$	1577.7	1574.4	17.58	8.28	−2.50	−9.00	1556.9	1553.6
c.5	$^2A_1$	795.7	792.4	15.82	7.04	−1.96	−9.00	776.0	772.7
a.6	$^2B_2$	2229.9	2225.2	21.13	9.33	−5.46	−10.80	2201.8	2197.1
n.6	$^1A_1$	2023.8	2018.9	21.02	11.49	−3.44	−10.80	2000.0	1995.1
c.6	$^2B_1$	1280.3	1275.5	21.20	10.40	−2.70	−10.80	1256.0	1251.2

[a] Based on CCSD(T) energies extrapolated using Eq. (1) with aug-cc-pVQZ and aug-cc-pV5Z basis sets at CCSD(T)/aug-cc-pVTZ optimized geometries. This gives TAE(1) values.
[b] Based on CCSD(T) energies extrapolated using Eq. (1) with aug-cc-pV(Q+d)Z and aug-cc-pV(5+d)Z basis sets at CCSD(T)/aug-cc-pVTZ optimized geometries. This gives TAE(2) values.
[c] Zero point energies taken from CCSD(T)/aug-cc-pVTZ harmonic vibrational frequencies.
[d] Core-valence corrections obtained with the aug-cc-pwCVTZ basis sets at CCSD(T) geometries.
[e] Scalar relativistic corrections based on CCSD(T)-DK/aug-cc-pVTZ-DK calculations and expressed relative to CCSD(T) results without the DK corrections.
[f] Corrections due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values based on C. Moore's Tables, Ref. [41].

Table 2
Total atomic energy (TAE) of the lowest-lying isomers of the anionic Si_n^-, neutral Si_n, and cationic Si_n^+ ($n = 2$–13) using G4 and CCSD(T)/CBS approaches.

Structure	TAE (kJ/mol)			
	G4	CBS(1)	CBS(2)	Exptl.[a]
a.2 ($^2\Sigma_g^+$, $D_\infty h$)	532.2	522.0	521.8	
n.2 ($^3\Sigma_g^-$, $D_\infty h$)	311.6	306.5	312.2	319 ± 7
c.2 ($^4\Sigma_g^+$, $D_\infty h$)	−450.1	−450.5	−450.7	
a.3 ($^2A_1$, C_{2v})	947.2	940.4	939.1	
n.3 ($^1A_1$, C_{2v})	723.9	717.8	716.5	705 ± 16
c.3 ($^2B_2$, C_{2v})	−75.9	−65.5	−67.0	
a.4 ($^2B_{2g}$, D_{2h})	1375.5	1367.5	1365.3	
n.4 (^1A_g, D_{2h})	1164.9	1161.1	1159.0	1151 ± 22
c.4 ($^2B_{2g}$, D_{2h})	393.1	394.1	392.1	
a.5 ($^2A''_2$, D_{3h})	1818.3	1795.6	1792.3	
n.5 ($^1A'_1$, D_{3h})	1577.1	1556.9	1553.6	1559 ± 24
c.5 ($^2A_1$, C_{2v})	788.8	776.0	772.7	
a.6 ($^2B_2$, C_{2v})	2229.2	2201.8	2197.1	
n.6 ($^1A_1$, C_{2v})	2021.7	2000.0	1995.1	1981 ± 32
c.6 ($^2B_1$, C_{2v})	1272.9	1256.0	1251.2	
a.7 ($^2A''_2$, D_{5h})	2631.5			
n.7 ($^1A'_1$, D_{5h})	2446.2			2381 ± 36
c.7 ($^2A_1$, C_{2v})	1672.0			
a.8 ($^2B_1$, C_{2v})	2975.8			
n.8 (^1A_g, C_{2h})	2729.1			2735 ± 65
c.8 ($^2B_1$, C_{2v})	2042.8			
a.9 (^2A, C_1)	3383.0			
n.9 ($^1A8$, C_s)	3172.2			
c.9 (^2A, C_2)	2427.3			
a.10 ($^2A_1$, C_{3v})	3886.2			
n.10 ($^1A_1$, C_{3v})	3660.0			
c.10 (^2A, C_1)	2892.9			
a.11 ($^2A'$, C_s)	4193.1			
n.11 ($^1A'$, C_s)	3946.7			
c.11 ($^2A'$, C_s)	3300.3			
a.12 ($^2A'$, C_s)	4581.2			
n.12 ($^1A'$, C_s)	4340.9			
c.12 ($^2A'$, C_s)	3628.4			
a.13 ($^2A'$, C_s)	5005.0			
n.13 ($^1A_1$, C_{2v})	4682.9			
c.13 ($^2B_2$, C_{2v})	4026.8			

[a] Experimental values taken from Refs. [13] for Si_2, Si_3, and Si_4, [15] for Si_5, [16] for Si_6, [17] for Si_7 and Si_8.

$n > 10$. In this context, accurate determination of TAEs for small silicon clusters remains a challenge for quantum chemical computations. Protocols using appropriate working reactions, in which the errors of energies in both sides could mutually be cancelled, could provide more balanced results.

3.3. Heats of formation ($\Delta_f H°$)

Calculated results are summarized in Table 3. As this parameter of each species is directly derived from its TAE and the $\Delta_f H°$(Si), the deviations discussed above for the TAEs will further be propagated. In addition, the discrepancy also arises from the value actually used for the element $\Delta_f H°$(Si). Due to the involvement of the latter quantity, the deviation is, as expected, getting increased with increasing cluster size. As a matter of fact, with an error of, for example, 5 kJ/mol, the atomic value $\Delta_f H°$(Si) invariably induces an error of $5n$ kJ/mol on the molecular parameter of Si_n. We can however note some reasonable agreements between both CBS and experimental values, as for Si_3, Si_4 and Si_6, but the deviations turn out to be more substantial for Si_2 and Si_5. As in the case for TAEs, the G4 values for Si_7 and Si_8 differ much from experiment for which the uncertainties reported are equally quite large (Table 4). Accordingly, the deviation for Si_7 amounts up to 45 kJ/mol, which is close to the upper bound of the error margin of ±36 kJ/mol [17]. As stated in Introduction, an even small difference in the atomic value leads to a significant deviation in the molecular parameter.

3.4. Electron affinities (EA) and ionization energies (IE)

The adiabatic EA of each neutral Si_n is calculated as the difference between the heats of formation of both corresponding neutral and anionic clusters at the same computational method. Similarly, the adiabatic IE is derived calculated from the heats of formation of the corresponding neutral and cationic structures. Calculated results are given in Table 4, together with available experimental values [4,9,48–52].

Results obtained using both sets of CBS TAEs are similar. To simplify the presentation of data, only the CBS(1) values are listed

Table 3
The heats of formation at 0 K [$\Delta_f H$ (0 K)] and 298 K [$\Delta_f H$ (298 K)] (kJ/mol) of the lowest-lying isomers of the anionic Si_n^-, neutral Si_n, and cationic Si_n^+ (n = 2–13), using G4 and CCSD(T)/CBS approaches.

Label	$\Delta_f H$						
	G4 (0 K)	CBS(1) (0 K)	CBS(2) (0 K)	G4 (298 K)	CBS(1) (298 K)	CBS(2) (298 K)	Exptl.[a] (298 K)
a.2 ($^2\Sigma_g^+, D_\infty h$)	364.9	375.0	375.3	367.6	377.8	378.1	
n.2 ($^3\Sigma_g^-, D_\infty h$)	585.5	590.5	584.8	588.3	593.4	587.7	575.5 ± 9.4
c.2 ($^4\Sigma_g^+, D_\infty h$)	1347.1	1347.5	1347.8	1350.2	1350.5	1350.7	
a.3 ($^2A_1, C_{2v}$)	398.3	405.2	406.5	401.5	408.3	409.5	
n.3 ($^1A_1, C_{2v}$)	621.7	627.8	629.0	624.7	630.7	632.0	631.3 ± 7.9
c.3 ($^2B_2, C_{2v}$)	1421.5	1411.1	1412.5	1425.2	1414.9	1416.3	
a.4 ($^2B_{2g}, D_{2h}$)	418.6	426.7	428.8	422.2	430.2	432.4	
n.4 ($^1A_g, D_{2h}$)	629.3	633.0	635.1	632.8	636.5	638.7	634.8 ± 8.3
c.4 ($^2B_{2g}, D_{2h}$)	1401.0	1400.0	1402.0	1404.8	1403.8	1405.7	
a.5 ($^2A''_2, D_{3h}$)	424.3	447.0	450.4	427.8	450.5	453.8	
n.5 ($^1A'_1, D_{3h}$)	665.5	685.8	689.0	669.0	689.0	692.3	661.3 ± 10.3
c.5 ($^2A_1, C_{2v}$)	1453.8	1466.6	1469.9	1458.4	1470.8	1474.1	
a.6 ($^2B_2, C_{2v}$)	462.0	489.3	494.0	466.7	494.0	498.7	
n.6 ($^1A_1, C_{2v}$)	669.4	691.1	696.05	674.6	696.3	701.2	702.8 ± 18.3
c.6 ($^2B_1, C_{2v}$)	1418.3	1435.2	1439.9	1423.2	1440.1	1444.9	
a.7 ($^2A''_2, D_{5h}$)	508.2			513.4			
n.7 ($^1A'_1, D_{5h}$)	693.5			698.5			743 ± 36
c.7 ($^2A_1, C_{2v}$)	1467.7			1473.7			
a.8 ($^2B_1, C_{2v}$)	612.4			619.3			
n.8 ($^1A_g, C_{2h}$)	859.1			866.0			837 ± 65
c.8 ($^2B_1, C_{2v}$)	1545.4			1552.7			
a.9 ($^2A, C_1$)	653.8			661.4			
n.9 ($^1A', C_s$)	864.6			872.2			
c.9 ($^2A, C_2$)	1069.4			1618.4			
a.10 ($^2A_1, C_{3v}$)	599.0			607.0			
n.10 ($^1A_1, C_{3v}$)	825.3			832.7			
c.10 ($^2A, C_1$)	1592.3			1601.2			
a.11 ($^2A', C_s$)	740.7			750.8			
n.11 ($^1A', C_s$)	987.0			996.2			
c.11 ($^2A', C_s$)	1633.5			1642.6			
a.12 ($^2A', C_s$)	801.1			810.1			
n.12 ($^1A', C_s$)	1041.4			1050.9			
c.12 ($^2A', C_s$)	1753.9			1764.0			
a.13 ($^2A', C_s$)	825.9			836.5			
n.13 ($^1A_1, C_{2v}$)	1148.2			1157.5			
c.13 ($^2B_2, C_{2v}$)	1804.0			1813.6			

[a] Experimental values taken from Refs. [12] for Si_2 and Si_3, Si_4, Si_5, and Si_6, [17] for Si_7 and Si_8.

Table 4
Adiabatic electronic affinities (EA) and ionization energy (IE) of Si_n clusters, n = 2–13 (G4 and CCSD(T)/CBS(1)).

Neutral (state)	Anion (state)	Cation (state)	EA (eV)			IE (eV)		
			G4	CBS(1)	Exptl.[a]	G4	CBS(1)	Exptl.[b]
$Si_2(^3\Sigma_g^-)$	($^2\Sigma_g^+$)	($^4\Sigma_g^+$)	2.29	2.23	2.20 ± 0.01	7.89	7.85	7.92 ± 0.05
$Si_3(^1A_1)$	($^2A_1$)	($^2A_1$)	2.31	2.31	2.29 ± 0.002	8.29	8.12	8.12 ± 0.05
$Si_4(^1A_g)$	($^2B_{2g}$)	($^2B_{2g}$)	2.18	2.14	2.13 ± 0.001	8.00	7.95	8.20 ± 0.10
$Si_5(^1A'_1)$	($^2A''_2$)	($^2A''_2$)	2.50	2.47	2.59 ± 0.02	8.17	8.09	7.96 ± 0.07
$Si_6(^1A_1)$	($^2B_2$)	($^2B_2$)	2.15	2.09	2.08 ± 0.14	7.76	7.71	7.80 ± 0.10
$Si_7(^1A'_1)$	($^2A''_2$)	($^2A''_2$)	1.92		1.85 ± 0.02	8.02		7.80 ± 0.10
$Si_8(^1A_g)$	($^2B_1$)	($^2B_1$)	2.56		2.36 ± 0.10	7.11		
$Si_9(^1A')$	(^2A)	(^2A)	2.18		2.31 ± 0.25	7.72		
$Si_{10}(^1A_1)$	($^2A_1$)	($^2A_1$)	2.35		2.29 ± 0.05	7.95		
$Si_{11}(^1A')$	($^2A'$)	($^2A'$)	2.55		2.5	6.70		
$Si_{12}(^1A')$	($^2A'$)	($^2A'$)	2.49		2.6	7.39		
$Si_{13}(^1A_1)$	($^2A'$)	($^2B_2$)	3.34			6.80		

[a] Experimental values taken from Refs. [48,49] for Si_2, [50] for Si_3, Si_4, Si_5, and Si_7, [51] for Si_6, Si_8, and Si_{10}, [52] for Si_9, [4] for Si_{11} and Si_{12}.
[b] Experimental values taken from Refs. [9] for Si_2, Si_3, Si_4, Si_5, Si_6, and Si_7.

in Table 4. Differences of a few hundredths of an eV between G4 and CBS(1) values can be noticed. Both sets of predictions are also in good agreement with available experimental data, with deviations <0.1 eV (Table 4). Let us note that previous DFT/B3LYP computations also gave rise to reasonable IEs for Si_n clusters [9]. A mutual cancellation of errors on the energies of both neutral and cationic forms is apparently occurred yielding good relative energetic quantities.

Figure 2 schematically illustrates the comparison, and also the evolution of both EA and IE values with respect to the cluster size. Si_4, Si_5 and Si_7 are the cases bearing relatively large deviations (0.2 eV), and in opposite directions, between calculated and measured IEs. On the contrary, calculated EAs for these sizes appear to be more consistent with experiment. Therefore they warrant some additional evaluations.
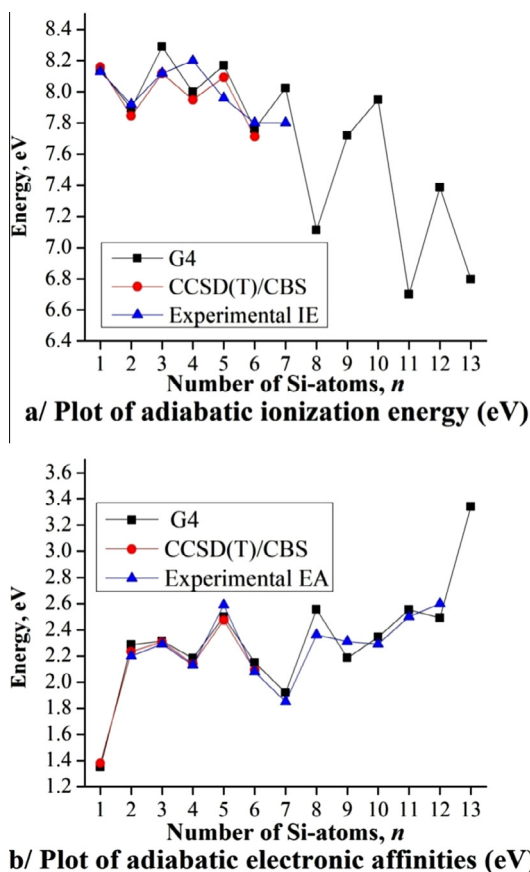
Figure 2. Comparison and evolution of adiabatic ionization energies (IE) and electron affinities (EA) of Si_n clusters obtained using G4 and CCSD(T)/CBS approaches and experiment.

In Section 3.2, we point out for Si_7 a large deviation of 45 kJ/mol of its G4 heat of formation relative to available experiment (Table 3). The G4 value for $EA(Si_7) = 1.92$ eV turns out to be comparable to the experimental result of 1.85 ± 0.02 eV [50]. On the contrary, the G4 value for $IE(Si_7) = 8.02$ eV represents the largest overestimation with respect to the experimental IE of 7.80 ± 0.10 eV [9].

For the tetraatomic system, a similar situation can be noted. Both calculated values of 2.18 (G4) and 2.14 eV (CBS) are close to the experimental EA of 2.13 eV [50] (Table 4). Again, the

predictions of 8.00 (G4) and 7.95 eV (CBS) for $IE(Si_4)$ correspond to the largest underestimation as compared to the experimental one of 8.20 ± 0.10 eV [9].

The EA and IE values for the pentaatomic system follow a comparable pattern including a good G4 prediction for EA (2.50 vs. 2.59 eV), but a less good G4 IE (8.15 vs. 7.96 eV). Overall, an error margin of, at most, ± 0.15 eV could be estimated on the G4 values for EAs and IEs of silicon clusters (Table 4). The EA of the element for which an experimental result is missing, can be predicted as $EA(Si) = 1.35 \pm 0.10$ eV.

3.5. Relative stability of clusters and dissociation energies

The relative stability of the Si_n clusters can be approached by using energetic parameters such as the average binding energy (E_b), and dissociation energies. The former properties can be defined as follows (Eqs. (3)–(5)):

$$E_b(Si_n) = [(n)E(Si) - E(Si_n)]/n \tag{3}$$

$$E_b(Si_n^-) = [(n-1)E(Si) + E(Si^-) - E(Si_n^-)]/n \tag{4}$$

$$E_b(Si_n^+) = [(n-1)E(Si) + E(Si^+) - E(Si_n^+)]/n \tag{5}$$

where $E(Si)$, $E(Si_n)$, $E(Si_n^-)$, and $E(Si_n^+)$ are the G4 total energies of Si atom, neutral, anionic, and cationic Si_n cluster, respectively. Calculated and experimental results listed in Table 5 point out a good agreement. The plots of their evolution are displayed in Figure 3.

The average binding energy (E_b) of cationic, neutral and anionic clusters uniformly increases with increasing size (Figure 3). The E_b values of smaller anionic clusters ($n \leqslant 6$) are slightly larger than those of corresponding neutral Si_n or cation Si_n^+. However, at larger sizes in ionic and neutral states, the E_b values are approximately close to each other, even though for $n \geqslant 13$, the E_b values of ions $Si_n^{+/-}$ tend to be somewhat larger than those of the neutral Si_n.

In order to probe further the thermodynamic stability, dissociation energies (D_e) for various fragmentation channels of Si clusters are considered. The dissociation energy for the channel (6) of the cluster:

$$Si_n^{+/0/-} \rightarrow Si + Si_{n-1}^{+/0/-} \tag{6}$$

is defined in Eq. (7) where ΔH_f° are enthalpies of formation at 0 K of the relevant clusters, respectively:

$$De(Si_n^{+/0/-}) = \Delta H_f^\circ(Si) + \Delta H_f^\circ(Si_{n-1}^{+/0/-}) - \Delta H_f^\circ(Si_n^{+/0/-}) \tag{7}$$

Table 5

Average binding energies (E_b) and dissociation energies (D_e) of Si_n^-, Si_n and Si_n^+, $n = 2$–13 (eV), using G4 and CCSD(T)/CBS(1) approaches.[a]

n	$E_b(Si_n^-)$		$E_b(Si_n)$		$E_b(Si_n^+)$		$D_e(Si_n^-)$		$D_e(Si_n)$			$D_e(Si_n^+)$	
	G4	CBS	G4	CBS	G4	CBS	G4	CBS	G4	CBS	Exptl.[b]	G4	CBS
2	2.08	2.02	1.61	1.59	1.74	1.75	4.17	4.03	3.23	3.18	3.21	3.48	3.49
3	2.82	2.79	2.50	2.48	2.45	2.49	4.30	4.34	4.27	4.26	4.09	3.88	3.99
4	3.23	3.21	3.02	3.01	3.05	3.06	4.44	4.43	4.57	4.59	4.60 ± 0.15	4.86	4.76
5	3.50	3.45	3.27	3.23	3.26	3.24	4.59	4.44	4.27	4.10		4.10	3.96
6	3.63	3.57	3.49	3.45	3.56	3.53	4.26	4.21	4.61	4.59		5.02	4.97
7	3.70		3.62		3.64		4.17		4.40			4.14	
8	3.69		3.54		3.66		3.57		2.93			3.84	
9	3.75		3.65		3.70		4.22		4.59			3.99	
10	3.89		3.79		3.81		5.22		5.06			4.83	
11	3.83		3.72		3.85		3.18		2.97			4.22	
12	3.84		3.75		3.81		4.02		4.09			3.40	
13	3.89		3.73		3.84		4.39		3.54			4.13	

[a] Average binding energies E_b of neutral, anionic and cationic Si_n clusters are defined as $E_b(Si_n) = [(n)E(Si) - E(Si_n)]/n$ for neutrals, $E_b(Si_n^-) = [(n-1)E(Si) + E(Si^-) - E(Si_n^-)]/n$ for anions and $E_b(Si_n^+) = [(n-1)E(Si) + E(Si^+) - E(Si_n^+)]/n$ for cations, and dissociation energy $D_e(Si_n^{+/0/-}) = \Delta H_f^\circ(Si) + \Delta H_f^\circ(Si_{n-1}^{+/0/-}) - \Delta H_f^\circ(Si_n^{+/0/-})$ of Si_n^+, Si_n and Si_n^- ($n = 2$–13).
[b] Experimental values taken from Refs. [53] for $D_e(Si_2)$, [54] for $D_e(Si_3)$, and [6] for $D_e(Si_4)$.
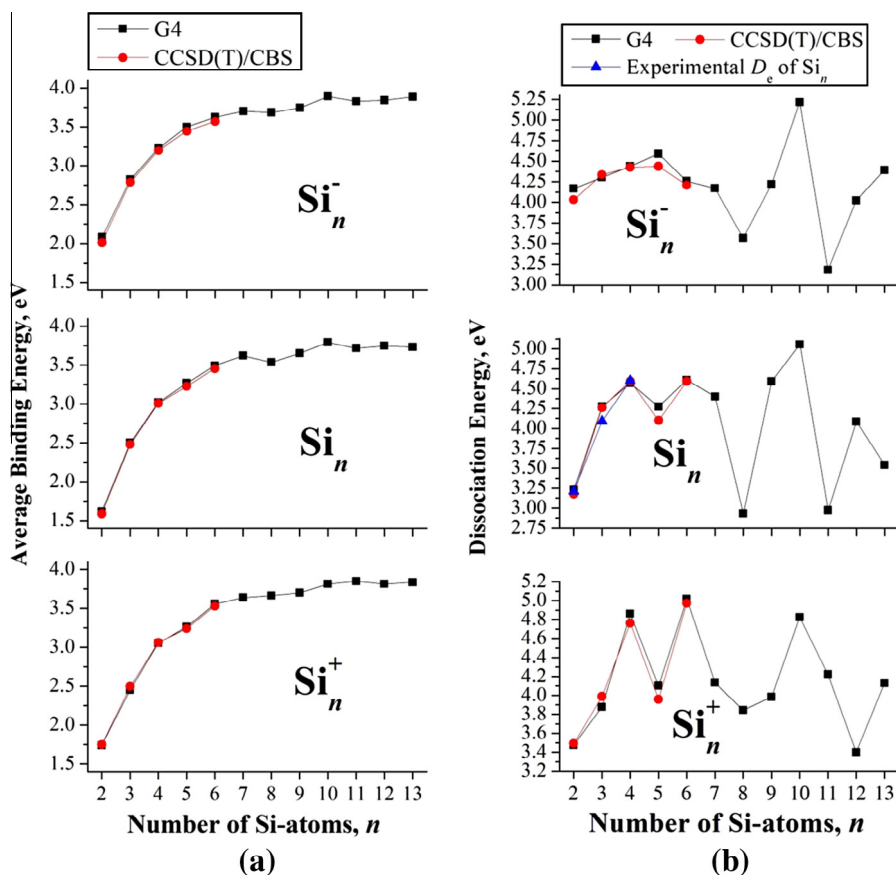
Figure 3. (a) Evolution of average binding energies (E_b) of Si_n clusters. These are defined as $E_b(Si_n) = [(n)E(Si) - E(Si_n)]/n$ for neutrals, $E_b(Si_n^-) = [(n-1)E(Si) + E(Si^-) - E(Si_n^-)]/n$ for anions and $E_b(Si_n^+) = [(n-1)E(Si) + E(Si^+) - E(Si_n^+)]/n$ for cations, and b) Evolution of dissociation energy $D_e(Si_n^{+/0/-}) = \Delta_f H^\circ(Si) + \Delta_f H^\circ(Si_{n-1}^{+/0/-}) - \Delta_f H^\circ(Si_n^{+/0/-})$ of Si_n^+, Si_n and Si_n^- ($n = 2$–13). The values are illustrated as a function of size using G4 and CCSD(T)/CBS methods.

The smallest D_e values are found for the fragmentation channels (6). This indicates that a Si_n cluster, irrespective of its charge state, prefers to decompose forming the immediately smaller cluster Si_{n-1} plus the atomic Si counterpart. An odd-oven oscillation is not always found for the plots of these fragment channels (Figure 3). The Si_{10} system reveals maximum local peaks in all charge states, in agreement with previous findings. For both neutral and cationic clusters, the sizes of 4 and 6 are more stable than their neighbours.

4. Concluding remarks

In this theoretical study, we determined molecular structures and predicted a set of thermochemical properties of a series of small silicon clusters Si_n with $n = 2$–13 in the neutral, +1 and –1 charged states.

To establish the global minima we used a stochastic search method along with high accuracy quantum chemical calculations. This search allowed us to locate a novel global minimum for the anion Si_{11}^-. Energetic parameters were evaluated using the G4 and CCSD(T)/CBS energies. In the latter, calculations using basis sets without and with tight d polarization functions were carried out.

We determined a uniform set of standard heats of formation for the cationic and anionic Si clusters that are missing up to now, using the value for the element $\Delta_f H^\circ(Si,298 \text{ K}) = 451.5$ kJ/mol. Differences between G4 and CBS TAE values are quite large. For these systems, experimental results in the current literature are also characterized by large uncertainties. This indicates that accurate

evaluation of this basic parameter for silicon clusters remains a challenge for quantum chemical computations.

Relative parameters such as ionization energies and electron affinities were however well predicted. The corresponding G4 results are expected to be accurate to ±0.15 eV. Again, the average binding energy of Si cluster tends to increase with increasing size toward a certain limit. Fragmentation giving a Si atom constitutes the favoured dissociation channel. Relative to this reaction mode, an enhanced stability is found for the sizes 4, 6 and in particular 10.

Appendix A. Supplementary data

Supplementary Tables containing the Cartesian coordinates of the lowest-lying structures and their total energies at various levels associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2013.08.051.

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