

THERMOCHEMICAL PARAMETERS OF SOME SMALL PURE AND DOPED SILICON CLUSTERS

Nguyen Minh Tam^{1,2,*}

¹Computational Chemistry Research Group, Ton Duc Thang University,
Ho Chi Minh City, Viet Nam

²Faculty of Applied Sciences, Ton Duc Thang University, Ho Chi Minh City, Viet Nam

*Email: nguyenminhtam@tdt.edu.vn

Received: 15 June 2017; Accepted for publication: 15 December 2017

ABSTRACT

Quantum chemical computations of thermochemical parameters of several series of small pure and doped silicon clusters are reviewed. We analyzed the performance of the coupled-cluster theory with energies extrapolated up to complete basis set, CCSD(T)/CBS and the composite G4 method in determining the total atomization energies (TAE), standard heats of formation ($\Delta_f H^0$), electron affinities (EA) and ionization energies (IE) and other thermochemical parameters with respect to available experimental data. The latter were determined with large error margins.

Keywords: Silicon Clusters, Doped silicon clusters, Thermochemical parameters, Total atomization energies, Heats of formation, Ionization energies, electron affinities.

1. INTRODUCTION

The heat of formation (or enthalpy of formation, denoted as ΔH_f , $\Delta_f H$, $\Delta_f H^0 \dots$), which is a key and characteristic physico-chemical parameter of a molecular system, is of common use in many fields of chemistry. It is necessary for the evaluation of thermochemical quantities of a chemical system, or the energetic outcome of a chemical process. In the latter, knowledge of the heats of formation of the compounds involved is primordial in its thermodynamic and kinetic studies. The standard heat of formation of a substance X, determined at a reference pressure and at a given temperature, is the enthalpy of the reaction accompanying the formation of one mole of that substance from its constituent elements in their reference states.

Reference states are defined as follows: i) for a gas: the standard state is at a pressure of exactly 1 atm (or 101.3 kPa), ii) for a solute present in an ideal solution: a concentration of exactly 1 M at a pressure of 1 atm, and iii) for an element: the form in which the element is the most stable under 1 atm of pressure. Since the pressure of formation reaction is usually fixed at $P = 1$ atm, the standard enthalpy of formation of a molecule (enthalpy of formation reaction), turns out to be dependent on temperature. In the symbol of $\Delta_f H^0(T)$, the superscript zero indicates that the process has occurred under standard conditions at the specified temperature T. Standard enthalpies of formation are commonly tabulated at a single temperature either $T = 0$ or 298.15 K.

For an element, its reference state is the thermodynamically most stable state at the stated conditions. The standard heats of formation of the elements in their reference states are, per definition, equal to zero at all temperatures [1]. Thus, the standard heat of formation of molecular hydrogen, the reference state of hydrogen in all temperatures, $\Delta_f H(H_2) = 0.0$, irrespective of the energy unit.

Due to their importance, determination of heats of formation has continuously been pursued using a variety of approaches and techniques by the physico-chemical community. The most common experimental measurements were based on the calorimetric and mass spectrometric techniques.[2] Among the latter, the Knudsen-effusion mass spectrometric measurements appear to be efficient for various types of elemental clusters.[3]

For a cluster $M_m N_n$ the enthalpy ΔH_r of the dissociation reaction (1):



corresponds to the total atomization energy (TAE) of the cluster $M_m N_n$, and this quantity can also be evaluated from the heats of formation of the cluster $\Delta H_f(M_m N_n)$ and the elements M and N, $\Delta H_f(M)$ and $\Delta H_f(N)$:

$$TAE = \Delta H_r = [m\Delta H_f(M) + n\Delta H_f(N)] - \Delta H_f(M_m N_n) \quad (2)$$

The wealth of experimental results obtained for heats of formation of chemical compounds in the gas phase has continuously been calibrated, evaluated and recommended in several books [4, 5, 6] and compilations [7]. Let us mention here the most known and employed compilations including the JANAF Thermochemical Tables [8], JANAF-NIST Tables [9], and the open and large compilations of the USA National Institute of Standard and Technology (NIST) webpage [10], the CODATA.... For small and medium-sized stable organic and inorganic compounds, their heats of formation in the gas phase were determined with high accuracy, attaining the chemical accuracy of ± 1.0 kcal/mol (± 4 kJ/mol or ± 0.04 eV) [8, 9, 10]. Determination of thermochemical data for unstable species or short-lived transient intermediates, such as the elemental clusters, whose productions are not straightforward, remains a challenge for experimental methods. In this context, computational thermochemistry emerged as a convenient, effective, economic and reliable alternative.

2. MATERIALS AND METHODS

Let us first briefly describe the current strategies for quantum chemical determination of heats of formation. The heats of formation cannot directly be derived from the total energies obtained from electronic structure computations. As in experiment, the use of thermochemical cycles involving the heat of a working reaction is necessary. This leads to two main theoretical approaches: while the first approach uses a working reaction where only the heat of formation to be determined is unknown, the second approach involves a complete dissociation of the substance yielding atoms (reaction 1) whose TAE needs to be computed.

2.1. Approach using a working chemical reaction.

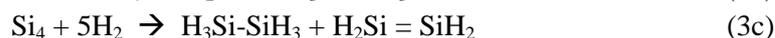
The selection of a suitable reaction is of essential importance. When several working reactions are equally possible, the reaction having the largest similarity between both reactant and product sides should be considered. Such a similarity minimizes the importance of correlation effects by a mutual cancellation of errors. For example, exchange reactions and isodesmic (bond separation) reactions for larger species, are often preferred over other types of

reaction. The main advantage of this approach is that it does not require a high level of theory in order to obtain good reaction energies. Its main inconvenience turns out to be the accuracy of the heats of formation of the compounds involved in the working reaction.

2.2. Approach using the total atomization energy (TAE).

This is a more direct way as it involves only the experimental heats of formation of the elements (cf. equation 2). Due to the intrinsic difference of electron correlation in atoms and molecules, use of massively correlated wavefunctions is imperative, and therefore evaluation of TAEs still represents a challenge for computations [11].

In both cases it is necessary to employ a quantum chemical method that is *size-consistent*, that is $E(A + B) = E(A) + E(B)$. Due to the fact that chemical bonding in elemental clusters is of non-classical nature, reactions such as the isodesmic (bond separation) reactions... that are successfully used for organic compounds could not be applied to clusters. The reactions (3) provide us with an example on silicon clusters. While the hydrogenation reaction (3a) could eventually be used, the bond separation reactions (3b) and (3c) are not suitable as the SiSi bonds in the tetramer Si_4 differ much from the single Si-Si bond in disilane and double Si=Si bond in disilene. The number of Si-Si bonds in the tetramer is not recovered in the products. More importantly, the experimental heat of formation of disilene is not known yet.



For this reason, the approach 2) involving first a theoretical determination of TAEs is commonly employed for elemental clusters. This is a straightforward but challenging approach, due to the intrinsic differences in electron correlation of the atoms and molecules. Only a careful strategy for treatment of electron correlation can give results attaining the chemical accuracy of ± 1.0 kcal/mol.

Quantum chemical results reported in this review were determined using both the composite G4 technique and coupled-cluster theory with energy extrapolated to the complete basis set limit, CCSD(T)/CBS. The main difference between both approaches is that the G4 is a fixed model chemistry whereas the CCSD(T)/CBS protocol allows more flexibility in the individual treatment of electron correlation.

The composite G4 technique[12] is the latest version the Gaussian-X (GX) method in which the G4 energy is actually based on that computed at the coupled-cluster CCSD(T) theory with the 6-31G(d) basis set. A sequence of single-point electronic energies is subsequently performed using perturbation theory (MP2 and MP2) computations with some larger basis sets, in conjunction with the additivity approximation, to arrive at an improved electronic energy of a given molecular species. Corrections for zero-point energies (ZPE) and spin-orbit (SO) and empirical higher level corrections (HLC) are also included.

In the CCSD(T)/CBS protocol, electronic energies are calculated using the restricted/unrestricted coupled-cluster R/UCCSD(T)[13] formalism (ROHF followed by UCCSD for open-shell structures) with the correlation consistent basis sets aug-cc-pVnZ (aVnZ n = D, T, Q, 5, 6...) [14] or aug-cc-pV(n+d)Z (aV(n+d)Z) where *d* stands for a set of tight *d* polarization functions. The CCSD(T) total energies are then extrapolated to the CBS limit using expression (4):

$$E(x) = E(\text{CBS}) + B\exp[-(x-1)] + C\exp[-(x-1)^2] \quad (4a)$$

where $x = 2, 3$ and 4 for the $aVnZ$ basis, $n = D, T$ and Q , respectively, and

$$E(x) = E(\text{CBS}) + B/x^3 \quad (4b)$$

where $x = 4$ and 5 (or 5 and 6) for the $aVnZ$ basis, $n = Q$ and 5 (or $n = 5$ and 6), respectively.

In the CCSD(T)/CBS protocol, the TAE (ΣD_0) of a compound is given by (5):

$$\Sigma D_0 = \Delta E(\text{CBS}) + \Delta E_{\text{CV}} + \Delta E_{\text{DKH-SR}} + \Delta E_{\text{SO}} - \Delta E_{\text{ZPE}} \quad (5)$$

in which ΔE_{CV} , $\Delta E_{\text{DKH-SR}}$, ΔE_{SO} and ΔE_{ZPE} stand for the corrections due to the core-valence correlation, relativistic effect, spin-orbit effect and zero-point energy, respectively. The most important corrections are the ZPEs, that are calculated, when possible, from either CCSD(T)/aug-cc-pVnZ ($n = D, T$) at CCSD(T) optimized geometries, or simply from density functional theory (DFT) harmonic vibrational frequencies at corresponding equilibrium geometries. The spin-orbit (SO) corrections of the atoms are obtained from their excitation energies. A value of 1.8 kJ/mol (0.43 kcal/mol) is taken for the Si atom. These corrections are relatively small but when taking their sum for a large cluster, they become non-negligible in the effort to attain a high accuracy of the TAEs.

It is of interest to examine the performance of the CBS extrapolation scheme. Table 1 lists the D_e values of Si_2 calculated with the aug-cc-pV($n+d$)Z basis sets going from $n = 2$ to 8 . The D_e value tends to be increased with increasing basis set, and smoothly converge to a limited value of ~ 318 kJ/mol. The latter value is actually the extrapolated CBS value obtained using also the aug-cc-pV($n+d$)Z basis sets with either $n = 2, 3$ and 4 or $n = 4$ and 5 for the extrapolation (Table 1).

Table 1. Atomization energy (D_e , kJ/mol) of Si_2 (${}^3\Sigma_g^-$) using coupled-cluster theory with different basis sets^{a)}.

Method	Basis set	D_e
R/UCCSD(T) (FC)	aug-cc-pV(D+d)Z	269.3
R/UCCSD(T) (FC)	aug-cc-pV(T+d)Z	301.0
R/UCCSD(T) (FC)	aug-cc-pV(Q+d)Z	311.5
R/UCCSD(T) (FC)	aug-cc-pV(5+d)Z	315.5
R/UCCSD(T) (FC)	aug-cc-pV(6+d)Z	316.5
R/UCCSD(T) (FC)	aug-cc-pV(7+d)Z	317.1
R/UCCSD(T) (FC)	aug-cc-pV(8+d)Z	317.4
R/UCCSD(T) (FC)	aug-cc-pV(n+d)Z CBS (n = 2,3,4)	318.0
R/UCCSD(T) (FC)	aug-cc-pV(n+d)Z CBS (n = 4, 5)	318.3

D_e is obtained at the optimized geometry using the same level and without vibrational correction.

The effect of higher-order correlation was also probed. Computations using full expansions of the triple excitations (T) in CCSDT/cc-pVQZ and quadruple excitations (Q) in CCSDTQ/cc-pVTZ give the $D_e(\text{Si}_2)$ values of 308 and 297 kJ/mol, respectively. [The latter values differ significantly from the CBS value of 318 kJ/mol. In going from the CCSD(T) to the full interaction configuration (FCI) with the same cc-pVDZ basis set, $D_e(\text{Si}_2)$ increases by 2.6

kJ/mol. This suggests that in the determination of TAEs, expansion of one-electron functions is a more important factor than incorporation of higher-order electron correlation. For this purpose, the CCSD(T)/CBS protocol is proved to be a reliable approach.

3. RESULTS AND DISCUSSION

3.1. The heat of formation of the silicon element

In a theoretical determination of heats of formation of silicon-based compounds, an inherent difficulty persists. As a matter of fact, the heat of formation of the silicon element is not well determined yet [15].

In their 1995 papers, Rocabois and coworkers [16, 17] reviewed the values of $\Delta_f H(\text{Si})$ 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 at 298 K. These authors [16] proposed after careful evaluating a value of 445.3 ± 5 kJ/mol. This differs by up to 10 k/mol from a previously established value of $\Delta_f H(\text{Si}, g) = 455.6 \pm 4.2$ kJ/mol at 298 K, tabulated in 1973 by Hultgren *et al.*[4].

In the 1998 JANAF database [18], a value of $\Delta_f H_{298.15}(\text{Si}) = 450 \pm 8$ 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 [19]. Other theoretical values for the Si heat of formation (0 K) include 452.3 ± 2.1 kJ/mol [20] and 449.3 ± 2.5 kJ/mol [21]. By means of high-accuracy quantum chemical computations on a few selected Si-compounds whose experimental data were well known [22], a value of 448.5 ± 0.8 kJ/mol (107.2 ± 0.2 kcal/mol) was proposed. This value appeared fortuitously to be an average of the values of Rocabois *et al.* [16] and JANAF/CODATA [18] mentioned above.

When determining the heats of formation of Si_7 and Si_8 from their experimental TAEs, Meloni and Gingerich [15] pointed out a large variation, up to 73-83 kJ/mol, between two sets of results derived from two different values for $\Delta_f H(\text{Si})$. The uncertainty on the $\Delta_f H(\text{Si}, g)$ mainly arises from the choice of the enthalpy of sublimation of solid silicon used in the thermodynamic cycle (ref. 15, page 5474). In our work, we have selected the latest value of $\Delta_f H(\text{Si}) = 448.5$ kJ/mol (107.2 kcal/mol) at 0 K.

3.2. Thermochemical parameters of pure neutral silicon clusters Si_n

3.2.1. Total Atomization Energies

Table 2 collects the total atomization energies (TAEs) of Si_n . There are only a few experimental results for small neutral Si_n clusters (refs. 15,16,17,23,24,25,26). Calculated results for the series Si_n with $n = 2-13$ are obtained using both G4 and CCSD(T)/CBS (denoted hereafter as CBS) methods. The CBS values are derived from extrapolation of the CCSD(T)/aug-cc-pV(n+d)Z energies. Inclusion of the tight d functions causes some reductions, up to 6 kJ/mol, of the TAEs, as compared to the CCSD(T)/aug-cc-pVnZ counterparts. This small but significant correction again demonstrates the importance of tight d polarisation functions in treatment of systems having multiple second-row atoms.

Of the calculated values for each cluster, the CBS value is the smaller one, except for Si_2 (Table 2). The G4 and CBS TAE values differ by 1, 7 and 6 kJ/mol for Si_2 , Si_3 and Si_4 ,

respectively. The deviations become larger for Si_5 (23 kJ/mol) and Si_6 (27 kJ/mol, cf. Table 1). Such a difference can in part be attributed to the inherent treatment of the Si atom in each protocol and the one-electron basis sets used. However, calculated TAEs compare relatively well with available experimental results when the large error bars of the reported experimental data are taken into account (Table 2).

Table 2. Total atomization energies (TAE) of the lowest-lying isomers of the neutral Si_n ($n = 2 - 13$) using G4 and CBS [CCSD(T)/CBS] protocols.

Structure ^{a)}	TAE (kJ/mol)		
	G4	CBS	Exptl. ^{b)}
Si_2 ($^3\Sigma_g^-, D_{\infty h}$)	311.6	312.2	319 ± 7
Si_3 ($^1A_1, C_{2v}$)	723.9	716.5	705 ± 16
Si_4 ($^1A_g, D_{2h}$)	1164.9	1159.0	1151 ± 22
Si_5 ($^1A'_1, D_{3h}$)	1577.1	1553.6	1559 ± 24
Si_6 ($^1A_1, C_{2v}$)	2021.7	1995.1	1981 ± 32
Si_7 ($^1A'_1, D_{5h}$)	2446.2		2381 ± 36
Si_8 ($^1A_g, C_{2h}$)	2729.1		2735 ± 65
Si_9 ($^1A', C_s$)	3172.2		
Si_{10} ($^1A_1, C_{3v}$)	3660.0		
Si_{11} ($^1A', C_s$)	3946.7		
Si_{12} ($^1A', C_s$)	4340.9		
Si_{13} ($^1A_1, C_{2v}$)	4682.9		

^{a)} Shape of the optimized geometries of the neutral Si_n clusters are displayed in Figure 1.

^{b)} Experimental values taken from refs. [23] for Si_2 and Si_3 , [24] for Si_4 , [25] for Si_5 , [26] for Si_6 , and [15] for Si_7 and Si_8 .

Si₂ ($^3\Sigma_g^-$): Computed values are apparently underestimated, but the G4 and CBS values of $\text{TAE}(\text{Si}_2) = 312$ kJ/mol is close to the experimental one of 319 ± 7 kJ/mol [16, 23]. Feller *et al.*[27] also used CCSD(T)/CBS but with basis set up to aug-cc-pV(6+d)Z, derived a value of 314 kJ/mol for $\text{TAE}(\text{Si}_2)$ including a correction of 2 kJ/mol for the higher-order correlation. If the latter correction of 2 kJ/mol is included, we thus obtain the same value for $\text{TAE}(\text{Si}_2)$ as in ref. [27].

Si₃: Calculated values $\text{TAE}(\text{Si}_3) = 724$ (G4) and 717 kJ/mol (CBS) are overestimated with respect to the experimental result of 705 ± 16 kJ/mol [16, 23] even though they are close to the upper limit of the error margin. Previous studies [28] found a singlet ground state with a small singlet-triplet separation (S-T) of ~4 kJ/mol.

To probe further this important parameter, Table 3 lists the S-T gap of Si_3 . Except for the CASPT2(12,12) level, the energy gaps obtained using wavefunction-based methods such as the composite G3 and G4 approaches and coupled-cluster theories agree well with each other. All suggest a marginally lower energy of the singlet state. The higher the level employed, the smaller the S-T gap. Table 4 presents the TAEs computed for both isomers of Si_3 including all the corrections necessary to reach a few kJ/mol accuracy. The best estimate including a correction from the CCSDTQ level, indicates that, at 0 K, the singlet state is 0.8 kJ/mol more stable than the triplet. However, a small error on different correction terms to the total energies, for example the ZPEs or the higher-order correlation could induce a change in the energy ordering in tipping the balance in one direction. We would thus conclude that at their vibrational ground state, both singlet and triplet states of Si_3 can be regarded as degenerate.

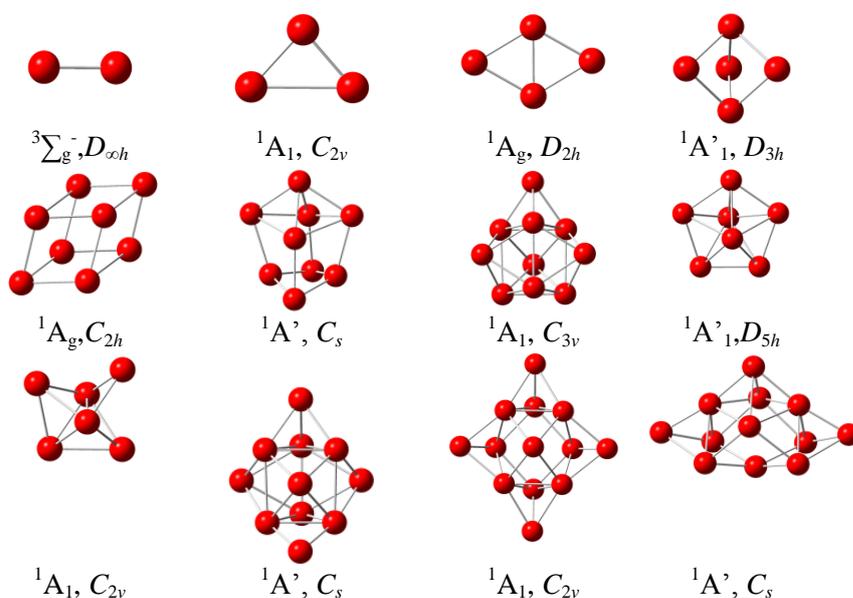


Figure 1. Shapes of the lowest-lying isomers of Si_n in the neutral state ($n = 2-13$).

Table 3. Singlet-triplet energy gap (ΔE_{ST}) of Si_3 calculated using different molecular orbital based methods.

Method	ΔE_{ST} , kJ/mol
G1	18.0
G2	14.9
G3	3.7
G3B3	4.1
G4	4.2
MP2/aug-cc-pVTZ	4.3
MP2/aug-cc-pVQZ	6.3
CASSCF(12,12)/ANO-L	19.2
CASSCF(12,12)/aug-cc-pVQZ	19.2
CASPT2(12,12)/ANO-L	-2.2
CASPT2(12,12)/ANO-L	-2.0
CCSD(T)/aug-cc-pV(D+d)Z	0.3
CCSD(T)/aug-cc-pV(T+d)Z	0.4
CCSD(T)/aug-cc-pV(Q+d)Z	0.3
CCSD(T)/aug-cc-pV(5+d)Z	0.5
CCSD(T)/aug-cc-pV(6+d)Z	0.5
CCSD(T)/CBS(D,T,Q)	0.6
CCSD(T)/CBS(Q,5)	0.6
CCSD(T)/CBS(5,6)	0.6
CCSD(T)/ aug-cc-pwCVQZ	0.4
CCSD(T)/ aug-cc-pwCV5Z	0.3
CCSDT/aug-cc-pV(T+d)Z	-1.3
CCSDT/aug-cc-pV(Q+d)Z	-0.7
CCSDTQ/ aug-cc-pV(D+d)Z	1.7
CCSDTQ/cc-pV(T+d)Z	0.6

Si₄: both computed values of 1165 (G4) and 1159 kJ/mol (CBS) for TAE(Si₄) are again overestimated but still within the experimental upper error margin of 1151 ± 22 kJ/mol.[16, 24].

Si₅: Of the values of 1577 (G4) and 1554 kJ/mol (CBS), the CBS can be compared with the experimental value of 1559 ± 24 kJ/mol.[16, 25] but the G4 still is within the experimental error bar.

Si₆: the CBS TAE(Si₆) = 1995 kJ/mol appears to be closer to the experimental data of 1981 ± 32 kJ/mol[16] than the G4 counterpart of 2022 kJ/mol.

Si₇ and Si₈. A disparate behavior of G4 values emerges. While TAE(Si₇) = 2446 kJ/mol is not consistent with the experimental results of 2381 ± 36 kJ/mol,[15] TAE(Si₈) = 2729 kJ/mol compares better with the experimental result of 2735 ± 65 kJ/mol.[15] 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 Si₈ appears again fortuitous.

For the larger Si_n from $n = 9$ to 13, the corresponding TAEs can now only be predicted by G4 results as summarized in Table 2. Overall, the CBS results (Table 2) represent the best values we have obtained so far for the small clusters. The large difference between G4 and CBS TAE values is rather 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 $n > 10$. Accurate determination of TAEs for medium-size silicon clusters remains a challenge for quantum chemical computations.

Table 4. Total atomization energy (TAE) of Si₃ determined using the R/UCC coupled-cluster treatment. Values in kJ/mol.

Components of the CBS protocol	Singlet ¹ A ₁	Triplet ³ A ₂
TAE _e /CCSD(T) CBS/aug-cc-pV(5+d)Z, aug-cc-pV(6+d)Z	726.0	724.5
Core (CCSD(T)/aug-cc-pwCV5Z)	3.3	3.7
Scalar relativistic CCSD(T)/aug-cc-pVTZ-DK	-1.8	-1.9
Spin Orbit	-5.3	-5.3
ZPE (anharmonic) ^{a)}	-7.5	-6.9
CCSDTQ-CCSD(T)	4.7	4.6
TAE at 0K	719.4	718.6

^{a)} Fundamental vibrational frequencies of the singlet state are 180, 524 and 549 cm⁻¹ and those of the triplet state are: 324, 325 and 502 cm⁻¹, obtained at the R/UCCSD(T)/cc-pV(T+d)Z level.

3.2.2. Heats of Formation

By combining the TAE (ΣD_0) values computed from either the G4 or CBS energies with the heat of formation at 0 K for the element Si (see above), we can derive the enthalpy of formation $\Delta_f H^\circ$ values at 0 K for a Si_n cluster in the gas phase (6):

$$\Sigma D_0(\text{Si}_n) = n \cdot \Delta H_f(\text{Si}) - \Delta H_f(\text{Si}_n) \quad (6)$$

Table 5. Heats of formation at 0K [$\Delta_f H(0\text{ K})$] and 298K [$\Delta_f H(298\text{ K})$] (kJ/mol) of the lowest-lying isomers of the neutral Si_n using G4 and CCSD(T)/CBS approaches.

n	G4 (0K)	CBS (0K)	G4 (298K)	CBS (298K)	Exptl.^{a)} (298K)
2	585.5	584.8	588.3	587.7	575.5 ± 9.4
3	621.7	629.0	624.7	632.0	631.3 ± 7.9
4	629.3	635.1	632.8	638.7	634.8 ± 8.3
5	665.5	689.0	669.0	692.3	661.3 ± 10.3
6	669.4	696.05	674.6	701.2	702.8 ± 18.3
7	693.5		698.5		743 ± 36
8	859.1		866.0		837 ± 65
9	864.6		872.2		
10	825.3		832.7		
11	987.0		996.2		
12	1041.4		1050.9		
13	1148.2		1157.5		

^{a)} Experimental values taken from refs. [17] for Si_2 , Si_3 , Si_4 , Si_5 , and Si_6 , ref. [15] for Si_7 and Si_8 .

The values at 298.15 K are subsequently determined by following the classical thermochemical cycle involving the thermal corrections. Calculated results are summarized in Table 5. As this parameter of each species is directly derived from its TAE and the $\Delta_f H^\circ(\text{Si})$, deviations discussed above for the TAEs will further be propagated. In addition, a discrepancy also arises from the value actually used for the element $\Delta_f H^\circ(\text{Si})$ (see Section 3). The deviation increases, as expected, with increasing cluster size. With an error of 5 kJ/mol, for example, the use of $\Delta_f H^\circ(\text{Si})$ invariably induces an error of $5n$ kJ/mol on the molecular parameter of Si_n . Reasonable agreement between both CBS and experimental values can be noted, 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 5). 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.[15] Overall, such deviations arise in part from the disparate selection of the value of the Si element.

3.2.3. Electron Affinities and Ionization Energies

Let us consider the electron affinities (EA) and ionization energies (IE) of the Si_n clusters as an amount of experimental results are available. Calculated G4 and CBS results are summarized in Table 6, together with available experimental values [29,30,31,32,33,34,35].

Differences of a few hundredths of an eV (1 eV = 96.49 kJ/mol) between both G4 and CBS values can be noticed. Both sets of predicted values are also in good agreement with experiment, with deviations < 0.1 eV (Table 6). Density functional theory (DFT/B3LYP) computations also give rise to reasonable IEs for Si_n [30]. A mutual cancellation of errors on the energies of both neutral and cationic forms appears to be effective yielding better relative energetic quantities.

The EA of the element Si for which an experimental result is missing, can be predicted as $\text{EA}(\text{Si}) = 1.35 \pm 0.10$ eV. There is a good agreement on both parameters of Si_2 , Si_3 and Si_6 . For Si_4 , both calculated values of 2.18 (G4) and 2.14 eV (CBS) are close to the experimental EA of 2.13 eV [33] (Table 6). Predictions of 8.00 (G4) and 7.95 eV (CBS) for $\text{IE}(\text{Si}_4)$ correspond to the

largest underestimation as compared to the experimental IE of 8.20 ± 0.10 eV.[30] The EA and IE values for Si_5 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).

While Si_7 has a large deviation of 45 kJ/mol of its G4 heat of formation relative to available experiment (Table 5), the G4 EA(Si_7) = 1.92 eV turns out to be comparable to the experimental result of 1.85 ± 0.02 eV.[33] On the contrary, the G4 IE(Si_7) = 8.02 eV represents the largest overestimation with respect to the experimental IE of 7.8 ± 0.1 eV [30].

Table 6. Adiabatic electronic affinities (EA) and ionization energies (IE) of Si_n clusters, $n = 2-13$ computed using G4 and CBS methods.

n	EA, eV			IE, eV		
	G4	CBS	Exptl. ^{a)}	G4	CBS	Exptl. ^{b)}
2	2.29	2.23	2.20 ± 0.01	7.89	7.85	7.92 ± 0.05
3	2.31	2.31	2.29 ± 0.002	8.29	8.12	8.12 ± 0.05
4	2.18	2.14	2.13 ± 0.001	8.00	7.95	8.20 ± 0.10
5	2.50	2.47	2.59 ± 0.02	8.17	8.09	7.96 ± 0.07
6	2.15	2.09	2.08 ± 0.14	7.76	7.71	7.8 ± 0.1
7	1.92		1.85 ± 0.02	8.02		7.8 ± 0.1
8	2.56		2.36 ± 0.10	7.11		
9	2.18		2.31 ± 0.25	7.72		
10	2.35		2.29 ± 0.05	7.95		
11	2.55		2.5	6.70		
12	2.49		2.6	7.39		
13	3.34			6.80		

^{a)} Experimental values taken from refs. [31, 32] for Si_2 , [33] for Si_3 , Si_4 , Si_5 , and Si_7 , [34] for Si_6 , Si_8 , and Si_{10} , [35] for Si_9 , [29] for Si_{11} and Si_{12} .

^{b)} Experimental values taken from refs. [30] for Si_2 , Si_3 , Si_4 , Si_5 , Si_6 , and Si_7 .

Table 7. Electron affinity (EA, eV) of Si_2 ($^3\Sigma_g^-$) and proton affinity (PA at 0 K, kJ/mol) of Si_3 (1A_1) calculated using the G4 and coupled-cluster theory with different basis sets.

Method ^{a)}	PA Si_3	EA Si_2
G4	820	2.29
CCSD(T)/aug-cc-pV(D+d)Z	820	2.07
CCSD(T)/aug-cc-pV(T+d)Z	826	2.18
CCSD(T)/aug-cc-pV(Q+d)Z	826	2.22
CCSD(T)/aug-cc-pV(5+d)Z	826	2.22
CCSD(T)/aug-cc-pV(6+d)Z	825	2.23
CCSD(T)/CBS(D,T,Q)	826	2.23
CCSD(T)/CBS(Q,5)	826	2.23
CCSD(T)/CBS(5,6)	825	2.23
CCSD(T)/CBS(Q,5,6)	825	2.23

a) Geometries and vibrational frequencies of neutral, protonated and anionic forms are computed at the same CCSD(T) level. For CBS computations, CCSD(T)/aug-cc-pV(T+d)Z geometries and frequencies (ZPE) are used.

The calculated EAs appear to be more consistent with experiment (Table 6). To test further the method dependence of these parameter, Table 7 lists the EA(Si₂) calculated using different basis sets and CBS extrapolation schemes. The EA(Si₂) value is rapidly converged, and a reliable EA value can already be obtained from the aug-cc-pV(T+d)Z basis set. At this level, a deviation of < 0.1 eV with respect to the CBS counterpart is expected. An error margin of, at most, ± 0.15 eV can be estimated for the G4 EAs and IEs of silicon clusters.

3.3 Thermochemical parameters of some doped silicon clusters Si_nM

Experimental results on thermochemical parameters of singly doped silicon clusters are rather scarce. Total atomization energies and heats of formation of only a few small Si_nM have been reported. These include the boron-doped Si₂B and Si₃B [36], carbon-doped Si₂C, Si₃C and Si₄C [16], and germanium-doped Si₂Ge [37]. Computational results for TAE, Δ_fH, IE, EA and other parameters are actually available for different series of doped silicon clusters including Si₃M (with M = Li, Na, K, Be, Mg and K) [38,39], Si_nB (*n* = 1-10) [40], Si_nAl_{*m*} (*n* = 1-11, *m* = 1-2) [41] and Si_nMg (*n* = 1-12). Experimental and computed ionization energies of multiply lithium-doped Si_nLi_{*m*} (*n* = 1-11, *m* = 1-5) were also reported [42,43].

Boron Doped Si_nB

Boron is widely used as a p-type dopant in crystalline silicon. These solid materials are known for their mechanical hardness. Gingerich and coworkers [36] used the Knudsen effusion mass spectrometric technique to determine the TAE and Δ_fH values of three Si_nB species with *n* = 1-3.

Table 8. Total atomization energies (TAE), adiabatic ionization energies (IE) and adiabatic electron affinities (EA) of B-doped silicon clusters Si_nB using G4 and CCSD(T)/CBS computations.

Structure	TAE (kJ/mol)			IE (eV)		EA (eV)	
	G4	CBS	Expt.	G4	CBS	G4	CBS
SiB	314.8	311.3	312 ± 12	9.15	9.03	1.69	1.67
Si ₂ B	780.6	774.9	767 ± 18	8.56	8.56	2.48	2.42
Si ₃ B	1179.5	1172.8	1199 ± 28	7.62	7.61	2.94	2.87
Si ₄ B	1610.5	1594.1		7.35	7.33	2.81	2.70
Si ₅ B	2079.4			7.65		3.37	
Si ₆ B	2468.5			7.15		3.60	
Si ₇ B	2841.0			6.60		2.93	
Si ₈ B	3222.4			6.12		3.25	
Si ₉ B	3722.5			6.89		3.65	
Si ₁₀ B	4064.3			5.30		3.09	

Table 8 compares the calculated and experimental TAEs for a series of Si_nB with *n* = 2-10, along with the adiabatic ionization energies (IE) and electron affinities (EA). Table 9 summarizes the results for heats of formation.

Where possible, there is a reasonable agreement between both sets of CBS and G4 results (Table 8). The CBS $\Delta_f H^0$ are larger than the G4 counterpart (Table 9). The difference varies in the range of 4–24 kcal/mol. The maximum difference between both sets of values is 0.11 eV for EA's and 0.12 eV for IE's. More importantly, both theoretical methods show a fair agreement with available experimental data, in view of the large experimental error margins.

Table 9. Heat of formation $\Delta_f H$ (0 K) and $\Delta_f H$ (298 K) (kcal/mol) of the global minima of $Si_n B$ obtained using G4 and CCSD(T)/CBS).

Structure	ΔH_f (0K)			ΔH_f (298K)		
	G4	CBS	Exptl. ^{a)}	G4	CBS	Exptl. ^{a)}
SiB ($C_{\infty v}$ $^4\Sigma^-$)	699.0	702.6	694 ± 14	703.5	707.1	698 ± 14
Si₂B (C_{2v} 2B_2)	681.7	687.6	685 ± 20	685.6	691.5	688 ± 20
Si₃B (C_{2v} 2A_1)	731.4	738.0	699 ± 31	735.8	742.4	701 ± 31
Si₄B (C_{2v} 2B_2)	748.9	763.0		754.0	767.5	
Si₅B (C_s $^2A''$)	728.5			733.8		
Si₆B (C_s $^2A''$)	787.9			794.6		
Si₇B (C_s $^1A'$)	863.9			870.4		
Si₈B (C_1 2A)	931.0			939.5		
Si₉B (C_s $^2A'$)	879.5			889.4		
Si₁₀B (C_s $^2A'$)	986.2			996.1		

^{a)} Experimental values taken from ref. [36].

Carbon Doped Si_nC and Germanium Doped Si_nGe

Only a few small silicon and germanium carbides have been the subject of thermochemical investigations. Using mass spectrometric techniques, Gingerich and coworkers [37, 44] were able to measure the TAE and subsequently derive the $\Delta_f H$ values of four $Si_n C_m$ (SiC_2 , Si_2C , Si_2C_2 and Si_3C) and four $Si_n Ge_m$ ($SiGe$, Si_2Ge , $SiGe_2$ and Si_2Ge_2). Parameters of the silicon carbides were also determined by Rocabois *et al.* [16, 17]. Table 10 lists the calculated and experimental results available for two triatomic Si_2C and Si_2Ge species. Again, a deviation between both G4 and CBS values for Si_2Ge amounts up to 30 kJ/mol, and both are only in fair agreement with experiment.

Table 10. TAE, ΔH_f (0 K) and ΔH_f (298 K) (kcal/mol) of Si_2C and Si_2Ge obtained using G4 and CCSD(T)/CBS Calculations.

Structure	TAE			ΔH_f (0K)		ΔH_f (298K)		
	G4	CBS	Exptl.	G4	CBS	G4	CBS	Exptl.
Si_2C	--	1059	1052 ± 10	-	549	--	553.7	566 ± 11 ^{a)} 563 ± 8 ^{b)}
Si_2Ge	676.8	706.9	700 ± 17	592.3	562.2	594.4	564.1	574 ± 19 ^{a)}

^{a)} Experimental results are taken from refs. [37,44];

^{b)} Experimental results are taken from refs. [17].

Aluminum Doped Si_nAl_m

As far as we are aware, no experimental data are available for Al-doped Si clusters. Table 11 summarizes the computed results obtained for not only for the singly-doped Si_nAl but also the doubly-doped Si_nAl_m counterparts. This includes the TAE, ($\Delta_f H^0$) and EA [41]. The ΔH_f^0 obtained using CCSD(T)/CBS are slightly larger than those obtained by G4, except for the diatomic SiAl . The difference varies in the range of 7 – 22 kJ/mol for the species considered (Table 11). The adiabatic electron affinities (EAs) are obtained with an overall agreement between both theoretical approaches. The maximum difference between two sets of values amounts to 0.17 eV for EAs of Si_nAl , and 0.11 eV for EAs of Si_nAl_2 .

Table 11. Total atomization energies (TAE), heats of formation at 0K [$\Delta H_f(0\text{ K})$] and 298K [$\Delta H_f(298\text{ K})$] (kcal/mol) and electron affinities (eV) of Si_nAl_m ($n = 1-11$, $m = 1-2$) in the neutral states obtained using G4 and CCSD(T)/CBS Calculations.

Structure	TAE		$\Delta H_f(0\text{ K})$		$\Delta H_f(298\text{ K})$		EA (eV)	
	G4	CBS	G4	CBS	G4	CBS	G4	CBS
SiAl	249.1	241.3	535.0	542.8	536.9	544.4	1.17	1.34
Si₂Al	619.1	609.9	613.5	622.8	616.2	625.5	2.27	2.24
Si₃Al	1031.7	1025.1	649.4	656.0	652.0	658.5	2.54	2.47
Si₄Al	1384.5		745.2		749.2		3.11	
Si₅Al	1885.6		692.6		696.6		2.95	
Si₆Al	2266.6		760.1		764.5		3.28	
Si₇Al	2613.5		861.8		868.1		2.85	
Si₈Al	3003.9		919.9		926.5		3.52	
Si₉Al	3461.1		911.2		918.3		3.96	
Si₁₀Al	3862.8		958.0		966.8		3.17	
Si₁₁Al	4183.6		1085.7		1094.0		3.57	
SiAl₂	503.4	486.3	616.3	633.3	617.3	634.1	1.90	2.01
Si₂Al₂	924.9	913.4	643.3	654.8	645.0	656.3	2.03	1.98
Si₃Al₂	1282.1	1270.7	734.5	746.0	738.7	747.6	2.18	2.07
Si₄Al₂	1755.2		710.0		713.5		2.56	
Si₅Al₂	2152.7		761.0		766.4		2.61	
Si₆Al₂	2554.1		808.1		813.0		2.14	
Si₇Al₂	2909.2		901.6		908.0		2.57	
Si₈Al₂	3382.1		877.3		884.1		2.64	
Si₉Al₂	3846.2		861.6		869.1		2.31	
Si₁₀Al₂	4118.9		1037.5		1044.2		2.65	
Si₁₁Al₂	4521.2		1083.7		1090.2		2.65	

4. CONCLUSION

In this short review, we attempted to assess the predictions made by high accuracy quantum chemical computations on the thermochemical parameters of a series of small pure Si_n and doped Si_nM silicon clusters. Energetic values were determined using both the composite G4 technique and the coupled-cluster protocol with energies extrapolated to complete basis set CCSD(T)/CBS. In the latter, calculations using basis sets with tight d polarization functions were carried out. Uniform sets of total atomization energies and thereby standard heats of formation as well as the ionization energies and electron affinities of Si clusters were determined. A number of factors emerge that appear to challenge the accurate computations of these thermochemical parameters.

i) Intrinsic differences in both protocols lead to large deviations between both G4 and CBS values for total atomization energies and heat of formation. The larger the molecule the larger the deviation.

ii) The heat of formation of the silicon element is not well established neither by experiment nor by theory. The value of $\Delta_f H^\circ(\text{Si}, 298 \text{ K}) = 451.5 \text{ kJ/mol}$ has been selected but the error margin is not known. This invariably leads to systematic errors in the evaluation of the standard heats of formation.

iii) Experimental results on TAEs of silicon clusters reported in the current literature are also characterized by large uncertainties, reaching $> \pm 60 \text{ kJ/mol}$. This indicates that accurate evaluation of this basic parameter for either pure or doped silicon clusters, attaining the chemical accuracy of $\pm 4.0 \text{ kJ/mol}$ or 1.0 kcal/mol , remains a great challenge for quantum chemical computations.

iv) Parameters based on relative energies such as adiabatic ionization energies, adiabatic electron affinities, proton affinities and low spin – high spin energy gaps... can be better predicted, thanks to a mutual cancellation of errors. For these thermochemical parameters, the corresponding G4 results are expected to be accurate to, at most, $\pm 12 \text{ kJ/mol}$ ($\pm 3 \text{ kcal/mol}$ or $\pm 0.15 \text{ eV}$).

Acknowledgements. The author is indebted to the KU Leuven Research Council for a postdoctoral fellowship. He also thanks ICST

REFERENCES

1. Atkin P. W. - Concepts in Physical Chemistry, Oxford University Press, U.K., 1995.
2. CODATA Task Group – CODATA recommended key values for thermodynamics, 1977 Report of the CODATA Task Group on key values for thermodynamics, 1977, J. Chem. Thermodyn **10** (1978) 903-906.
3. Gingerich K. A. - Gaseous Metal Nitrides, II. The Dissociation Energy, Heat of Sublimation, and Heat of Formation of Zirconium Mononitride, J. Phys. Chem. **49** (1968) 14-18.
4. Hultgren R., Desai P. D., Kawkins D. T., Gleiser M., Kelly K. K., and Wagman D. D. - Selected Values for the Thermodynamic Properties of the Elements, American Society of Metals, Metals Park, OH, 1973.
5. Cox J. D. and Pilcher G. - Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970.
6. Gurvich L. V., Veyts I. V, and Alcock C. B. - Thermodynamic Properties of Individual Substances, Hemisphere, New York, 1991.

7. A large number of thermochemical data were compiled in the Journal of Physical Chemistry and Reference Data published by the American Chemical Society.
8. Chase M. W., Davis C. A., Downey J. R., Frurip D. J., McDonald R. A., and Syverud A. N. - JANAF Thermochemical Tables, J. Phys. Chem. Ref. Data, Supplement **14** (1985).
9. Chase M. W. - NIST-JANAF Thermochemical Tables, J. Phys. Chem. Ref. Data, Monograph Nr. 9, 4th Edition, Supplement 1, 1998.
10. National Institute of Standard and Technology, Chemistry Web Book, <http://webbook.nist.gov/chemistry/>
11. Peterson K. A., Feller D., and Dixon D. A. - Chemical accuracy in ab initio thermochemistry and spectroscopy: current strategies and future challenges, Theor. Chem. Acc. **131** (2012) 1079-20.
12. Curtiss L. A., Redfern P. C., and Raghavachari K. - Gaussian-4 theory, J. Chem. Phys. **126** (2007) 084108-12.
13. Bartlett R. J. and Musial M. - Coupled-cluster theory in quantum chemistry, Rev. Mod. Phys. **79** (2007) 291-352.
14. Kendall R. A., Dunning T. H., and Harrison R. J. - Electron affinities of the first- row atoms revisited. Systematic basis sets and wave functions, J. Chem. Phys. **96** (1992) 6796-6806.
15. Meloni M. and Gingerich K. A. - Thermodynamic investigation of the Si₇ and Si₈ clusters by Knudsen cell mass spectrometry, J. Chem. Phys. **115** (2001) 5470-5476.
16. Rocabois P., Chatillon C., and Bernard C. - Thermodynamics of the Si-C system I. Mass spectrometric studies of the condensed phases at high temperature, High Temp. High. Press. **27** (1995) 3.
17. Rocabois P., Chatillon C., Bernard C., and Genet F. - Thermodynamics of the Si-C system II. Mass spectrometric determination of the enthalpies of formation of molecules in the gaseous phase, High Temp. High. Press. **27** (1995) 25.
18. Chase W. Jr. - NIST-JANAF Thermochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph **9** (1998) 1.
19. NIST Chemistry Web Book, <http://webbook.nist.gov/chemistry/>
20. Grev R. S. and Schaefer H. F. III. - Thermochemistry of CH_n, SiH_n (n = 0-4), and the cations SiH⁺, SiH₂⁺, and SiH₃⁺: A converged quantum mechanical approach J. Chem. Phys. **97** (1992) 8389-8406.
21. Feller D. and Dixon D. A. - Theoretical Study of the Heats of Formation of Small Silicon-Containing Compounds, J. Phys. Chem. A **103** (1999) 6413-6419.
22. Karton A. and Martin J. M. L. - Heats of Formation of Beryllium, Boron, Aluminum, and Silicon Re-examined by Means of W4 Theory, J. Phys. Chem. A, **111** (2007) 5936-5944.
23. Schmude R. W., Ran Q., Gingerich K. A., and Kingcade J. E. - Atomization enthalpy and enthalpy of formation of gaseous Si₂ and Si₃ from mass spectrometric equilibrium measurements, J. Chem. Phys. **102** (1995) 2574-2579.
24. Schmude R. W., Ran Q., and Gingerich K. A. - Atomization enthalpy and enthalpy of formation of gaseous Si₄ from mass spectrometric equilibrium measurements, J. Chem. Phys. **99** (1993) 7998-8004.

25. Ran Q., Schmude R. W., Miller M., and Gingerich K. A. - Mass spectrometric investigation of the thermodynamic properties of the Si₅ molecule, *Chem. Phys. Lett.* **230** (1994) 337.
26. Gingerich K. A., Ran Q., and Schmude R. W. - Mass spectrometric investigation of the thermodynamic properties of the Si₆ molecule, *Chem. Phys. Lett.* **256** (1996) 274-278.
27. Feller D., Peterson K. A., and Dixon D. A. - A survey of factors contributing to accurate theoretical predictions of atomization energies and molecular structures, *J. Chem. Phys.* **129** (2008) 204105-32.
28. Kitsopoulos T. N., Chick C. J., Zhao Y., and Neumark D. M. - Study of the low-lying electronic states of Si₂ and Si₂⁻ using negative ion photodetachment techniques, *J. Chem. Phys.* **95** (1991) 1441-1448.
29. Cheshnovsky O., Yang S. H., Pettiette C. L., Craycraft M. J., Liu Y., and Smally R. E. - Ultraviolet photoelectron spectroscopy of semiconductor clusters: Silicon and germanium, *Chem. Phys. Lett.* **138** (1987) 119-124.
30. Kostko O., Leone S. R., Duncan M. A., and Ahmed M. - Determination of Ionization Energies of Small Silicon Clusters with Vacuum Ultraviolet Radiation, *J. Phys. Chem. A* **114** (2010) 3176-3181.
31. Nimlos M. R., Harding B. L., and Ellison G. B. - The electronic states of Si₂ and Si₂⁻ as revealed by photoelectron spectroscopy, *J. Chem. Phys.* **87** (1987) 5116-5124.
32. Arnold C. C., Kitsopoulos T. N., and Neumark D. M. - Reassignment of the Si₂⁻ photodetachment spectra, *J. Chem. Phys.* **99** (1993) 766-768.
33. Xu C., Taylor T. R., Burton G. R., and Neumark D. M. - Vibrationally resolved photoelectron spectroscopy of silicon cluster anions Si_n⁻ (n = 3 -7), *J. Chem. Phys.* **108** (1998) 1395-1406.
34. Kawamata H., Negishi Y., Kishi R., Iwata S., Nakajima A., and Kaya K. - Photoelectron spectroscopy of silicon-fluorine binary cluster anions (Si_nF_m⁻), *J. Chem. Phys.* **105** (1996) 5369-5376.
35. Kishi R., Kawamata H., Negishi Y., Iwata S., Nakajima A., and Kaya K. - Geometric and electronic structures of silicon-sodium binary clusters. II. Photoelectron spectroscopy of Si_nNa_m⁻ cluster anions, *J. Chem. Phys.* **107** (1997) 10029-10043.
36. Viswanathan R., Schmude R. W., and Gingerich K. A. - Thermochemistry of BSi(g), BSi₂(g), and BSi₃(g), *J. Phys. Chem.* **100** (1996) 10784-10786.
37. Viswanathan R., Schmude R. W., and Gingerich K. A. - Molar atomization enthalpies and molar enthalpies of formation of GeSi, GeSi₂, Ge₂Si, and Ge₂Si₂ by Knudsen-effusion mass spectrometry, *J. Chem. Thermodyn.* **27** (1995) 763-770.
38. Tam N. M., Hang T. D., Pham H. T., Nguyen H. T., Pham-Ho M. P., Denis P. A., and Nguyen M. T. - Bonding and singlet-triplet gap of silicon trimer: Effects of protonation and attachment of alkali metal cations, *J. Comput. Chem.* **36** (2015) 805-815.
39. Hang T. D., Hung H. M., Nguyen H. T., and Nguyen M. T. - Structures, Thermochemical Properties, and Bonding of Mixed Alkaline-Earth-Metal Silicon Trimers Si₃M^{+0/-} with M = Be, Mg, Ca, *J. Phys. Chem. A* **119** (2015) 6493-6503.

40. Tam N. M., Tai T. B., and Nguyen M. T. - Thermochemical Parameters and Growth Mechanism of the Boron-Doped Silicon Clusters, Si_nB^q with $n = 1-10$ and $q = -1, 0, +1$, *J. Phys. Chem. C* **116** (2012) 20086-20098.
41. Tam N. M., Tai T. B., Ngan V. T., and Nguyen M. T. - Structure, Thermochemical Properties, and Growth Sequence of Aluminum-Doped Silicon Clusters Si_nAl_m ($n = 1-11$, $m = 1-2$) and Their Anions, *J. Phys. Chem. A* **117** (2013) 6867-6882.
42. Tam N. M., Ngan V. T., de Haeck J., Bhattacharyya S., Le H. T., Janssens E., Lievens P., and Nguyen M. T. - Singly and doubly lithium doped silicon clusters: Geometrical and electronic structures and ionization energies, *J. Chem. Phys.* **136** (2012) 024301-11.
43. de Haeck J., Bhattacharyya S., Le H. T., Debruyne D., Tam N. M., Ngan V. T., Janssens E., Nguyen M. T., and Lievens P. - Ionization energies and structures of lithium doped silicon clusters, *Phys. Chem. Chem. Phys.* **14** (2012) 8542-8550.
44. Schmude R. W., and Gingerich K. A. - Thermodynamic Study of Small Silicon Carbide Clusters with a Mass Spectrometer, *J. Phys. Chem. A* **101** (1997) 2610-2613.