Eur. Phys. J. D **1**, 197-205 (1998)

THE EUROPEAN PHYSICAL JOURNAL D

Can we rationalize the structure of small silicon-carbon clusters?

M. Bertolus[a], V. Brenner, and P. Millié

Laboratoire de Chimie Théorique CEA-CE Saclay DSM/DRECAM/SPAM 91191 Gif-sur-Yvette, France

Received: 20 October 1997 / Received in final form: 16 December 1997 / Accepted: 17 December 1997

Abstract. A theoretical study of Si_mC_n clusters with $m + n \in \langle 3, 6\rangle$ using density functional theory is presented. Tests of various functionals demonstrate that local spin density approximation (LSDA) is the most adequate functional for the study of these systems. Structures, vibrational frequencies, and IR intensities of the lowest energy isomer of the studied clusters obtained using LSDA are described, and the unusual properties of the Si-C clusters are discussed. A quantitative analysis of the obtained structures was carried out, and relations between the coordinations, interatomic distances, and angles observed in the Si-C clusters were obtained through introduction of the notion of coordination. This analysis also shows that the carbon atoms mainly exhibit sp and sp^2 hybridizations, and that a majority of silicon atoms do not hybridize. This study is the first step of the implementation of a semi-empirical potential, which would describe the moderately small Si-C clusters.

PACS. 31.15.Ew Density-functional theory – 36.40.Mr Spectroscopy and geometrical structure of clusters

Introduction

Recently, numerous experimental and theoretical studies have been published on the structures and properties of mixed silicon-carbon clusters. Several reasons justify this increasing interest. First, investigation of such clusters allows the chemist to gain further understanding of the differences between carbon and silicon, and the bonds they form. Second, SiC, SiC_2, and SiC_4 have been observed in circumstellar space [1–3], and are thought to play important roles in chemical reactions in the interstellar medium. Since it is likely that other Si-C clusters are also present, the study of these clusters is important to investigate the chemical processes in the interstellar and circumstellar environments. Third, Si-C clusters are involved in technological processes such as chemical vapor deposition used for the manufacture of SiC thin films [4,5]. They are therefore important to electronics related technologies and materials science.

Experimental data available in the existing literature mainly consist of IR vibrational frequencies and relative intensities for Si_mC_n clusters with $m + n \leq 5$ [6–18] and Si_2C_4 [19], as well as photoelectron spectra [20]. As for theoretical studies, the development of the use of methods allowing the calculation of correlation effects, such as MP2, MP4, many body perturbation theory (MBPT), and more recently diffusion Monte Carlo methods [21], coupled-cluster calculations or density functional theory (DFT) enabled precise calculations on these clusters, for which correlation effects are far from negligible. Several studies have yielded structures and a few vibrational frequencies for the Si_mC_n clusters with $m + n \leq 6$ [10,18, 19,21–38]. A recent systematic study by Hunsicker and Jones [39] combining DFT and molecular dynamics yielded the structures of numerous isomers of Si_mC_n clusters with $m + n \leq 6$, Si_2C_5, Si_6C, and Si_7C, as well as vibrational frequencies for lowest energy isomers of the clusters with $m + n \leq 5$. These studies have resulted in unusual structures and properties compared to usual molecules, such as notably multicentric bonding and dangling bonds, as well as structure differences between carbon-rich and silicon-rich clusters.

Little is known, however, concerning the structures of larger Si-C clusters containing up to 50-100 atoms. Mass spectrometry experiments performed on Si_mC_n with $m + n < 100$ have been carried out by Pellarin *et al.* [40]. These experiments showed that, contrary to the case of pure clusters, no particularly stable size is detected, and that fragmentation occurs through evaporation of Si_2C and Si_3C for $m + n \geq 10$, evaporation of Si_2C and SiC_2 for $m + n < 10$. Pellarin *et al.* proved moreover that carbon-rich and silicon-rich clusters exhibit structures similar to pure carbon and similar clusters, respectively. It seems difficult to study these clusters theoretically using precise quantum chemistry *ab initio* methods, and, to our knowledge, no semi-empirical potential exists that describes the properties of the silicon-carbon clusters. For instance, we tested the potential developed by Tersoff using the bulk properties of silicon carbide [41]. We implemented this potential in our Monte Carlo growth method program [42], and carried out global explorations of the potential energy surfaces (PES) of the C_n and Si_n clusters with $n \leq 9$, and of various Si_mC_n clusters (SiC_2, SiC_3, Si_2C_2, Si_2C_3,

---

[a] e-mail: `marjorie@callisto.saclay.cea.fr`

Si_3C_2, Si_2C_4, and Si_3C_3). For all clusters, the structures obtained are very different from those found in the literature [6–8,10,16–19,27,30,31,34–36]. For instance, no linear structure has been obtained whereas, according to precise quantum chemistry *ab initio* calculations, the ground states of SiC_n with $n = 4, 5$, Si_2C_n with $n = 3, 4$ and those of C_{2m+1} with $m = 1, 2$ are linear. Furthermore, because of the specific form of the many-body interaction term, a large majority of the resulting structures containing C-C bonds exhibit (CCC) or (SiCC) angles equal to 124,79°. Therefore, this potential cannot reproduce the variety of structures found in small Si_mC_n clusters, and cannot even be used to obtain starting geometries for PES explorations.

The aim of our study is therefore the implementation of a potential which could describe the properties of the moderately small Si-C clusters. The first step is a systematic study of the smaller Si-C clusters, for which reasonable starting geometries can be obtained either through chemical intuition or from the literature or both. The purpose of this step is the construction of a database of structures and IR frequencies for the implementation of the potential. We present here a systematic study of all possible Si_mC_n clusters obtained for all values of m and n such that $m + n \in \langle 3, 6\rangle$ (twenty-two clusters) using density functional theory. We first present the test of several functionals which we carried out so as to determine the most adequate functional for the study of these systems. Next, we briefly describe the results yielded by calculations of the equilibrium structures, IR frequencies and intensities. Finally, we present a qualitative and quantitative analysis of the data yielded by our calculations, as well as the properties that we were able to deduce from this analysis.

1 Computational details

Because of the importance of correlation effects in such systems [36], we decided to study the Si-C clusters using the DFT methods. This approach enables the calculation of correlation effects at a much lower cost than standard quantum chemistry *ab initio* methods through an effective exchange-correlation potential. Because of the complexity of the potential energy surface, several starting geometries obtained from the literature or through chemical intuition were considered and local optimizations were performed in the symmetry group of the starting geometry. The harmonic vibrational frequencies were then calculated at the obtained stationary point to determine its nature: minimum or saddle-point.

For all optimizations and frequency calculations, several density functionals were tested: two local spin density approximations (LSDA), two non-local spin density approximations including gradient-corrected exchange or correlation or both, and a hybrid method, where the exchange potential is calculated as a linear combination of the Hartree-Fock and gradient-corrected exchanges. The two local spin density functionals used were combinations of Slater exchange functional [43] and Vosko-Wilk-Nusair or Vosko-Wilk-Nusair 5 correlation functionals [44] (VWN, VWN5). For the two non-local spin density approximations, we tested Becke 88 [45] associated with VWN (BVWN), and with Perdew-Wang 91 [46] (BPW). The hybrid method tested was the Becke's three parameter hybrid method [47], where the correlation is gradient-corrected, and provided by the expression of Lee, Yang, and Parr [48] (B3LYP). All calculations were performed using the GAUSSIAN94 [49] (for VWN and B3LYP) and the DMOL 95.0 [50] (for VWN5, BVWN, BPW) program suites run on the Cray C94 of the *Commissariat à l'Énergie Atomique* at Grenoble. The basis set used in all calculations is the standard 6-31G* in GAUSSIAN94 and its numerical equivalent in DMOL. No orbitals were frozen in GAUSSIAN94, while built-in pseudo-potentials were used in DMOL [51].

2 Comparison of the various functionals

We compared the results obtained by the five tested functionals on the twenty-two possible Si_mC_n clusters ($m + n \in \langle 3, 6\rangle$) with the experimentally obtained values and results of precise *ab initio* calculations of the articles quoted in the introduction. To limit the number of references in the text, the clusters studied in references 6 to 38 have been added to each reference in the bibliography. The comparison was made based on four different criteria: determination of the correct energetic order, precision of the computed bond distances and of the computed IR vibrational frequencies, and calculation times. The results are listed in Table 1.

We first compare the obtained lowest energy isomers with experimentally obtained isomers for $m + n \le 5$, C_6, Si_2C_4, and Si_6, and with results of standard quantum chemistry *ab initio* calculations for SiC_5, Si_3C_3, Si_4C_2, and Si_5C. For the twenty-two Si-C clusters considered, VWN5 yields in each case the experimentally observed lowest energy isomer. VWN and BPW, however, misassign the ground state for C_3 which is a fairly pathological case [52]. B3LYP misassigns the ground state for the five clusters C_3, SiC_2, Si_2C, C_6, Si_6, while BVWN yields eight misassignments for C_3, SiC_2, Si_2C, C_4, SiC_3, C_6, Si_3C_3, and Si_6. The calculations using BPW and BVWN yielded energetic orders for higher energy isomers which are correlated poorly with results of precise quantum chemistry *ab initio* calculations. This can be seen on Table 2, which shows the energetic orders of the four energy lowest isomers of Si_3C_3 as obtained by the various functionals studied, as well as those obtained by Mühlhäuser *et al.* [36] and Hunsicker and Jones [39]. We observe that the ground states of the C_3, SiC_2, Si_2C, C_6, and Si_6 clusters are particularly difficult to determine correctly because of the small energy differences between the two lowest energy isomers, and that BVWN and B3LYP both fail to determine the correct ground state for these clusters. In addition we see that six atoms remains a pathological size, since there are several problems in the determination of clusters with this size.

Second, we compiled statistics on thirty-six bond distances observed in fourteen lowest energy structures which appear in the literature. We compared the relative error

Table 1. Comparison of the five tested functionals.

	VWN	VWN5	B3LYP	BPW	BVWN
correct ground state determination (%)	96	100	77	96	64
relative error on distances (%)	0.1	0.09	0.72	1.39	1.98
relative error on frequencies (%)	2.8	2.1	3.3	7.5	7.0
relative error on IR intensities (%)	42	520	41	560	580
calculation rate (arbitrary unit)	10.0	4.3	4.5	1.8	2.4
frequency calculation time for Si_3C_3 (min.)	9'45"	22'27"	22'05"	49'40"	38'24"

Table 2. Energetic orders of the four energy lowest isomers of Si_3C_3 obtained by the various functionals studied compared to those obtained by Mühlhäuser *et al.* [36] and Hunsicker and Jones [39]. The energies are given in mhartrees.

Isomer	VWN	VWN5	B3LYP	BPW	BVWN	MP2 [36]	MD+LSDA [39]
1 C_s	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2 C_{2v} [a]	+18.97	+16.39	+23.94	+18.69	+22.88	+14.34	[c]
3 C_{2v} [b]	+23.29	+18.93	+13.98	[d]	−33.90	[d]	+18.74
4 C_1	+30.23	+26.99	+10.55	+21.32	+1.40	+44.14	[c]

[a] transition state,
[b] this isomer is slightly deformed and has a C_s symmetry in reference [39],
[c] energy not given in the paper,
[d] isomer not obtained using this method.

Table 3. Bond distances (in Å) obtained for Si_2C, Si_4, C_5, Si_3C_2 and Si_5 by the various functionals compared to the bond distances found in the literature. Atom numbers are shown Figure 1.

Cluster	Bond	VWN	VWN5	B3LYP	BPW	BVWN	Literature	Ref.
Si_2C	C_1-Si_1	1.699	1.706	[a]	1.716	1.708	1.703	25
C_{2v}	Si_1-Si_2	3.021	2.945		3.189	3.117	2.942	
Si_4	Si_1-Si_2	2.395	2.410	2.429	2.440	2.460	2.413	23
D_{2h}	Si_1-Si_3	2.313	2.319	2.331	2.354	2.360	2.312	
C_5	C_1-C_2	1.300	1.294	1.291	1.307	1.301	1.290	29
$D_{\infty h}$	C_2-C_3	1.290	1.284	1.287	1.298	1.294	1.282	
	C_1-C_2	1.366	1.365	1.368	1.378	1.370	1.380	
Si_3C_2	C_1-Si_1	1.732	1.736	1.725	1.748	1.737	1.738	31
C_{2v}	C_1-Si_2	1.917	1.925	1.940	1.958	1.967	1.929	
	Si_1-Si_2	2.538	2.543	2.640	2.636	2.670	2.563	
Si_5	Si_1-Si_2	2.294	2.308	2.328	2.340	2.356	2.290	
D_{3h}	Si_1-Si_3	2.967	2.969	2.944	2.934	2.936	2.959	23
	Si_1-Si_5	3.037	3.060	3.124	3.159	3.192	3.050	

[a] the C_{2v} geometry is not a stationary point.

yielded by the five functionals with several experimental distances [6,52], but mostly with results of very precise quantum chemistry *ab initio* calculations such as coupled-cluster calculations [22,29,33] and many body perturbation theory [25,28,30]. Examples of the bond lengths obtained for several clusters by the various functionals studied are given in Table 3. As can be seen from Table 1, the relative errors obtained are very low, but local functionals yield errors eight, fifteen, and twenty times smaller than B3LYP, BPW and BVWN, respectively.

Third, we calculated the relative error between the results obtained by the five functionals using the harmonic approximation and the experimental vibrational frequencies and infrared intensities. As far as the frequencies are concerned, statistics were taken on twenty-four experimental values measured on SiC_2, Si_2C, Si_2C_2, Si_3C, Si_3C_2, C_5, and Si_2C_4 clusters. A few frequencies and intensities yielded by the five functionals studied, as well as those obtained experimentally are tabulated in Table 4. It can be observed from Tables 1 and 4 that the best results are obtained by the VWN, VWN5, and B3LYP functionals, while BVWN and BPW yields errors twice as large. Hartree-Fock, by comparison, yields a relative error on the frequencies of approximately 10% in these systems.

Table 4. Vibrational frequencies (in cm^{-1}) and *IR relative intensities* (arbitrary unit) obtained for Si_2C_2, Si_3C and Si_3C_2 by the various functionals compared to the experimentally obtained values.

Cluster	VWN	VWN5	B3LYP	BPW	BVWN	Experience
Si_2C_2	368.9 *(0.18)*	372.2 *(0.22)*	350.3 *(0.17)*	333.4 *(0.35)*	327.0 *(0.31)*	382.2 *(0.18)*
D_{2h}	974.6 *(1.00)*	969.5 *(1.00)*	970.9 *(1.00)*	895.0 *(1.00)*	910.1 *(1.00)*	982.9 *(1.00)*
	306.9 *(0.05)*	305.0 *(0.29)*	296.3 *(0.05)*	278.4 *(0.35)*	270.6 *(0.40)*	309.5 *(0.11)*
Si_3C	361.0 *(0.11)*	361.0 *(1.45)*	333.3 *(0.14)*	325.1 *(1.59)*	305.7 *(1.61)*	357.6 *(0.16)*
C_{2v}	511.7 *(0.24)*	497.2 *(1.32)*	510.7 *(0.31)*	463.9 *(1.37)*	461.7 *(1.37)*	511.8 *(0.32)*
	671.4 *(0.61)*	660.4 *(0.37)*	647.9 *(0.60)*	603.0 *(0.41)*	583.3 *(0.44)*	658.2 *(0.52)*
	1111.9 *(1.00)*	1095.6 *(1.00)*	1108.7 *(1.00)*	1037.0 *(1.00)*	1067.0 *(1.00)*	1101.4 *(1.00)*
Si_3C_2	607.0 *(0.82)*	596.8 *(0.94)*	586.1 *(0.88)*	572.7 *(1.13)*	528.9 *(1.32)*	597.8 *(0.98)*
C_{2v}	710.7 *(0.60)*	703.0 *(0.08)*	671.9 *(0.60)*	643.9 *(0.07)*	616.4 *(0.07)*	681.1 *(0.31)*
	956.7 *(1.00)*	949.2 *(1.00)*	977.4 *(1.00)*	909.5 *(1.00)*	924.6 *(1.00)*	956.7 *(1.00)*

Furthermore, we observed that the error made by HF on low frequencies is even larger, often yielding imaginary frequencies in cases where experiments or precise quantum chemistry *ab initio* calculations would yield real frequencies, and *vice versa.* This makes it difficult to distinguish minima from saddle-points. The frequencies calculated using the various functionals are not systematically higher than those measured experimentally. This means that carbon and silicon atoms are heavy enough to significantly reduce the anharmonicity in the first vibrational levels. Application of the harmonic approximation is therefore justified for the systems in our study, and thus differences of a few percentage points in the calculated relative errors can be considered significant. Hence, it can be concluded that for Si-C clusters VWN, VWN5 and B3LYP are more precise for frequency calculation than BPW, BVWN and HF. For the infrared intensities, statistics were compiled on sixteen experimentally measured relative intensities. It can be seen that VWN and B3LYP on GAUSSIAN94 reproduce the order of intensities found experimentally, and yield relative intensities with a 40% error (see Tab. 1). This 40% error, while not excellent, is satisfactory since it is well known that vibration frequency intensities are extremely difficult to calculate accurately. To our knowledge, no IR intensity has been calculated at the coupled-cluster level for Si-C clusters, and a sophisticated and time-consuming quantum chemistry *ab initio* method such as many body perturbation theory (MBPT) yields a 33% error in the relative intensities of the five experimentally observed frequencies of Si_3C [28]. On the other hand, the intensities obtained using all functionals on DMOL are, for unknown reasons, not reliable (more than 500% error). This makes the comparison between theoretical and experimental results rather difficult.

Finally, we compared the calculation times necessary for the optimization of the geometries and the determination of the vibrational frequencies. We calculated statistics on the twenty-two Si_mC_n lowest energy isomers, and determined a "calculation rate" for each functional for the optimization and the frequency calculation. These rates, in arbitrary units, as well as the time necessary to calculate the vibrational frequencies of the Si_3C_3 ground state on the Cray C94, are listed in Table 1. It can be seen that VWN on GAUSSIAN94 is by far the quickest method, showing fairly short calculation times for the frequency determination, followed by B3LYP and VWN5 on DMOL, which are more than twice as slow. The difference between the two local methods on GAUSSIAN94 and DMOL 95.0 results from the fact that the GAUSSIAN94 program uses analytical basis sets and calculates gradients and second derivatives analytically, whereas DMOL uses numerical basis sets and calculates gradients and second derivatives numerically.

In conclusion, we observe that the gradient-corrected methods are surprisingly non reliable in the case of the Si-C clusters, and that the LSDA functionals are the most precise methods. They yield correct ground states and energetic orders, distances within 0.1% of the most precise quantum chemistry *ab initio* calculations, and vibrational frequencies within 3% of the experimental values, allowing for a quantitative prediction of frequencies not yet measured experimentally. In addition, VWN on GAUSSIAN94 is the most rapid method. Therefore, the LSDA functional VWN will be used for further studies and the results presented in the following are those obtained by VWN.

3 Results of calculations

We present here the structures, vibrational frequencies, and IR intensities obtained for the silicon-carbon clusters using the LSDA, as well as the properties of these clusters, which can be derived from the results obtained.

Numerous studies dealing with the Si-C clusters have been published since 1989 (see introduction), but there has been no systematic study, except for the very recent one by Hunsicker and Jones (HJ) [39]. Combining molecular dynamics and DFT, HJ carried out explorations of the PES of the Si-C clusters with up to eight atoms, and of their anions. HJ did not perform a complete study, however, since they only tested the local spin density approximation, and they did not systematically calculate the vibration frequencies. Furthermore, they only represented the various isomers obtained for the anions, and not

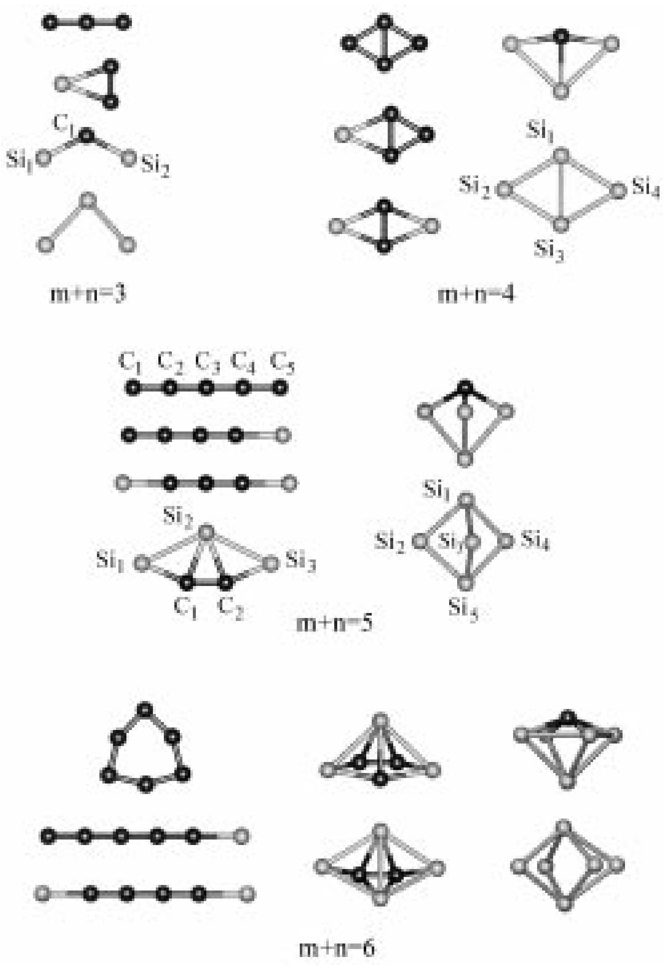

Fig. 1. Structures of the lowest energy isomers of the Si_mC_n clusters with m and n such as $m + n \in \langle 3, 6\rangle$.

those of the neutral clusters. We will not present here the numerous isomers found, which have been thoroughly discussed by HJ, but only the structures of the ground state of each cluster yielded by the LSDA, which will be used in the following. Figure 1 shows the lowest energy isomers of the Si_mC_n clusters with $m + n \in \langle 3, 6\rangle$. Light and dark spheres represent silicon and carbon atoms, respectively. Bonds between the atoms have been drawn for C-C distances less than 1.62 Å, Si-C distances less than 2.20 Å, and Si-Si distances less than 2.60 Å (see Sec. 4 for justification of these thresholds). All ground states are singlet states, except linear clusters with even size, which are triplet states. The results obtained are in very good agreement with previous experimental and theoretical studies. The only disagreement with experimental results is for C_3, where the LSDA on GAUSSIAN94 yields a linear ground state, whereas the correct ground state is thought to have the C_{2v} symmetry, with a (CCC) angle approximately equal to 160° [53]. Furthermore, there is a total agreement between our results and those of HJ for the ground states and isomeric orders. Very few additional high energy isomers have been obtained by HJ through the dynamic exploration. This confirms our initial hypothesis that chemical intuition would allow us to explore the PES of the Si_mC_n clusters with up to six atoms.

Table 5 lists the ground state vibrational frequencies and infrared intensities of all considered clusters calculated by the LSDA on GAUSSIAN94 using the harmonic approximation. It should be noted that the frequencies and intensities of the six atom clusters presented here, other than Si_2C_4 which was the object of a recent combined theoretical and experimental study [19], are either far more accurate than those found in the literature (Si_3C_3), or have never been published (SiC_5, Si_4C_2, and Si_5C). Since the agreement of the calculated frequencies with existing experimental data is very good, these frequencies are likely to be accurate enough to allow the observation of as yet undetected Si-C clusters.

Section 4 presents a quantitative analysis of the data yielded by the calculations, but several phenomena can be deduced from a qualitative analysis of the structures obtained. First, the PES of the Si-C clusters exhibit numerous minima and saddle-points. Our explorations yielded fifty-one minima and eighty-three saddle-points, and, while we are reasonably sure that we found the lowest energy stationary points, the explorations were probably not exhaustive. Furthermore, the number of stationary points increases rapidly and their structures become less intuitive as the cluster size increases. This would make surface explorations for larger sizes difficult, justifying the use of molecular dynamics processes such as the Car-Parrinello method [54], or of methods of global minimum search, such as genetic algorithms [55], simulated annealing, or Monte Carlo growth method [42]. Second, for the cluster structures themselves, we observe an increase in dimension with the increase in silicon content, from linear or cyclic carbon-rich clusters to three-dimensional silicon-rich clusters. This phenomenon, which had already been observed by Froudakis *et al.* [34], is best seen on five atom clusters. Third, a segregation occurs between the silicon and the carbon atoms: because the C-C bond is stronger than the Si-C bond, which is itself stronger than the Si-Si bond [56], there is a tendency to maximize first the number of C-C bonds, then the number of Si-C bonds. The result is the formation of carbon kernels surrounded by silicon atoms, which can be observed in the six atom clusters, and especially in Si_3C_3. Finally, it seems that some silicon atoms (and even some carbon atoms) exhibit a hypervalence phenomenon, *e.g.*, in the Si_3C_3 and Si_2C_4 ground states. This will be discussed in further detail in the analysis of observed coordinations in the next section.

4 Quantitative data analysis

In this section, a quantitative analysis of the data obtained by the LSDA calculations is presented.

4.1 Distances

For the implementation of a semi-empirical potential for the Si-C clusters, it seemed simpler to have at our disposal a criterion distinguishing bonded from non-bonded

Table 5. Theoretical and experimental vibrational frequencies and IR intensities of the $\mathrm{Si}_m\mathrm{C}_n$ ground states with $m + n \in \langle 3, 6\rangle$.

Cluster	Symmetry	Calculated frequencies cm^{-1} *(absolute intensities* km/mol*)*	Experimental frequencies cm^{-1} *(relative intensities arb. unit)*
$\mathrm{C_3}$	$D_{\infty h}$	141.3 *(20)* 1218.3 *(10)* 2130.5 *(618)*	
$\mathrm{SiC_2}$	C_{2v}	216.8 *(78)*, 811.9 *(119)*, 1823.6 *(12)*	160.4 ; 824.3 ; 1741.3
$\mathrm{Si_2C}$	C_{2v}	95.7 *(1)*, 785.9 *(13)*, 1257.0 *(238)*	839.5 *(0.07)* ; 1188.4 *(1)*
$\mathrm{Si_3}$	C_{2v}	169.1 *(5)* 542.1 *(31)* 550.3 *(7)*	
$\mathrm{C_4}$	$D_{\infty h}$	128.8 *(0)*, 144.3 *(30)*, 928.9 *(0)*, 1582.2 *(281)*, 2111.7 *(0)*	
$\mathrm{Si_3}$	C_{2v}	125.4 *(25)*, 429.3 *(34)*, 676.7 *(38)*, 1027.5 *(44)*, 1077.9 *(2)*, 1412.6 *(153)*	
$\mathrm{Si_2C_2}$	D_{2h}	200.0 *(1)*, 368.9 *(47)*, 513.1 *(0)*, 967.9 *(0)*, 974.6 *(260)*, 1164.2 *(0)*	382.2 *(0.18)* ; 982.9 *(1)*
$\mathrm{Si_3C}$	C_{2v}	186.3 *(0.5)*, 306.9 *(4)*, 361.1 *(8)*, 511.7 *(18)*, 671.4 *(45)*, 1111.9 *(73)*	309.5 *(0.11)* ; 357.6 *(0.16)* ; 511.8 *(0.32)* ; 658.2 *(0.52)* ; 1101.4 *(1)*
$\mathrm{Si_4}$	D_{2h}	81.1 *(3)*, 250.1 *(1)*, 355.4 *(0)*, 443.8 *(0)*, 477.3 *(0)*	
$\mathrm{C_5}$	$D_{\infty h}$	131.0 *(17)*, 275.0 *(0)*, 653.1 *(1)*, 789.8 *(0)*, 1475.0 *(133)*, 2015.8 *(0)*, 2271.2 *(1699)*	1544.0 *(0.02)* ; 2164.0 *(1)*
$\mathrm{SiC_4}$	$C_{\infty v}$	105.2 *(1)*, 256.8 *(11)*, 574.3 *(21)*, 629.9 *(4)*, 1176.1 *(107)*, 1866.3 *(0)*, 2198.7 *(1718)*	2095.5
$\mathrm{Si_2C_3}$	$D_{\infty h}$	90.2 *(1)*, 225.2 *(0)*, 465.7 *(0)*, 604.8 *(12)*, 905.6 *(171)*, 1576.5 *(0)*, 2077.3 *(1582)*	898.9 *(0.07)* ; 1955.2 *(1)*
$\mathrm{Si_3C_2}$	C_{2v}	148.9 *(0.3)*, 189.5 *(1)*, 195.7 *(0.6)*, 456.6 *(0)*, 467.5 *(4)*, 607.0 *(35)*, 710.7 *(28)*, 956.5 *(43)*, 1525.8 *(1)*	597.8 *(0.98)* ; 681.1 *(0.31)* ; 956.7 *(1)*
$\mathrm{Si_4C}$	C_{3v}	238.0 *(2)*, 322.4 *(20)*, 348.6 *(1)*, 424.2 *(5)*, 692.7 *(28)*, 739.5 *(5)*	
$\mathrm{Si_5}$	D_{3h}	173.0 *(1.4)*, 231.6 *(0)*, 391.7 *(0)*, 417.6 *(2.1)*, 450.4 *(1.1)*, 482.2 *(0)*	
$\mathrm{C_6}$	D_{3h}	468.7 *(9)*, 540.2 *(0)*, 574.2 *(0)*, 611.7 *(18)*, 1223.4 *(0.3)*, 1236.9 *(0)*, 1539.5 *(0)*, 1832.5 *(301)*	
$\mathrm{SiC_5}$	$C_{\infty v}$	85.5 *(3)*, 203.6 *(10)*, 404.7 *(0.3)*, 496.4 *(11)*, 647.0 *(1)*, 959.7 *(36)*, 1538.6 *(12)*, 1966.5 *(388)*, 2140.2 *(261)*	
$\mathrm{Si_2C_4}$	$D_{\infty h}$	71.8 *(0.2)*, 184.5 *(0)*, 390.0 *(4)*, 412.5 *(0)*, 625.3 *(0)*, 732.8 *(32)*, 1255.7 *(0)*, 1869.1 *(118)*, 2078.4 *(0)*	719.1 *(0.14)* ; 1807.4 *(1)*
$\mathrm{Si_3C_3}$	C_s	196.2 *(8)*, 210.8 *(0.2)*, 267.3 *(5)*, 278.7 *(9)*, 439.2 *(5)*, 471.4 *(37)*, 480.1 *(12)*, 554.8 *(72)*, 657.5 *(11)*, 665.7 *(79)*, 912.2 *(42)*, 1624.8 *(0.2)*	
$\mathrm{Si_4C_2}$	C_{2v}	158.2 *(3)*, 195.7 *(2)*, 323.6 *(0)*, 379.1 *(15)*, 379.4 *(4)*, 388.2 *(0)*, 426.4 *(0.3)*, 434.5 *(15)*, 505.9 *(48)*, 630.5 *(22)*, 775.1 *(100)*, 1635.9 *(1)*	
$\mathrm{Si_5C}$	C_{4v}	76.8 *(0)*, 148.9 *(0.4)*, 312.8 *(0)*, 380.8 *(3)*, 412.3 *(0)*, 435.8 *(38)*, 595.0 *(28)*, 819.3 *(60)*	
$\mathrm{Si_6}$	C_{2v}	36.9 *(0.1)*, 41.0 *(0.2)*, 153.3 *(0)*, 265.3 *(0.1)*, 326.5 *(0)*, 330.8 *(0.4)*, 394.5 *(0.1)*, 418.5 *(0.3)*, 422.3 *(0)*, 464.5 *(9)*, 468.0 *(7)*, 471.0 *(19)*	

atoms. We reasoned that this would enable us to define the notion of coordination of an atom, which is absolutely necessary to study and discuss hybridization. It would moreover enable us to deduce relations between the coordination, distances and angles that our potential should reproduce. This criterion is not, however, as obvious as in usual molecules, where there is a large gap between the longest bonding and the shortest non bonding distance [57]. Therefore, in order to define bonding distance threshold for the various present bonds, C-C, Si-C and Si-Si, we compiled statistics on the interatomic distances found in the clusters studied. Figure 2 shows histograms of these three types of distances found in the 134 structures yielded by the calculations (minimum and transition states).

As for C-C, two distinct gaussian distributions can be observed. The first one is centered at 1.30 Å, which is the typical double-bond distance in allenes, or in other molecules with cumulated double bonds [58]. Further analysis shows that this distribution is mainly due to linear structures, and that no other distances are present in these structures. The second distribution is centered at 1.43 Å, which is slightly longer than the distance of an aromatic bond. In addition a peak is observed at 1.60 Å. It can be noted that there is no distribution centered on 1.54 Å, *i.e.*, that almost no single C-C bonds are present. From this C-C distance histogram, two bonding distance boundaries could be chosen: 1.56 or 1.62 Å, whether or not we include the peak at 1.60 Å.

As for the Si-Si bond, the determination of the threshold is less obvious. Three distributions can be seen: one for distances from 2.10 to 2.24 Å, one from 2.26 to 2.42 Å, and the last one neatly separated, from 2.44 to 2.60 Å. In this case as well, two choices for the bonding criterion are possible: 2.60 Å if we want to take the third distribution into account, or 2.42 Å if we take as reference the typical single Si-Si bond, equal to 2.35 Å.

Finally, the Si-C histogram can also be separated into three distributions, one centered on 1.70 Å, a second one from 1.78 to 1.98 Å, with a maximum for 1.85 Å, the Si-C single bond distance, and one much smaller, from 2.00 to 2.20 Å, which strongly decreases if we consider only the stable structures. Here again two bonding distance thresholds could be chosen: 2.20 Å if we consider all the distributions observed, or 2.00 Å, if we consider the fact that distances longer than 2.00 Å are above all present in transition states.

It can therefore be seen that if reasonable bonding criteria can be found, uncertainties remain: we have two possible bonding distance boundaries for each bond type: 1.56 or 1.62 Å for C-C, 2.00 or 2.20 Å for Si-C, and 2.42 or 2.60 Å for Si-Si.

4.2 Coordinations

To remove this uncertainty, we calculated the coordinations obtained using the various criteria. Figure 3 shows the carbon and silicon coordinations observed in the fifty-one stable structures. For the sake of readability the two C-C possible bonding distance thresholds, which have no influence on the histograms, have not been represented.

The carbon coordination histogram shows that, with the chosen criteria, neither coordination 0 nor coordination five atoms are present. That means that no carbon atom is hypervalent if we consider these thresholds. Furthermore, the majority of carbon atoms have a coordination equal to 2, a condition which has little to do with the fact that only small clusters have been considered. Two third of the clusters have five or more atoms, and it is therefore possible for a large majority of atoms to have a coordination of up to four. Finally, it can be observed that the number of carbon atoms four-times-coordinated is very low, which is related to the preference of carbon

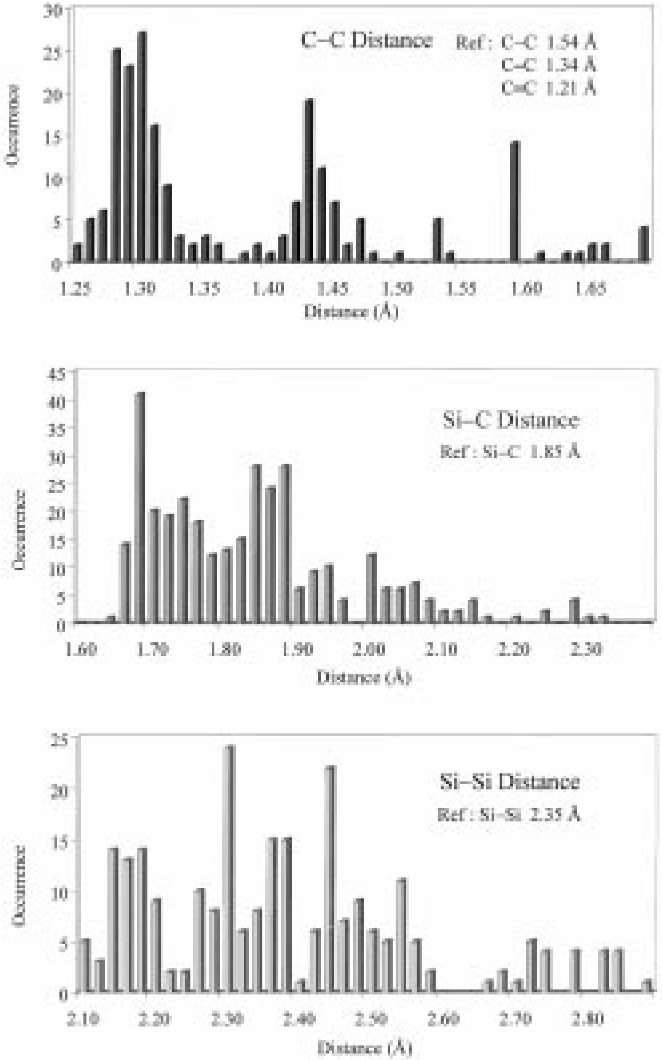

Fig. 2. Histograms of the C-C, Si-C, and Si-Si distances less than 1,70 Å, 2.40 Å and 2.90 Å, respectively, observed in the 134 structures yielded by the LSDA calculations.

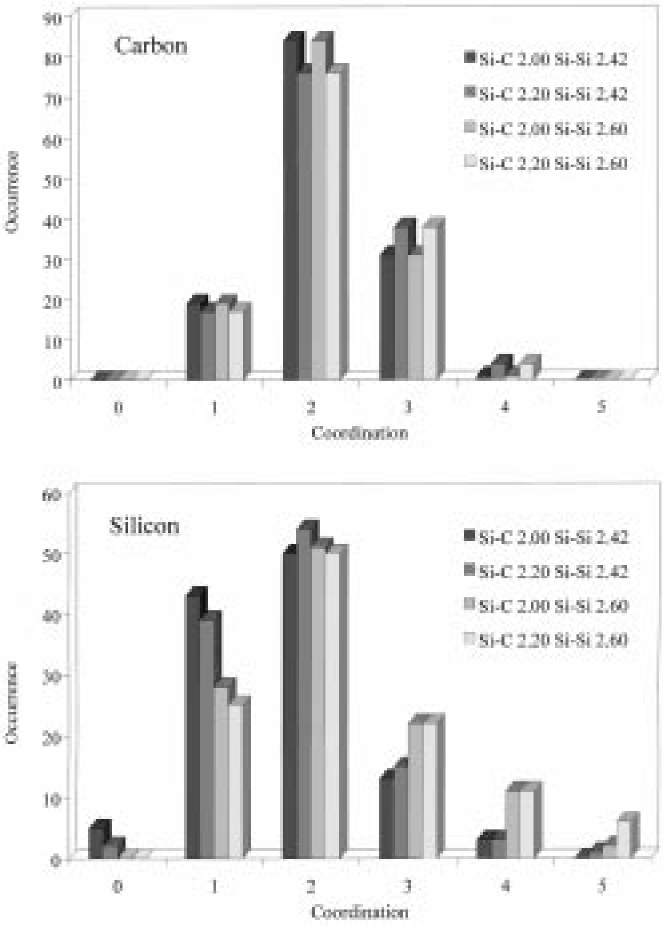

Fig. 3. Histograms of the C and Si coordinences observed in the fifty-one stable structures as a function of bonding criteria.

atoms for C-C bonds, and to the absence of C-C distances corresponding to single bonds.

As for Si coordination, the histogram shows how with fixed Si-C and Si-Si bonding criteria, either non-bonded or hypervalent atoms are present. Since it does not seem reasonable to have non-bonded atoms in stable structures, the Si-Si bonding distance threshold has to be 2.60 Å. Consequently, several silicon atoms exhibit hypervalence, especially in Si_3C_3 and Si_4C_2, whatever the Si-C bonding distance boundary which only has a small effect on the coordinations observed. This hypervalence phenomenon is also observed in Si_7, for which the ground state is a pentagonal bipyramid [23]. As well as for carbon atoms, a majority of silicon atoms exhibit a coordination 2.

Detailed study of the obtained coordinations using various bonding criteria has enabled us to reduce the uncertainty on these criteria: the Si-Si bonding distance boundary has to be 2.60 Å. However, it has not allowed us to eliminate the uncertainty since the C-C and Si-C bonding criteria only have a small influence on the observed coordinations in stable structures. However, to choose the C-C bonding criterion, we have to take into account that the longest C-C bonding distances observed are approximately 1.85 Å in exotic organic compounds such as bisnorcaradiene derivatives, and that bonding distances between 1.60 and 1.62 Å are commonly observed in polycyclic bridged molecules [59]. We therefore choose the C-C bonding criterion equal to 1.62 Å. For Si-C, we also decide to take all the distributions observed into account as in the case of the C-C and of the Si-Si bonds, and choose a bonding distance threshold equal to 2.20 Å.

4.3 Angles

On the basis of the cutoff distances chosen, we then determined the most likely angles formed by an atom as a function of its coordination.

In the case of carbon atoms, most likely angles depend on the atom coordination, and there is an especially big difference between coordination 2 atoms on the one hand, and three-or-four-times-coordinated atoms on the other hand. The large majority of coordination 2 carbon atoms form angles equal to 180°, *i.e.*, are involved in linear structures. Other angles observed are 60°, 90° and 120°. The most likely angles for three-times-coordinated atoms form a distribution from 60° to 90°, and there are also small peaks at 120° and 160°. Coordination 4 carbon atoms preferentially form angles between 60° and 80°, as well as angles equal to 120° and 150°, but it is not really significant since there are very few of these carbon atoms. This confirms that there is a majority of sp^2 and above all sp hybridizations, and that the sp^3 hybridization is unfavorable.

For the silicon, the most likely angles for coordination 2 and 3 atoms form a distribution from 45° to 80°, with a maximum for 55°, whereas for four-times-coordinated atoms they form a distribution between 45° and 100°. It can therefore be seen than silicon atoms never form angles larger than 100°. This results from the difficulty with which silicon atoms form π bonds, and, as a consequence, from their tendency to only form single-bonds. If we link this to the fact that a majority of silicon atoms are two-times-coordinated, it seems to imply that a majority of silicon atoms do not hybridize.

5 Conclusion

Test of various functionals demonstrate that gradient corrections are surprisingly ineffective when applied on the mixed Si-C clusters. LSDA, on the other hand, is fast and accurate for isomeric orders, interatomic distances, and IR frequencies. It is therefore a good tool for the study of these clusters.

Qualitative analysis of the structures obtained using LSDA shows a variety of geometries and unusual properties of the Si_mC_n clusters: the large number of isomers and transition states, a segregation between Si and C atoms, an increase in dimension as the silicon content increases, and Si hypervalence. Quantitative data analysis yields relationships between the interatomic distances, coordinations and angles observed in the Si-C clusters.

The results obtained show that a potential which satisfactorily describes the properties of Si-C clusters must be extremely versatile. It must be able to reproduce the various possible hybridizations of carbon atoms, as well as the competition between linear and cyclic structures. For silicon atoms, the potential must also allow for a description of a variety of situations ranging from non-hybridized single or double-bonded atoms to hypervalent atoms. Such a potential is currently being developed.

In addition, a study of clusters containing up to ten atoms is being carried out using Car-Parrinello method [54] in order to extend our database of structures and vibrational frequencies. This method, combining molecular dynamics and DFT, enables exhaustive global PES explorations, and will allow us to study clusters with sizes greater than six, for which increasing PES complexity prevents the use of local optimizations combined with chemical intuition as an effective exploration method. Little is known about clusters with size between seven and ten, and especially about Si_mC_n with m between $n-1$ and $n+1$ (HJ only studied Si_2C_5, Si_6C, and Si_7C). The study of these clusters will enable us to confirm the trends observed on the smaller clusters, and will yield useful information for the implementation of the potential.

References

1. J. Cernicharo, C.A. Gottlieb, M. Guélin, P. Thaddeus, J.M. Vrtilek, Ap. J. **341**, L25 (1989).
2. P. Thaddeus, S.E. Cummins, R.A. Linke, Ap. J. **283**, L45 (1984).
3. M. Otoshi, N. Kaifu, K. Kawaguchi, A. Murakami, S. Saito, S. Yamomoto, S.-I. Ishikawa, Y. Fujita, Y. Shiratori, W.M. Irvine, Ap. J. **345**, L83 (1989).
4. J. Drowart, G. De Maria, M.G. Inghram, J. Chem. Phys. **29**, 1015 (1958).
5. J.D. Parsons, R.F. Bunshah, O.M. Stafsudd, Solid State Technol. **28**, 133 (1985).
6. D.L. Michalopoulos, M.E. Gensic, P.R.R. Langridge-Smith, R.E. Smalley, J. Chem. Phys. **80**, 3556 (1984); SiC_2.
7. R.A. Shepherd, W.R.M. Graham, J. Chem. Phys. **82**, 4788 (1985); SiC_2.
8. J.D. Presilla-Márquez, W.R.M. Graham, R.A. Shepherd, J. Chem. Phys. **93**, 5424 (1990); SiC_2.
9. J.D. Presilla-Márquez, W.R.M. Graham, J. Chem. Phys. **95**, 5612 (1991); Si_2C.
10. J.D. Presilla-Márquez, S.C. Gay, C.M.L. Rittby, W.R.M. Graham, J. Chem. Phys. **102**, 6354 (1995); Si_2C_2.
11. J.D. Presilla-Márquez, W.R.M. Graham, J. Chem. Phys. **96**, 6509 (1992); Si_3C.
12. M. Vala, T.M. Chandrasekhar, J. Szczepanski, R. Van Zee, W. Weltner Jr., J. Chem. Phys. **90**, 595 (1989); C_5.
13. R.H. Kranze, W.R.M. Graham, J. Chem. Phys. **96**, 2517 (1992); C_5.
14. P.A. Withey, W.R.M. Graham, J. Chem. Phys. **96**, 4068 (1992); SiC_4.
15. A. Van Orden, R.A. Provençal, T.F. Giesen, R.J. Saykally, Chem. Phys. Lett. **237**, 77 (1995); SiC_4.
16. J.D. Presilla-Márquez, W.R.M. Graham, J. Chem. Phys. **100**, 181 (1994); Si_2C_3.
17. A. Van Orden, T.F. Giesen, R.A. Provençal, H.J. Wang, R.J. Saykally, J. Chem. Phys. **101**, 10237 (1994); Si_2C_3.
18. J.D. Presilla-Márquez, C.M.L. Rittby, W.R.M. Graham, J. Chem. Phys. **104**, 2818 (1996); Si_3C_2.
19. J.D. Presilla-Márquez, C.M.L. Rittby, W.R.M. Graham, J. Chem. Phys. **106**, 8367 (1997); Si_2C_4.
20. A. Nakajima, T. Taguwa, K. Nakao, M. Gomei, R. Kishi, S. Iwata, K. Kaya, J. Chem. Phys. **103**, 2050 (1995).
21. J.C. Grossman, L. Mitas, Phys. Rev. Lett. **74**, 1323 (1995); Si_n, $n \leq 20$.
22. J.M.L. Martin, P.R. Taylor, J. Phys. Chem. **100**, 6047 (1996); C_2-C_9.
23. L.A. Curtiss, P.W. Deutsch, K. Raghavachari, J. Chem. Phys. **96**, 6868 (1992); Si_2-Si_5.
24. C. Ross, T.J. Butenhoff, E.A. Rohlfing, C.M. Rohlfing, J. Chem. Phys. **100**, 4110 (1994); SiC_2.
25. C.M.L. Rittby, J. Chem. Phys. **95**, 5609 (1991); Si_2C.
26. E. Bolton, B.J. Deleeuw, J.E. Fowler, R.S. Grev, H.F. Shaefer III, J. Chem. Phys. **97**, 5586 (1992); Si_2C.
27. I.L. Alberts, R.S. Grev, H.F. Shaefer III, J. Chem. Phys. **93**, 5046 (1990); SiC_3.

28. C.M.L. Rittby, J. Chem. Phys. **96**, 6509 (1992); Si_3C.
29. P. Botschwina, J. Chem. Phys. **101**, 853 (1994); C_5.
30. C.M.L. Rittby, J. Chem. Phys. **100**, 175 (1994); Si_2C_3.
31. G.E. Froudakis, M. Mühlhäuser, A.D. Zdetsis, Chem. Phys. Lett. **233**, 619 (1995); Si_3C_2.
32. A.D. Zdetsis, G.E. Froudakis, M. Mühlhäuser, H. Thümmel, J. Chem. Phys. **104**, 2566 (1996); Si_4C.
33. S. Schmatz, P. Botschwina, Chem. Phys. Lett. **235**, 5 (1995); C_6.
34. G.E. Froudakis, A.D. Zdetsis, M. Mühlhäuser, B. Engels, S.D. Peyerimhoff, J. Chem. Phys. **101**, 6790 (1994); Si_2C_4, Si_3C_3, Si_4C_2.
35. M. Mühlhäuser, G.E. Froudakis, A.D. Zdetsis, S.D. Peyerimhoff, Chem. Phys. Lett. **204**, 617 (1993); Si_3C_3.
36. M. Mühlhäuser, G.E. Froudakis, A.D. Zdetsis, B. Engels, N. Flytzanis, S.D. Peyerimhoff, Z. Phys. D **32**, 113 (1994); Si_3C_3.
37. P.W. Deutsch, L.A. Curtiss, Chem. Phys. Lett. **226**, 387 (1994); Si_mC_n, $m+n$=3.
38. R. Kishi, M. Gomei, A. Nakajima, S. Iwata, K. Kaya, J. Chem. Phys. **104**, 8593 (1996); Si_nC, $n \in \langle 2, 5 \rangle$.
39. S. Hunsicker, R.O. Jones, J. Chem. Phys. **105**, 5048 (1996).
40. M. Pellarin, C. Ray, P. Mélinon, J. Lermé, J.L. Vialle, P. Kéghélian, A. Perez, M. Broyer, Chem. Phys. Lett. **277**, 96 (1997).
41. J. Tersoff, Phys. Rev. B. **39**, 5566 (1989).
42. M. Bertolus, V. Brenner, P. Millié, J.-B. Maillet, Z. Phys. D **39**, 239 (1997).
43. J.C. Slater, *Quantum Theory of Molecular and Solids Vol 4: The Self-Consistent Field for Molecular and Solids* (New York, McGraw-Hill, 1974).
44. S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. **58**, 1200 (1980).
45. A.D. Becke, Phys. Rev. A **38**, 3098 (1988).
46. J.P. Perdew, Y. Wang, Phys. Rev. B **45**, 13244 (1992).
47. A.D. Becke, J. Chem. Phys. **98**, 5648 (1993).
48. C. Lee, W. Yang, R.G. Parr, Phys. Rev. B **37**, 785 (1988).
49. M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian94, Revision C.2, Gaussian, Inc., (Pittsburgh, Pennsylvania, 1995).
50. Biosym/MSI, San Diego (1995).
51. B. Delley, IJQC Proceedings of the Symposium on DFT and Applications, Duke University, Durham, North Carolina, 3-7 June 1997 (to be published).
52. W. Weltner Jr., R.J. Van Zee, Chem. Rev. **89**, 1713 (1989).
53. P. Jensen, Collect. Czech. Chem. Commun. **54**, 1209 (1989).
54. R. Car, M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
55. Y. Xiao, D.E. Williams, Chem. Phys. Lett. **215**, 17 (1993).
56. K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure Vol IV: Constants of Diatomic Molecules.* (New York, Van Nostrand Reinhold Company 1979).
57. R. Daudel, R. Lefebvre, C. Moser, *Quantum Chemistry: Methods and Applications*, (New York, Intersciences, 1959).
58. H.J.M. Bowen, J. Donohue, D.G. Jenkin, O. Kennard, P.J. Wheatley, D.H. Whiffen, *Tables of Interatomic Distances and Configuration in Molecules and Ions*, edited by A.D. Mitchell, L.C. Cross, (London, The Chemical Society Burlington House W.1, 1958).
59. E. Osawa, K. Kanematsu, *Molecular Structures and Energetics Vol 3: Studies of Organic Molecules*, edited by J.F Liebmann, A. Greenberg, (Deerfield Beach, Florida: VCH 1986).