I. INTRODUCTION

The structures and properties of mixed silicon–carbon hetero-clusters have attracted much attention over the past several years. One of the main reasons for this being that SiC, SiC₂, SiC₃, and SiC₄ have been detected in the interstellar space and in the atmosphere of carbon stars. It is quite probable that bigger clusters are also present in these stars. Their detection, therefore, is important for an understanding of chemical processes in interstellar environments, and their discovery has inspired several works which reported the production of such clusters in the laboratory. Moreover, silicon carbide is an attractive material from a technological point due to its high potential in electrical and high temperature mechanical devices.

Even though carbon and silicon are contiguous in the same column (Group IV) of the periodic table, their chemical and bonding properties are rather different. While carbon exhibits huge flexibility by forming single and multiple bonds, this characteristic is not shared by silicon which prefers multidirectional single bonds. The different behavior in the bonding is reflected in the structure of small pure clusters. Small carbon clusters (n = 10) form planar structures, linear for odd n and cyclic for even n. By contrast, silicon clusters are known to prefer three-dimensional structures from clusters as small as n = 5. These striking differences are also evident in the bulk phase, since no graphitic structure exists for Si. In the intermediate size silicon–carbon hetero-clusters it is reasonable to expect to find a transition from carbonlike to siliconlike behavior as we go from carbon-rich to silicon-rich clusters. This trend has been experimentally confirmed in previous works. For example, Nakajima et al. measured the photoelectron spectra of Si₃C₄⁺ anion clusters (1 ≤ n ≤ 7 and 1 ≤ m ≤ 5), and found that the spectra of the SiₙC₄⁺ (3 ≤ n ≤ 7) are similar to those of pure Siₙ⁺ clusters, and attributed it to being of similar geometry. However, this similarity is not present between Cₘ⁺ and SiₙCₘ⁺, and this they attribute to structural change from chains to rings. More recently, another study by Pellarin et al. covered different composition regimes of binary SiₙCₘ clusters by means of photolysis experiments. For clusters containing n = 20 carbon atoms, they reported an enhanced stability for the most likely C₅Si₅⁺ clusters and evidences for carbon chains terminated by one Si atom in each end rather than more compact structures.

There are several theoretical studies dealing with the topic of small SiₙCₙ clusters. Presilla-Márquez et al. have combined measurements of frequencies, relative intensities, and isotopic shifts of vibrational fundamentals with ab initio calculations to identify new species or new modes of known species including SiC₂, Si₂C, Si₃C, Si₄C, Si₅C, Si₆C, Si₇C, Si₈C, and Si₉C. Froudakis et al. have performed an ab initio study of Si₄C₄, Si₅C₅, and Si₆C₆ clusters and point out that, in the building-up mechanism of silicon–carbon clusters, strong C–C bonds are favored over Si–C bonds, while Si–Si bonds are much less important and, in addition, multicenter bonding plays an important role. More recently, Bertolus et al. made a systematic study of SiₙCₙ with m + n ∈ {3,6} using the density functional theory. Their results showed that gradient corrections are ineffective when applied to this system. Furthermore, they predicted a segregation between silicon and carbon atoms, an increase in dimension as the silicon content increases, and the existence of a large number of isomers and transition states.

Despite these studies, to the best of our knowledge, no theoretical work has been reported for clusters of intermediate sizes in the range n = 10 to n = 20. This is a challenging issue since the lack of symmetry, that we might find for the SiC hetero-clusters, would make the ab initio calculations computationally prohibitive. Also, the high number of sta-
tionary points in the potential energy surface (PES) and their proximity to each other would make the exploration of the surface formidable. Consequently, the use of a computationally efficient method that allows us to sweep the PES as exhaustively as possible, is crucial. In this respect, the generalized tight-binding molecular dynamics scheme (GTBMD) provides us with a powerful tool to study the SiC hetero-clusters. This method has been proven to yield geometries for silicon and carbon clusters in agreement with ab initio results. Recently, it has also been successfully applied to the study of small size Si$_n$C$_m$ clusters and SiC hetero-fullerenes.

II. THEORETICAL PROCEDURE

In order to effectively explore the PES of the SiC hetero-clusters we use a combination of methods that includes GTBMD scheme in conjunction with ab initio methods. The first step involves scanning the surface using the GTBMD scheme, thereby allowing us to go through a large number of configurations in a reasonable time and make a first guess. The structures found with this technique are then further relaxed using Hartree–Fock (HF) method using the 6-31G* basis set. The stability of the clusters was examined by evaluating the harmonic frequencies with the same method and basis set. Even though correlation effects are very significant in this system and are not taken into account with HF, it can help us approach the minima and eliminate some of the geometries considered. However, a careful look at the vibrational analysis is necessary. For low frequencies HF is often unable to distinguish real frequencies from imaginary ones, confusing minima with saddle points and vice versa.

In the final step, the structures were optimized using the density functional theory (DFT) within the local spin density approximation (LSDA). The functional used was a combination of Slater exchange functional and Vosko–Wilk–Nusair correlation functional (SVWN) using the 6-31G* basis set. This method has been found to yield the best results for small SiC clusters in accordance with experiment and accurate ab initio calculations among several functionals, including gradient-corrected functionals. All the HF and DFT calculations were performed using the GAUSSIAN 98 program.

When the final geometry corresponds to a saddle point, a small displacement is applied along the eigenvectors of the normal mode associated with the imaginary frequency. Further relaxing of the system would then yield a true minima connected to this stationary point.

III. GEOMETRIES OF THE LOW-ENERGY CONFIGURATIONS

Following the techniques discussed in Sec. II, we have examined the structures and energies of carbon clusters substitutionally doped with up to three silicon atoms (C$_{n}$Si$_{m}$, n + m = 11, 12, m = 1, 2, 3). The initial geometries were based on the lowest-lying structures of C$_{11}$ (Ref. 40) and C$_{12}$ (Ref. 41), including in both cases linear, planar, and three-dimensional configurations. In the search of the PES, many minima and saddle points were found very close in energy among themselves, supporting the trend previously reported in the calculations of SiC clusters of smaller sizes. The three-dimensional structures, however, were found to be sufficiently higher in energy when compared to linear and planar structures and can be ruled out as candidates for ground state. We, therefore, limit our discussion mainly to the linear and planar structures and a few cage structures. Also, only the final structures resulting from the relaxation with the sequence of methods described are shown. All the molecular states corresponding to the structures discussed are singlets, except for the chains with 12 atoms, where the triplets were found to be more stable.

It is worth noting that qualitative differences exist in the frequencies and order of energies predicted by HF and SVWN. As mentioned earlier, HF is only used as a tool to approach the minima in the relaxation process. The omission of correlation effects, extremely important in this system, makes any predictions using this method inaccurate and unreliable, and this task is performed using the more accurate SVWN LSDA method. Nevertheless, the use of the HF method is justified here. Mühlhäuser et al. have studied the effects of correlation in the Si$_3$C$_4$ cluster by relaxing it using the HF and calculations based on the Møller–Plesset (MP) theory, which does include correlation. Change in the resulting geometry was found to be minimal (around 1% in distances and 3–5 degrees in angles) and correlation was found to affect only the relative energies of the different isomers studied. This provides proof that HF, even with its deficiencies, can still be a useful tool to perform relaxation for obtaining different starting configurations and to locate stationary points in the PES.

A. Substitutional doping of the C$_{11}$ cluster with silicon: C$_{10}$Si, C$_{9}$Si$_2$, and C$_{9}$Si$_3$ clusters

The search results for the minima of the C$_{11}$ cluster substitutionally doped with up to three silicon atoms is summarized in Table I and Fig. 1. In the three situations many minima with energies very close among each other were found. Consequently, the accuracy of the method used does not allow us to determine exactly the true minima of the PES. However, it appears that both linear and planar struc-

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Isomer</th>
<th>$E_B$ (eV)</th>
<th>$\delta E$</th>
<th>$N_{imag}$</th>
<th>SVWN</th>
<th>$E_B$ (eV)</th>
<th>$\delta E$</th>
<th>$N_{imag}$</th>
</tr>
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<td>C$_{10}$Si</td>
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<td>0</td>
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</tr>
<tr>
<td></td>
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<tr>
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<tr>
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<td>C$_{9}$Si$_2$ (a)</td>
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<td>0</td>
<td>-5.94</td>
<td>0.05</td>
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<tr>
<td></td>
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<tr>
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<td>0.28</td>
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<tr>
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<td>C$_{9}$Si$_3$ (a)</td>
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<td>-5.36</td>
<td>0.18</td>
<td>2</td>
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</tr>
<tr>
<td></td>
<td>C$_{9}$Si$_3$ (b)</td>
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<td>0</td>
<td>-5.54</td>
<td>0</td>
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<td></td>
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<td>-5.35</td>
<td>0.19</td>
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</table>
these clusters are competitive as most stable isomers, while three-dimensional arrangements lie higher in energy, even when up to three atoms are substituted (0.51 eV/atom for C$_{10}$Si, 0.54 eV/atom for C$_9$Si$_2$, and 0.12 eV/atom for C$_8$Si$_3$).

Another characteristic worth noting is that the presence of silicon atoms in a carbon cluster introduces some degree of asymmetry. The original geometries are deformed to accommodate the silicon atom, which has a longer bond length and prefers the directional single bonds. As a result, many of the relaxed structures show very low degree of symmetry. These binding preferences of silicon are clear in the linear chain C$_8$Si$_3$ (Fig. 1) where a bending at the edge containing two silicon atoms is seen. The angle between the Si–C and Si–Si bonds is $\approx 150^\circ$.

B. Substitutional doping of the C$_{12}$ cluster with silicon: C$_{11}$Si, C$_{10}$Si$_2$, and C$_9$Si$_3$

In Fig. 2 we show low energy geometries of C$_n$Si$_m$ clusters with $n + m = 12$. Table II contains a summary of results. As seen in the table, the various isomers lie very close in energies to each other, making it virtually impossible to list one single structure as the most stable.

![Diagram of C$_{11}$Si, C$_{10}$Si$_2$, and C$_9$Si$_3$ clusters](image)

**TABLE II.** Energy of the most stable silicon doped C$_{12}$ clusters, where the energy is given in eV/atom and $\delta E$ denotes energy relative to the lowest energy isomer found. The linear isomer C$_5$Si$_2$ was not found to be a stationary point using HF.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Isomer</th>
<th>$E_B$ (eV)</th>
<th>$\delta E$</th>
<th>$N_{imag}$</th>
<th>$E_B$ (eV)</th>
<th>$\delta E$</th>
<th>$N_{imag}$</th>
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<tr>
<td>C$_{11}$Si (c)</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>C$_{10}$Si$_2$ (b)</td>
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<td>C$_{10}$Si$_2$ (c)</td>
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<td>C$_{10}$Si$_2$ (d)</td>
<td>-8.56</td>
<td>0.21</td>
<td>1</td>
<td>-5.77</td>
<td>0.01</td>
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<tr>
<td>C$_9$Si$_3$</td>
<td>C$_9$Si$_3$ (a)</td>
<td>-8.35</td>
<td>0</td>
<td>0</td>
<td>-5.87</td>
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<tr>
<td>C$_9$Si$_3$ (b)</td>
<td>-8.24</td>
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<tr>
<td>C$_9$Si$_3$ (c)</td>
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<td>0.15</td>
<td>0</td>
<td>-5.68</td>
<td>0.19</td>
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<tr>
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<td>-5.68</td>
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</tr>
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</table>

In this case, planar or nearly planar single and double rings and linear chains appear to be likely candidates for the ground state. As in Sec. III A, three-dimensional structures can be ruled out as possible candidates in this range of composition, except perhaps for the C$_5$Si$_2$ cluster, where a bowl structure (Fig. 2) is among the lowest in energy. These results lead us to conclude that the ground state of clusters with these compositions are geometries with low dimensions, consisting of either chains or single and double rings. This may seem counter intuitive because silicon atoms prefer single bonds ($sp^3$ hybridization) which is not compatible with the $sp^2$ hybridization found in planar and linear structures. However, we note that this behavior was also found in experiments. Pellarin et al. proposed linear chains in this regimen of composition and found an enhanced stability for the C$_n$Si$_2$ clusters.

**IV. BONDS AND COORDINATION**

It is well known that silicon and carbon behave quite differently when forming bonds. With this in mind we analyze the different types of bonds formed by the two elements and present a histogram with the interatomic distances of 37 clusters studied (see Fig. 3). This group of clusters includes the more stable isomers of all the stoichiometries considered in this work.

For the C–C bonds, there are four distributions centered at 1.28 Å, 1.35 Å, 1.41 Å, and 1.54 Å. As expected, the geometry of the clusters determines, for the most part, the range of the bonds. The smallest set of bonds arises mainly from one-dimensional chains, and it is coincident with the double bond in allenes. Two-dimensional structures contribute mainly to the maximum at 1.35 Å. The distribution at 1.41 Å (distance between carbons in a graphene layer) derives contribution from both; two- and three-dimensional structures, the latter showing another peak at 1.54 Å (the single bond length for carbon).

For the Si–C interdistances, the histogram shows two distributions: one at 1.70 Å and a fairly broad distribution centered at 1.84 Å, which is the bond length of the single
Si–C bond. As before, it can be seen that the dimensionality of the structures is closely related to the distances between neighbors in the molecule. In fact, only linear structures contribute to bond lengths of 1.70 Å. For the Si–Si bond the lack of statistics does not allow us to make a reliable analysis.

It is worth noting that hypervalence (more than four bonds per atom) was not found for any clusters and that most of the atoms contained a coordination of two. This finding is consistent with the results reported by Bertolus et al. in a similar study of small Si–C clusters, where up to six atoms were considered. The results for both the coordination and the bond lengths are fairly close to the values obtained in our analysis.

V. SUMMARY AND CONCLUSIONS

In this work we have used the GTBMD scheme to search for possible ground state candidates for silicon doped carbon clusters, \( C_nSi_m \), \( n + m = 11,12, \ m = 1,2,3 \). The efficiency of this technique allowed us to analyze up to hundred of configurations and make a first guess. This was followed by more accurate calculations, based on the DFT and the LSDA approximation, to further relax the geometries and get the binding energies. As a result, it was found that Si–C hetero-clusters present a fairly complex PES with numerous minima and saddle points that lie very close in energies, making the task difficult in the search for the minima and defying the resolution of the theoretical methods used. Moreover, a strong competition between linear chains and planar or nearly planar structures occurs, while three-dimensional structures are not seen as possible candidates for the ground state, even when three silicon atoms are inserted in the cluster. This is quite surprising as silicon is known to prefer single bonds which would form three-dimensional geometries. Nevertheless, our finding is consistent with photoysis experiments performed by Pellarin et al. However, due to the complexity of the problem, it is not possible to propose one single structure as the global minimum in the PES.

Additionally, we have also presented a study of bond length distribution, analyzing both neighbor distances and the coordination. The trend found is similar to the one proposed by Bertolus et al. in a similar study of smaller Si–C clusters.

We believe that the method would be equally valid for the Si clusters doped with carbon. The candidates for ground state geometries, however, will be dominated by three-dimensional structures. This is because orbitals in Si atoms favor form multidirectional single bonds. The ability of C atom to form various bonding configurations makes substitutional doping relatively easy. The mass spectroscopy experiments of Pellarin et al. suggest that in clusters containing up to 11 Si atoms a simple substitution of carbon atoms seems to be highly plausible.

ACKNOWLEDGMENTS

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23. M. Pellarin, C. Ray, J. Lermé, J. L. Vialle, M. Broyer, X. Blase, P. Kég-