NUCLEATION OF SMALL SILICON CARBIDE DUST CLUSTERS IN AGB STARS

DAVID GOBRECHT, SERGIO CRISTALLO AND LUCIANO PIERSANTI
Osservatorio Astronomico di Teramo, INAF, 64100 Teramo, Italy

AND

STEFAN T. BROMLEY
Departament de Cincia de Materials i Química Física and Institut de Química Teràpica i Computacional (IQTCUB), Universitat de Barcelona, E-08028 Barcelona, Spain and
Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Spain

ABSTRACT

Silicon carbide (SiC) grains are a major dust component in carbon-rich AGB stars. The formation pathways of these grains are, however, not fully understood. We calculate ground states and energetically low-lying structures of \((\text{SiC})_n\), \(n = 1,16\) clusters by means of simulated annealing (SA) and Monte Carlo simulations of seed structures and subsequent quantum-mechanical calculations on the density functional level of theory. We derive the infrared (IR) spectra of these clusters and compare the IR signatures to observational and laboratory data. According to energetic considerations, we evaluate the viability of SiC cluster growth at several densities and temperatures, characterising various locations and evolutionary states in circumstellar envelopes. We discover new, energetically low-lying structures for \(\text{Si}_4\text{C}_4\), \(\text{Si}_5\text{C}_5\), \(\text{Si}_{15}\text{C}_{15}\) and \(\text{Si}_{16}\text{C}_{16}\), and new ground states for \(\text{Si}_9\text{C}_{10}\) and \(\text{Si}_{15}\text{C}_{15}\). The clusters with carbon-segregated substructures tend to be more stable by 4-9 eV than their bulk-like isomers with alternating Si-C bonds. However, we find ground states with cage (“bucky”)-like geometries for \(\text{Si}_{12}\text{C}_{12}\) and \(\text{Si}_{16}\text{C}_{16}\) and low-lying, stable cage structures for \(n \geq 12\). The latter findings indicate thus a regime of clusters sizes that differs from small clusters as well as from large-scale crystals. Thus, and owing to their stability and geometry, the latter clusters may mark a transition from a quantum-confined cluster regime to crystalline, solid bulk-material.

The calculated vibrational IR spectra of the ground-state SiC clusters shows significant emission. They include the 10-13 \(\mu\)m wavelength range and the 11.3 \(\mu\)m feature inferred from laboratory measurements and observations, respectively, though the overall intensities are rather low.

Keywords: dust grains, clusters: general — silicon carbide: individual

1. INTRODUCTION

Dust is ubiquitous in the Universe and plays a crucial role in astrophysical environments. Dust impacts the synthesis of complex organic molecules in molecular clouds, the wind-driving of evolved stars and the formation of celestial bodies (e.g. asteroids, planets) in protoplanetary discs (Ehrenfreund & Charnley 2000; Dori & Hoeftner 1991; Testi et al. 2014). Dust is thus essential for the chemical evolution of galaxies and its formation in late-type stars is the subject of this paper. The dust formation from a gaseous medium requires several thermodynamic conditions: densities above a certain threshold to ensure sufficient collisions between the constituent particles, moderate temperatures below the stability threshold of the dust component, and sufficient time for the nucleation and growth of molecular clusters into larger grains. Such conditions are found in the warm and dense molecular layers in circumstellar environments of Asymptotic Giant Branch (AGB) stars (Woitke et al. 1999). It is thus not surprising, that, among the stellar sources of dust, AGB stars are a significant contributor. We note, however, that, arguably, the bulk of dust present in the local Universe could be the result of grain growth and reprocessing in the interstellar medium (Draine 2009).

The amount and nature of the dust depends on stellar mass, metallicity, and not least on the photospheric C/O ratio. For C/O <1 (M-type AGB stars) the circumstellar chemistry is oxygen-dominated and the type of dust that is forming is made of silicates, alumina and other metal oxides (Gobrecht et al. 2016). In carbon-rich stars with C/O >1, carbonaceous molecules prevail and condensates such as amorphous carbon and silicon carbide constitute the dust grains (Henning 2010). About 90% of SiC grains are thought to come from low-mass AGB stars of approximately solar metallicity (Davis 2011) and SiC accounts for about \(\sim 10\%\) of carbonaceous dust of solar and moderately subsolar metallicity (Zhukovska & Henning 2013).

S-type AGB stars are reckoned as transitional objects between M-type and C-type stars, respectively, and have little excess of either carbon or oxygen. However, these stars may produce dust in the form of pure metals (Ferrarotti & Gail 2006).

Often, it is argued that dust formation and the related mass loss phenomena is less understood in M-type stars, owing to the low opacity of oxygen- rich condensates in the near infrared range (Woitke 2006; Höfner 2008). The wind-driving in carbon-rich AGB atmospheres is better understood. However, the synthesis of carbonaceous dust clusters and the formation routes towards (silicon)-carbon grains is not yet fully understood.

One of the major dust components is silicon carbide (SiC) showing a spectral emission/absorption in the 10-13 \(\mu\)m range, in particular a strong and characteristic
feature around $\sim 11.3 \, \mu m^{[6]}$\cite{Speck1996,2006}. Laboratory studies have shown that the spectral band profile depends on size, shape and purity, respectively, of the SiC dust grains, but is less affected by its crystal type \cite{Mutschke1999}. Fundamental lattice vibrations (i.e. phonons) dominate the interaction of infrared radiation with crystalline SiC. For small dust clusters, however, the situation is different. Owing to the lack of periodicity and lattices it is impossible to excite collective lattice vibrations such as phonons in small clusters. However, clusters possess distinct and non-bulk-like vibrational and rotational modes arising due to bending and stretching of internal bonds.

Moreover, SiC dust grains have been found in primitive meteorites \cite{Bernatowicz1987} and have typical sizes of 0.3-3 $\mu m^{[6]}$\cite{Amari1994}. The analysis of the SiC grain isotope composition, in particular the excess of $^{13}$C and $^{15}$N compared with scaled-solar abundances, revealed unambiguously that SiC grains originate from extended atmospheres of AGB stars \cite{Hoppe1996}. In addition, the majority of the SiC grains exhibit s-process isotopic signatures arising in the atmospheres of Carbon-rich AGB stars \cite{Gallino1994,Liu2014,Liu2015}. More recently, new instruments like the NanoSIMS \cite{Zinner2007} became available and allowed the analysis of SiC grains with sizes as small as a few nm \cite{Hynes2009}. The investigation and analysis of rather small SiC grains (0.2-0.5 $\mu m$) have revealed that submicrometer-sized grains originating from AGB stars are much more abundant than their larger, micron-sized counterparts \cite{Hoppe2010,Amari2014}. The classification of individual SiC grains into different groups named “Mainstream”, AB and X grains, respectively, is based on the isotopic excess. “Mainstream” grains are associated with carbon-rich AGB stars. About 90% of the presolar SiC grains are thus thought to come from low-mass AGB stars of approximately solar metallicity \cite{Davis2011}.

Owing to the interaction with the stellar radiation field, SiC grains are promising candidates to trigger the mass-loss in carbon-rich AGB stars. However, the formation of the SiC grains in stellar winds remains poorly understood.

In the bulk phase, SiC exists in about 250 crystalline forms, so called polytypes. The most commonly encountered polytypes are α-SiC and β-SiC with tetrahedrally coordinated Si atoms. All SiC grains extracted from meteorites have proven to be either cubic $\beta$(3C)-SiC ($\sim 80 \%$) or hexagonal $\alpha$(2H)-SiC \cite{Daulton2003,Bernatowicz2005}. These two polytypes do not differ systematically in their spectral signatures \cite{Mutschke1999}. The band profile is rather affected by grain size, shape, and impurities, respectively. Moreover, the analysed SiC grains do not contain any seed nuclei of different chemical type in their centres \cite{Stroud2005}, thus indicating a homogeneous (homo-molecular) grain formation. The properties of nanoparticles with sizes below 50 nm, however, differ significantly from bulk properties. Quantum and surface effects of these small particles lead to non-crystalline structures, whose characteristics (geometry, coordination, density, binding energy) may differ by orders of magnitude, as compared to the bulk material. In the smallest clusters, namely dimers and polymers of a dust species, the inter-atomic bonds are often unsaturated (in terms of atomic coordination), owing to the high surface-to-volume ratio. A top-down approach, i.e. deducing cluster characteristics from bulk material properties, is thus inappropriate. Contrary, a bottom-up approach, starting with prevalent molecules in the gas phase (e.g. SiC, SiO) and successive growth to clusters by molecular (addition) reactions, seems to be suitable. Such a method has been applied for clusters of magnesium oxide \cite{Koehler1997}, titanium dioxide \cite{Lee2015}, silicates of enstatite and forsterite stoichiometry \cite{Goumans2012}, and silicon oxide \cite{Bromley2010}, respectively.

In Section II we describe the computational methods used to characterise the SiC cluster structures and energetics. Section III gathers and summarises the results for the most stable clusters. Finally, the results are discussed with particular attention on implications for circumstellar dust formation and spectroscopic signatures.

2. METHODS

In this study, global optimisation techniques and Molecular Dynamic (MD) simulations are used to determine the energetically most stable cluster structures. The more atoms a cluster contains, the larger its size is and the number of possible structural isomers increases drastically. The investigation of large clusters is therefore computationally demanding. In order to reduce the computational effort, we apply several pre-selection methods to find potential minimum energy SiC cluster structures. Seed cluster structures are constructed by hand according to their geometries reported in the literature.

2.1. Monte-Carlo Basin-Hopping search on the Buckingham potential energy landscape

Some of the candidate structures are found with the Monte Carlo - Basin Hopping (MC-BH) global optimization technique \cite{Wales1997}, with inter-atomic Buckingham pair potentials. The general form of the inter-atomic Buckingham pair potential reads:

$$U(r_{ij}) = \frac{q_i q_j}{r} + A \exp(-\frac{r_{ij}}{B}) - \frac{C}{r_{ij}^6} \tag{1}$$

where $r_{ij}$ is the relative distance of two atoms, $q_i$ and $q_j$ the charges of atom i and j, respectively and A, B and C the Buckingham pair parameters. The first term represents the Coulomb law, the second term the short-range, steric repulsion term accounting for the Pauli principle, and the last term describes the van-der-Waals interaction. The steric repulsion term is motivated by the fact that atoms are not dot-like but occupy a certain volume in space.

In the case of silicon carbide, parameter sets for the Si-C system are lacking in the literature for several reasons. As an integral part the electrostatic Coulomb potential appears in Equation [1]. It describes the repulsion and attraction of charged particles, in this case of the silicon and carbon ions within a SiC cluster. As lightest Group IV elements in the periodic table, Si and C form strong covalent bonds. The electronegativity (EN) of carbon (EN(C) = 2.55) is too small to allow carbon to form C$^{4-}$ or C$^{4+}$ ions. The Buckingham potential is thus mainly used for materials with an ionic character and as for example metal oxides. Nevertheless, there is
a significant amount of charge transfer of 2.5 electrons between Si and C atoms (Watkins et al. 2009). Nonetheless, Watkins et al. (2009) have shown the similarity of zincblende ZnO (a cubic crystal type with face-centred lattice points), and β SiC, despite the first is generally regarded as ionic II-VI system and the latter as covalent IV-IV system. Moreover, they found that the Buckingham parameters for ZnO also describe SiC clusters fairly well. We therefore performed MC-BH with a simplified version of the parameter set for ZnO given by Whitmore et al. (2002).

The ZnO forcefield we employ has been shown to be able to stabilize a wide range of different cluster isomers (Al-Sumaidi et al. 2008) and bulk polymorphs (Demiroglu et al. 2014) which exhibit alternating cation-anion ordering. However, to reduce the probability to miss stable cluster isomers in our searches, we also ran some test calculations for several sizes with a forcefield parameterized for ZnS (Wright & Jackson 1995) which potentially provides an additional source of cluster isomers not easily found with the ZnO forcefield. However, the few structures that we found exclusively with the ZnS parameters had high energies (when converted to SiC clusters) and did not compete with the ZnO cluster analogues. Although the use of forcefields is an approximation, their use enables us to perform tractable thorough searches. With our mixed-forcefield approach (see also section 2.2) we hope to have minimized the probability to miss a stable SiC isomer.

2.2. Tersoff potential simulated annealing

As already explained, the Buckingham pair potential may fail to describe stable cluster configurations, which show segregation of the Si and C atoms. In this case, the stable clusters are characterised by rather covalent than ionic bonds. A simple two-body interaction is thus not sufficient to properly describe the Si-C system. In addition, a three-body potential is needed to describe the covalent character of bond bending and stretching (Stillinger & Weber 1985; Vashishta et al. 2007). In order to properly describe internal interactions of the most stable SiC clusters, empirical bond-order potentials are favourable, in particular for small clusters (Erhart & Albe 2005). This class of interatomic potentials include the Tersoff type (Tersoff 1989), the Brenner (Brenner 1990), or, ReaxFF (van Duijn et al. 2001), which take into account the bonding environment, namely the bond length, the angle and the number of bonds. As a consequence of geometry, the bonding angle in a tetrahedrally coordinated system like SiC is \( \Theta = \arccos(-1/3) = 109.47^\circ \). The general form of a bond-order potential reads:

\[
V(r_{ij}) = f_c(r_{ij}) \left[ V_{rep}(r_{ij}) + \beta_{ij} V_{att}(r_{ij}) \right] \tag{2}
\]

where \( V_{rep}(r_{ij}) = A_{ij} \exp(-\lambda_{ij} r_{ij}) \) is the repulsive part of the potential and \( V_{att}(r_{ij}) = B_{ij} \exp(-\mu_{ij} r_{ij}) \) the attractive effective potential. \( \beta_{ij} \) modifies the strength of the bond, depending on the environmental parameter like the bonding angle \( \Theta \) as reported in Tersoff (1989). In the Tersoff parametrisation of inter-atomic Si-C molecular system, which is chosen in our approach, the potential is modified by a taper function \( f_c \). \( f_c \) is 1 for inter-atomic distances \( r_{ij} \) smaller or equal of typical bonding distances and falls quickly to 0 for distances larger than \( S \) and thus restricts the interaction to the first neighbouring atoms within a distance \( S \).

\[
f_c(r_{ij}) = \begin{cases} 
1, & r_{ij} < R \\
0.5 + 0.5 \cos(\frac{z(r_{ij}-R)}{S-R}), & R < r_{ij} < S \\
0, & r_{ij} > S 
\end{cases} \tag{3}
\]

The parameter set given by Tersoff (1989) suffers from an underestimation of the dimer binding energy and may not be satisfactory for the description of small gas-phase molecules and clusters. A revised set of parameters is available (Erhart & Albe 2005). In the updated parameter set, the bond-order term \( \beta_{ij} \) is formulated differently from the original description. Unfortunately, the new formulation is not compatible for calculations in most molecular dynamics programs. However, the classic Tersoff parametrisation is sufficient for our purposes, as the results are subsequently refined using a quantum mechanical level of theory. We use the programme GULP (General Utility Lattice Programme) (Gale 1997) which is tailored for the classic parametrisation by Tersoff (1989).

Some SiC cluster structures have been reported in the literature (Pradhan & Ray 2004; Hou & Song 2008; Duan et al. 2013). We tested their stability against (small) distortions in molecular dynamics runs with GULP. Furthermore, we applied the classic Tersoff potential to these structures. In the majority of the cases, this potential suffices to stabilise the structures. In some cases, however, the Tersoff potential fails to stabilize the clusters, and hand-constructed structures were taken instead for the subsequent computation. In some of these failure cases new, unreported clusters appeared.

We also perform simulated annealing runs using the Tersoff-optimised structures - an imitation of a cluster cooling process. The melting point, where crystalline SiC decomposes, is around 3000 K, which is chosen to be the maximal temperature in the annealing routine. By varying the starting temperature \( T_{max} \) and the cooling timescales, we performed several hundred simulated annealing runs for the previously defined seed cluster structures. All the structures were cooled to a final temperature of 200 K. We distinguished between four regimes:

- High temperature annealing with \( T_{max}=3000 \) K
- Moderate temperature annealing with \( T_{max}=1800 \) K
- Low temperature annealing with \( T_{max}=1000 \) K
- Molecular dynamics at a constant temperature of 300 K

The majority of the investigated clusters already stabilize around 600-800 K. In order to reinforce the convergence of the MD runs, the structures were optimised to the Tersoff potential at every step where the temperature is decreased. In the MD runs at constant temperature, snapshots of the lowest potential energy configurations were selected and further inspected.
2.3. Quantum-mechanical refinement

Once pre-optimised, the clusters are refined using quantum-mechanical DFT (Density Functional Theory) calculations to obtain structure-specific infrared spectra (i.e., vibrational frequencies) rotational constants, and zero-point-energies. By comparing the obtained infrared spectra with observational data, the specific isomers present in circumstellar envelopes can thus be identified. The (SiC)$_n$ cluster structures, so far reported in the literature, rely on various theoretical quantum chemistry methods. They include DFT methods using generalized gradient approximation (GGA, PBE), local density approximation (LDA), B3LYP and M11 functionals, respectively, and post-Hartree Fock methods using Möller-Plesset (MP2, MBPT) and coupled-cluster (LCCD, CCSD) techniques. For DFT methods the computational cost scales with the system size as between the order $O(N^3)$ and $O(N^4)$, where $N$ is the number of electrons in the cluster. This means that they can be readily applied to systems containing 10s of atoms. However, many DFT methods can suffer from artificial electron self-interaction that results in overly strong electron delocalisation and too low potential energies. In contrast, Post-Hartree-Fock methods do not suffer from these effects. However, the computational cost of these latter methods is very high and scales with the system size as $O(N^7)$, where $N$ is the number of atoms. Functionals such as B3LYP and M11 attempt to compensate for the above mentioned shortcomings of typical GGA/LDA functionals. The recent extensive benchmark study by Byrd et al. (2016) confirms that the M11 functional is able to correctly identify all investigated (SiC)$_n$ ground states. Although B3LYP was found to be less accurate than M11 for SiC clusters, we also include data calculated with this widely used functional for comparison. We conclude that, for our purposes, the M11 functional method is the best compromise between a reasonable computational cost and the required accuracy.

Owing to its high computational costs, DFT calculations are performed on supercomputers using the well-parallelised code Gaussian 09. These calculations approximate the wave functions and the energy of a quantum many-body system in a stationary state. In the case of SiC clusters, the hybrid B3LYP functional with a cc-pVTZ (correlation-consistent polarized Valence Triple Zeta) basis set is used (Becke, 1993). Recent investigations, however, revealed that the B3LYP functional may fail to predict the correct ground states and spacings in relative energies for SiC clusters (Byrd et al., 2016). Moreover, the authors indicated in their benchmark study that the Minnesota functionals (e.g., M11, Peverati & Truhlar, 2012) have a more adequate accuracy, compared with B3LYP. Owing to this reason we additionally performed DFT calculations using the M11 functional for the majority of the investigated clusters.

Gaussian 09 optimises cluster structures at standard conditions (i.e., pressure of 1 atm and temperature of 298 K). In circumstellar envelopes, however, very different conditions prevail: pressures are 4-9 orders of magnitude lower and temperatures factors of ~5-200 higher. In order to account for the above mentioned temperatures and pressures, the thermodynamic potential functions (enthalpy, entropy, Gibbs energy) are evaluated with the help of partition functions. These functions and their derivatives are calculated from the electronic energies, moments of inertia and vibrational frequencies within the rigid-roter harmonic oscillator approximation (McQuarrie & Simon, 1999, Goumans & Bromley, 2012).

As a consequence, the relative energy spacings of the individual clusters shift and may cross. This implies that the initial lowest energy isomer may not be the most favourable structure in circumstellar conditions and a different cluster structure is preferred. It is thus necessary to study a range of the energetically lowest-lying structures for each cluster size. The use of partition functions relies on the validity of thermodynamic equilibrium. We note, however, that AGB atmospheres may depart from equilibrium as they are periodically crossed by pulsational shock waves. The resulting Gibbs Free energies thus have limited validity. Nonetheless, they provide a good approximation for the individual cluster stability in circumstellar conditions.

3. RESULTS

In this Section we describe our results on the (SiC)$_n$, $n=1-16$, clusters. We constrain our calculations to a maximum size of $n \leq 16$. On one hand the DFT calculations rapidly become increasingly costly with increasing size. On the other hand, we follow a bottom-up approach thus focusing on the initial steps of SiC dust nucleation. These steps often represent the bottleneck of cluster nucleation processes. The displayed numbers correspond to values obtained with the M11 functional, whereas the values in parenthesis correspond to B3LYP results.

**SiC**: As a diatomic molecule the SiC monomer is a linear structure. The SiC triplet represent the ground state of this molecule and is 1.34 (0.96) eV lower in energy than the corresponding singlet state. We find an average bond length of 1.707 (1.813) Å, a rotational constant of 20.6 (18.3) GHz and a vibrational frequency of 1008.7 (862.2) cm$^{-1}$, which corresponds to a wavelength of 9.9 (11.6) μm.

**Si$_2$C and SiC$_2$**: The SiC$_2$ ground state is a triangle and lower by 2.29 (1.98) eV than the linear triplet isomers B in Figure [I]. The isomer with a linear C-Si-C chain is unstable (6.82 eV above the ground state). Regarding the large differences in energy, we assume that isomer A is the dominant state of SiC$_2$ and the geometry of B is negligible for all temperatures and pressures. Reilly et al. (2015) have characterized the ground electronic state of Si$_2$C. The singlet isomer with two off-axis Si atoms bounded by an angle of 114.87 deg. and a C$_{2v}$ symmetry, reported in McCarthy et al. (2015); Cernicharo et al. (2015), is found by our M11 calculations, but not with the B3LYP functional. In the latter case, the molecule relaxes into linear C-Si-C or fails to converge. This result demonstrates the advantage of the M11 functional, compared with B3LYP. The linear Si-Si-C isomer exhibits imaginary frequencies in their IR spectra. Structures showing imaginary frequencies (vibration modes) represent a saddle point (and not a minimum) in the complex potential energy landscape. These saddle points have, as the real minima, a zero gradient and are interpreted as transition states.

Thus, the bended C-Si-C structure is the only stable
SiC2: Two structures of SiC2 are commonly proposed as ground states: the linear triplet structure and the closed rhomb. They usually show a tiny difference in binding energies and are thus considered as degenerate isomers. The exact energy separation depends on the used functional and basis set. This is consistent with our B3LYP findings, where these two structures are separated by only 0.03 eV, as can be seen in Figure 2. Contrary, we show that the M11 functional predicts the rhombic structure (A) to be more stable than the linear chain (C) by 0.69 eV at standard conditions. Isomer B is characterized by threefold-coordinated (Si and C) atoms and is 0.39 (0.26) eV above the lowest-lying state. The linear triplet structure D has potential energy 2.77 (2.20) eV higher with respect to the ground state. The structures shown here have been previously found by Pradhan & Ray (2004), Hou & Song (2008), and Duan et al. (2010), respectively. Several further isomers have been investigated by Pradhan & Ray (2004). Our calculations show, however, that the structures G, H and I in Figure 3 are transition states and the force constants indicate a relaxation into isomer B of Figure 2.

Si3C3: For Si3C3 clusters an extensive and comprehensible study has been carried out by Mühlhäuser et al. (1994) who examined 17 structure in total. Further studies by Hou & Song (2008), Pradhan & Ray (2004), and Duan et al. (2010) have revealed that some of these structures are particularly stable. In Figure 4 we summarise our findings.

Apparently, the isomers in Figure 4 are characterised by planar structures as well as three-dimensional forms with triangular faces. All clusters contain three adjacent C atoms. The majority of the found Si3C3 clusters show a carbon chain (like C and D) but also triangular C arrangement is observed (A and B). Ground state A and next higher-lying isomer B are non-planar and have triangular faces. Structure D is the lowest-lying isomer within the B3LYP level of theory. In the M11 functional frame, however, D is 0.88 eV above the minimum structure and the C3 chain is slightly bent. Some structures that have been reported in the literature, however, exhibit imaginary infrared frequencies indicating a transition state rather than a minimum structure. By identifying the bond causing the imaginary vibration and re-optimising a slightly distorted structure, we found that structures M, N, and O in Figure 5 relax into other low-lying structures. All linear structures are triplet states and are energetically unfavourable or exhibit imaginary frequencies and can thus not be considered as minimum
structures.

**Si₃C₄**: The ground state (A) of Si₃C₄ displayed in Figure 5 is a non-planar structure having one Si atom out of the plane. The second lowest energy structure (B) is a planar structure with a C₂ᵥ symmetry. It is composed of a 4-member-trans-carbon chain and can be viewed as two connected Si₂C₂ clusters (isomer B in Figure 2), bridged by C-C bonding. The corresponding cis-isomer (structure C) has an energy 0.33 eV above the ground state and 0.07 (0.09) above the trans-isomer. Trans- and cis-isomers differ only by a rotation of 180° along the C-C double bond axis. The structures A-D have been reported in Duan et al. (2013) and references therein.

**Si₄C₄**: The most stable Si₄C₄ clusters and relative energies (in eV).

**Si₅C₅**: This is the smallest cluster size, where a carbon ring appears. The ground state cluster (A) exhibits a C₅ ring and a mirror plane, thus belonging to the Cᵥ symmetry group. Structure B shows a C₅ symmetry as well, and a six member ring with 5 C and 1 Si atoms. Both structures (A and B) have the lowest potential energy in the B3LYP calculations as well. All low-lying structures displayed in Figure 8 exhibit either a bended carbon chain with five members or a ring and are non-planar. These structures were previously reported by Duan et al. (2013).

**Si₆C₆**: The ground state of Si₆C₆ contains a C₆-ring and laterally distributed Si atoms as can be seen in Figure 9. Isomer B and and C show 5 member carbon rings. Structure D has the lowest potential in the B3LYP frame and is a planar configuration containing two five-member-rings consisting of four carbon and one silicon atom. Among the lowest lying isomers, compound A is the only one found with an aromatic C₆ ring. The other aromatic isomers have significantly higher potential energies. We found that structures B and C exhibit a C₅ ring and a one-sided silicon segregation (apart from single Si atoms conjugating the cluster). Clusters obeying a strict alternation of Si and C atoms are 5-9 eV higher in energy.
energy compared with the ground state. Structures A–D were reported in [Duan et al. (2013)].

Si$_7$C$_7$: The ground state of Si$_7$C$_7$ (cluster A in Figure 10) consists of aromatic ring connected to a Si$_5$ sub-cluster and two individual Si atoms. Structures C and D have a five-member carbon ring in common, where the dangling bonds are saturated by two individual Si atoms. MC-BH generated structures with alternating Si and C atoms have energies 7–8 eV higher than isomer A.

Si$_8$C$_8$: In the most stable Si$_8$C$_8$ clusters the carbon atoms tend to form planar 5- or 6-member rings as can be seen in Figure 11. The Si atoms surround the carbon sub-cluster and segregate spatially. Structures A and C contain a C$_5$-ring, whereas B and D have a C$_6$-ring. The remaining carbon atoms arrange as side-chains to form a silicon-substituted ring. Structures A, B and C are reported in [Duan et al. (2013)]. Other candidate isomers (except structure D) obtained through simulated annealing are 3–5 eV above the minimum structure. The highly symmetric double-ring structure (G) proposed by [Belenkov et al. (2012)] and the “keyhole” isomer (H) in Figure 12 have potential energies of 5.29 (6.04) eV and 4.46 (5.35) eV above the ground state, respectively. Further structures with alternating arrangement of atom types (Si and C) have energies 4–9 eV above the ground state.

Si$_9$C$_9$: The energetically favourable structures A, B and C in Figure 13 contain fused C$_6$ and C$_5$ rings. Only isomer D has an exceptional character with a C$_6$ and two side chains. A C$_{2v}$ symmetric structure with alternating Si and C atoms was obtained by the MC-BH method, but it has an energy of 7.15 (7.84) eV above the ground state. Other isomers obtained by simulated annealing have potential energies 2–6 eV above the ground state.

Si$_{10}$C$_{10}$: The lowest-lying isomer using the B3LYP functional (structure A’) is reported for the first time and can be seen in Figure 14. Applying the M11 functional, Structure A’ relaxes into state A. We thus consider A as the true ground state. Clusters A, B and C have been found by [Duan et al. (2013)]. It is prominent that fused double C$_6$ rings of naphthalene type form for the four favourable clusters A’, A, B, and C. Compared to smaller
SiC cluster sizes, the most stable Si_{10}C_{10} clusters have spatial and open cage-like forms rather than planar configurations. We find that the eleven energetically most favourable clusters reside in a narrow energy range of 1 eV. This is more than for any other size of the investigated SiC clusters. Further isomers we found by means of simulated annealing of seed clusters have energies 2-4 eV above the minimum energy structure. MC-BH synthesised isomers have energies 4-6 eV above the ground state.

**Figure 14.** The most stable Si_{10}C_{10} clusters and relative energies (in eV).

**Si_{11}C_{11}:** The most stable isomers (see Figure 15) are characterised by presence of a C_6 and two C_5 rings, respectively, each one sharing an edge with another ring. Structures A-D are found in Duan et al. (2013). All structures, except the ground state A, have a carbon subunit characterised by a fusion of two C_5 and one C_6 ring. The ground state A contains one C_5 and one C_6 ring, and two Si-substituted 5-member-rings (C_5Si rings). For this cluster size, stable cage-like clusters found with the MC-BH method possess potential energies 1.2 - 4.5 eV the ground state.

**Figure 15.** The most stable Si_{11}C_{11} clusters and relative energies (in eV).

**Si_{12}C_{12}:** The ground state (A) of Si_{12}C_{12} is displayed in Figure 16 and represents a particular case in the series of Si_{n}C_{n} ground states. It exhibits a highly symmetric tetrahedral configuration (symmetry group T_H) with alternating SiC-bondings and was proposed by Watkins et al. (2009) as a potential nano building block of larger structures. Having a “bucky”-like configuration, the almost spherical structure resembles the chemical family of fullerenes. The cluster has a mass of \( \sim 480 \) a.m.u. and a diameter of \( \sim 5.9 \) Å. This would result in a mass density of 0.919 g cm\(^{-3}\), which is about 30 % of 3.217 g cm\(^{-3}\), a reference mass density for all polytypes (Pattanak 2003). Owing to its properties, structure A may link the segregated clusters with the crystalline bulk material observed in pristine SiC dust grains. In contrast to other isomers, structure A may be identified spectroscopically, owing to its strong infrared vibration mode intensities (see Figure 21). Moreover, it is the smallest ground state among the most stable Si_{n}C_{n} clusters that we found with the Buckingham pair potential applying the MC-BH method. Owing to its stability, shape and atomic coordination, structure A may be a candidate for the basic building blocks of SiC dust grains and may trigger the molecular size where cluster chemistry crosses over to dust chemistry (i.e. condensation and coalescence).

The second most stable polymer (B) exhibits a dihedral D\(_{2h}\) symmetric structure with two unconnected C_6 rings. Despite classified as member of the C_1 group, cluster D is almost symmetric with a quasi mirror plane. These two structures B and D have been reported by Song et al. (2010). Apart from structure C, all these cluster exhibit a fused C_6-C_5-C_5 ring segregation. Isomers C has not been reported previously.

We found several other stable clusters with higher potential energies. However, they are not displayed as they have a similar open-cage like configurations such as structures C and higher lying isomers. Among the lowest-lying Si_{12}C_{12} configurations a high degree of symmetry is prominent. The symmetric structures obtained with the MC-BH method are, apart from the ground state, 8-9 eV higher in potential energy than isomer A.

**Figure 16.** The most stable Si_{12}C_{12} clusters and relative energies (in eV).

**Si_{13}C_{13}:** Among the lowest-lying Si_{13}C_{13} isomers, we find carbon segregations with one C_6 and three C_5 rings (structures A and B) and four C_5 rings (C) (see Figure 17). Also the Si atoms start to develop segregated rings with 5 to 6 members (A,B and C). A, B and C
have been found by Song et al. (2010), however, owing to the different functional/basis set used in their study, in a different energy ordering. We find that the energetic ordering is preserved by comparing our M11 and B3LYP results. Further structures found by simulated annealing are 0.5-4 eV higher in potential energy. Structure D is a MC-BH generated structure and contains seven 6-member rings and 1 large 8-member ring. We find three further structures with cage-like geometries that have potential energies 0.56-1.93 eV above the ground state and thus, they are comparable to the segregated clusters obtained by simulated annealing.

**Figure 17.** The most stable Si_{13}C_{13} clusters and relative energies (in eV).

**Si_{14}C_{14}:** The two most stable isomers of Si_{14}C_{14} both show symmetries as can be seen in Figure 18. The first (A) shows two mirror planes and a two fold symmetry axis (C_2v group), the second (B) has one mirror plane (C_s group). The most stable structures (A, B and D) show a complete carbon segregation consisting of two C_6 and two C_5 rings. Whereas in B and D the C_6 rings are connected and share a C-C bonding, in A the C_5 rings share binding electrons and the C_6 rings are separated from each other. Moreover, B and C show an overall open cage geometry, whereas A represents a closed hollow ellipsoid. Isomers A, B and C were found in Song et al. (2010), D is reported for the first time. Further structures obtained by simulated annealing are not displayed here and have 1-4 eV above the ground state. With the MC-BH approach we found a structure with alternating Si-C bonds and an energy 0.64 eV above the ground state. It is the fifth lowest energy structure for Si_{14}C_{14}. Other structures obtained with the MC-BH method have energies 1.4 - 1.7 eV above the global minimum. The latter findings indicate that for n=14 the segregated forms cease to dominate and cage-like clusters can compete against the latter in terms of potential energy.

**Si_{15}C_{15}:** The ground state of Si_{15}C_{15} is a symmetric structure with alternative bond Si-C bonds found with the MC-BH method. It is composed of eleven 6-member and four 4-member rings obeying strict alternation of Si and C atoms. This ground state is reported for the first time. Its low potential energy indicates that the symmetric cage-like configurations with alternating Si-C bonds can compete against segregated structures at this size regime and even represent the lowest energy structure for n=15.

The second lowest isomer showing two separate carbon segregations and a quasi-mirror plane is displayed in Figure 19. It shows similarity with the smaller-sized (n=12) structure B in Figure 16. The two low-lying isomers (C and D) are almost identical in terms of their B3LYP potential energy and can be termed degenerate. The investigation of these cluster with the M11 functional, however, reveals a larger spacing in energy, and that they can be regarded as independent and discrete clusters. Moreover, they show distinct geometries, vibrational IR spectra and rotational constants. Their carbon subunit is almost identical and resembles structure D in Figure 6 of Song et al. (2010). However, the silicon atoms are arranged differently, giving rise to the change in potential energy.

Structure B has been reported previously by Song et al. (2010).

**Figure 18.** The most stable Si_{14}C_{14} clusters and relative energies (in eV).

**Si_{16}C_{16}:** The ground state of Si_{16}C_{16} shows a particular high degree of symmetry (point group T_d) and is composed of 6-member rings with alternating Si-C bondings. The structure has been put forward as building units of larger SiC frameworks by Watkins et al. (2009). The overall structure is a closed hollow fullerene-like cage and shows strong IR features (around 9.3-9.5 and 18.9 µm, see Figure 21), compared to isomer B (and the other iso-

**Figure 19.** The most stable Si_{15}C_{15} clusters and relative energies (in eV).
mers of this size). As for n=12, we found the ground state structure by applying the Buckingham pair potential using MC-BH. The “bucky”-like structure has an approximately spherical shape and exhibits alternating Si-C bonds. The hollow spheres with a Tₐ symmetry have a mass of ~ 640 a.m.u. and a diameter of ~ 6.5 Å. This would result in a mass density of 0.924 g cm⁻³, which is very similar as for the n=12 case and about 30 % of 3.217 g cm⁻³, a reference mass density for all polytypes (Patnaik 2003). Owing to its strong and characteristic infra-red features, this particular isomer can be spectroscopically identified. As for n=12, the ground state (A) may link the segregation-dominated small clusters (n<12) with larger clusters and crystalline SiC bulk material.

The next higher lying isomer of Si₁₆C₁₆ (structure B) shows two carbon segregations, a C₆C₅-ring and a C₆-ring with a one-C-atom arm, and exhibits a distorted symmetry with a quasi mirror plane, as can be seen in Figure 20. Isomer B has been found for the first time and is the lowest energy structure using the B3LYP functional. Despite its low potential energy, it is challenging to observationally detect structure A, owing to low vibrational IR intensities (see Figure 21).

For sizes n≤12 we clearly show the emergence of a new family of stable clusters, the cage-like structures with alternating Si-C bonds. Some properties (alternating atomic arrangement, bond lengths) of the latter strongly resemble the bulk phase of 3C-SiC, compared to the segregated clusters. Though the “bucky” clusters are void in their interior which is not the case for any SiC crystal lattice. We thus expect a transition from cage- to bulk-like at some not further specified size n ≥ 16.

3.1. Gas conditions in the circumstellar envelope

| T / p | 500 | 100 | 10 | 1 | 0.1 | 0.01 |
|-------|-----|-----|----|---|-----|------|
| 5000 | ×   | ×   | ×  | × | ×   | ×    |
| 3000 | ×   | ×   | ×  | × | ×   | ×    |
| 2500 | Si₃C₃ | Si₃C₄ | Si₂C₃ | × | ×   | ×    |
| 2000 | Si₃C₂ | Si₃C₃ | Si₂C₂ | × | ×   | ×    |
| 1500 | Si₂C₂ | Si₂C₂ | Si₂C₃ | × | ×   | ×    |
| 1000 | Si₂C₂ | Si₂C₂ | Si₂C₃ | × | ×   | ×    |
| 500 | Si₂C₂ | Si₂C₂ | Si₂C₃ | × | ×   | ×    |

In Table 1, the energetic feasibility for SiC cluster growth at characteristic circumstellar conditions are displayed.

The left upper part of Table I represents gas conditions shortly after the passage of a pulsational shock, where the gas is hot and compressed (T=3000-5000 K, p= 100 - 500 dyne·cm⁻² = 10 - 50 P). In this case, the SiC dimerisation, representing the initial process to start the particle growth, is suppressed by an energy barrier of several eV.

Also for the larger clusters (n ≥ 3) the Gibbs free energy of formation, ΔG, of the lowest-lying clusters become largely positive and nucleation is unlikely to occur, owing to the lack of stability and high activation barriers.

The left intermediate part of Table I (T=2000-2500 K, p= 10 - 100 dyne·cm⁻² = 1-10 P) reflects typical conditions at the visual photosphere where the optical depth τ is 2/3. Under such conditions, the initial steps for SiC cluster growth are likely to occur, as they proceed under the excess of energy. At some point of the nucleation chain, however, owing to energy barriers, the growth may not proceed (we refer to this as a waiting point) until the conditions in the wind have relaxed to lower temperatures and densities, where subsequent nucleation is favourable. Examples for waiting points are Si₂C₂ and Si₂C₃, but also also Si₃C₉ at high temperatures as can be seen in Figure 22.

Cooler and more diluted gas conditions prevail further away from the star (~ 10 Rₖ), where the pulsational shocks have strongly weakened and damped and the wind has accelerated up to its terminal velocity (and it is assumed that a considerable amount of dust has already formed). Such conditions (T=500 K, 10⁻⁵ dyne·cm⁻² = 10⁻⁶ Pa) are found in the right lower part of the table. In this regime, the complete nucleation pathway is energetically favourable. However, the densities are so low, that particle collision events with subsequent nucleation become rare. Nevertheless, previously synthesized
dust clusters may stochastically coalesce and form dust grains.

In summary, SiC cluster formation and growth favours dense and cool conditions; vice versa, the SiC cluster synthesis is hampered in hot and dilute environments. As circumstellar envelopes cover a broad range of temperatures and pressures in space (due to the radial distance from the star) as well as in time (owing to dynamical pulsations and wind acceleration), a combination and exposures of various pressures and temperatures involving waiting points is more realistic than assuming thermodynamic equilibrium. Yasuda & Kozasa (2012) showed in their calculations that SiC grains hardly form in local thermodynamic equilibrium (LTE), and that nonequilibrium processes (like pulsations) are necessary to explain the observed ratio of SiC dust (0.01-0.3) in carbonaceous dust grains inferred from the radiative transfer model.

For a constant pressure of p=100 dyne·cm⁻² (which corresponds to gas density of 3.6 · 10¹⁴ cm⁻³) and T=2500 K, the cluster growth is energetically feasible up to n=3, or Si₂C₃. The synthesis of larger cluster sizes is strongly hampered by energy barriers of the order of 100 kJ/mol (~1 eV). At T≤2000 K and reasonably high densities, the processes increasing the cluster size are energetically downhill up to the maximum size n=16 considered in this study.

Figure 22. Gibbs energy of formation of the ground state clusters versus cluster size for different sets of gas temperatures and pressures.

In Figure 23, the relative binding energy of the lowest lying SiₙCₙ cluster (ground state) is plotted versus cluster size n according to the prescription:

\[
\Delta E_b(SiₙCₙ) = \frac{E_b(SiₙCₙ)}{n} - E_b(SiC)
\]

The largest incremental in the binding energy (4.3 eV) between clusters of size n and (n+1) occurs between the SiC monomer and the dimer. For larger cluster sizes the binding energy increases almost monotonically and saturates around 6.0 eV. However, we also note that the ground states of n=9 and n=12 are particularly stable. \(\Delta E_{MO}\) denotes the energy gap of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This quantity describes the strength and stability of a given electronic configuration. A large \(\Delta E_{MO}\) indicates a high cluster stability against thermal and radiative excitations. Evidently, for \(\Delta E_{MO}\), there is no correlation with cluster size n. However, it reveals that some cluster sizes (n=3,12,16) have a higher stability and that the closed cage structures are particularly stable, compared to other cluster sizes. Generally, \(\Delta E_{MO}\) tends to decrease the larger the system is, as the density of (unoccupied) states increases with cluster size n. For a given cluster size, the HOMO-LUMO energy gap is not necessarily the largest for the ground state.

Figure 23. The relative binding energy \(\Delta E_b\) (filled squares and solid line) of the ground state SiₙCₙ clusters (normalised to cluster size n) and the HOMO-LUMO energy gap \(\Delta E_{MO}\) (triangles and dashed line) of the ground state SiₙCₙ clusters.

In Figure 24, curves with vanishing Gibbs energy of formation, \((\Delta G_f=0)\) for small ground state clusters. The corresponding cluster formation is energetically favourable \((\Delta G_f < 0)\) for temperatures/pressures left/above of these curves. In contrast, for temperatures/pressures right/below these curves, the corresponding cluster formation is unlikely \((\Delta G_f > 0)\)

In Figure 24 curves with vanishing Gibbs energy of formation, \((\Delta G_f=0)\), for small SiₙCₙ, n ≤ 7, and Si₂C and SiC₂ are shown. Our results indicate that the latter (SiC₂) is the first silicon-carbon molecule to emerge from the hot atmosphere, as it is more stable over a broad range of gas pressures, compared with the other considered compounds. The formation of Si₂C and SiC₂ becomes exogenic \((\Delta G_f < 0)\) at very similar pressures and temperatures. In contrast, the formation of the SiC molecule is more likely at lower temperatures assuming a constant pressure. For the larger SiₙCₙ clusters, the formation probability shifts successively to lower temperatures (or higher pressures). From Figure 24 we conclude that a homogeneous nucleation is viable, presuming a bottom-up approach in the formation of SiₙCₙ clusters. It should be noted that, in the presence of stellar pul-
sations, a trajectory of a gas parcel will not be represented by a single line in the T-p diagram, but rather by a complex zigzag. It implies that certain clusters with a particular high stability (i.e. waiting points) form at several times during the nucleation process and thus can be considered as candidates for a possible observational detection. In summary, we conclude that a homogeneous nucleation of SiC clusters is definitely viable in circumstellar environments and that, owing to their thermal stability, the molecular species \( \text{Si}_2\text{C}_2 \) and \( \text{Si}_2\text{C} \) may play an important role in the initial steps of SiC nucleation.

![Image of vibrational spectra](image-url)

**Figure 25.** Vibrational spectra of the ground state \( \text{Si}_n\text{C}_n \) clusters. The fit is a Lorentzian distribution with a FWHM parameter of 0.033.

In Figure 25 the calculated vibrational IR spectra of the \( \text{Si}_n\text{C}_n \) ground state clusters are displayed. A cluster of size \( n \) (i.e. the number of SiC units) exhibits at maximum 6-(\( n-1 \)) individual vibrations accounting for bending and stretching modes. Clusters with symmetric arrangement, however, show fewer emission modes, owing to the multiplicity of identical vibrations.

The unit conversion from \( \text{km} \cdot \text{mole}^{-1} \) to the opacity in \( \text{cm}^2\text{g}^{-1} \) is obtained by

\[
1 \text{km} \cdot \text{mole}^{-1} = \frac{10^5}{\nu} \text{cm}^2\text{mole}^{-1} = \frac{10^5}{\nu M} \text{cm}^2\text{g}^{-1}
\]

where \( \nu \) is the vibrational frequency in units of \( \text{cm}^{-1} \) and \( M \) the molecular mass in atomic mass units (e.g. \( \sim 40 \) for the SiC monomer).

4. DISCUSSION

The 11.2-11.5 \( \mu \text{m} \) feature observed in the spectra of carbon-rich stars represents the most prominent emission attributed to SiC dust particles. About 4% of the stars in the sample of Little-Marenin (1986) show a feature shifted to 11.6 \( \mu \text{m} \) corresponding to the wavelength of the SiC molecule (monomer) vibration mode. Some carbon stars exhibit a peak around 11.7 \( \mu \text{m} \) (Goebl et al. 1995). These stars are characterised by a lower feature strength and broadened emission indicating larger SiC particles. A spectral feature at 9 \( \mu \text{m} \) that correlates with the 11.3 \( \mu \text{m} \) is observed as well in carbon stars (Speck et al. 2005). The authors concluded that the carrier of the 9 \( \mu \text{m} \) is either amorphous SiC or Si-doped nanodiamond. Moreover, the authors find that as the star evolves and increases its mass loss rate, the SiC dust grain sizes become smaller. Finally, in the superwind phase, owing to the high mass loss rate, the SiC feature appears in absorption, broadens, weakens, and is shifted towards shorter wavelengths. Speck et al. (2009) investigated spectral features in the 10-13 \( \mu \text{m} \) range in a sample of extreme carbon stars and attributed them to carbonaceous solids including a fraction of SiC dust. In our study, \( \text{Si}_2\text{C}_2 \) at 10.237 \( \mu \text{m} \) and \( \text{Si}_3\text{C}_3 \) at 12.507 \( \mu \text{m} \) show the strongest emission in this range among the \( \text{Si}_n\text{C}_n \) cluster ground states. [Rau et al. (2015)] showed that, apart from the spectral feature around 11.4 \( \mu \text{m} \), amorphous carbon and SiC dust particles exhibit absorption distributions that are fairly similar in the small particle limit. This feature is thus a unique and distinct tracer for the presence of SiC dust grains. Also laboratory spectra show a wide variety of the SiC phonon features in the 10-13 \( \mu \text{m} \) wavelength range, both in peak wavelength and band shape (Mutschke et al. 1999). It is the only relatively broad band that is attributed to SiC. As previously mentioned the SiC crystal type (\( \alpha \) vs. \( \beta \) SiC) plays a minor role in the 10-13 \( \mu \text{m} \) emissivity.

In our study, we found several clusters with vibrational emissions in the 11.2-11.5 \( \mu \text{m} \) wavelength. Their overall IR intensity is, however, too small in order to explain the observed emission. The investigated cluster sizes (up to \( n=16 \)) may be too small to reproduce the bulk-related phonon emission around 11.3-11.4 \( \mu \text{m} \). The SiC molecule (monomer) exhibits a vibrational emission feature at 11.599 \( \mu \text{m} \). However, its IR Intensity is weak (0.1274 \( \text{km} \cdot \text{mole}^{-1} = 0.3694 \text{cm}^2\text{g}^{-1} \)), compared with the IR intensities of the other SiC clusters. Also the three-atomic species \( \text{Si}_2\text{C} \) and \( \text{SiC}_2 \), the latter being a by-product of SiC dust formation, cannot account for the 11.3 \( \mu \text{m} \) feature in their spectra. \( \text{Si}_3\text{C}_3 \) (isomer F) exhibits a feature at 11.325 \( \mu \text{m} \) with a reasonable intensity of 106.2789 \( \text{km} \cdot \text{mole}^{-1} = 0.3694 \text{cm}^2\text{g}^{-1} \). However, the cluster is 0.84 eV above the ground state at standard conditions, and the situation is similar (0.8-1.2 eV) at characteristic wind conditions. \( \text{Si}_4\text{C}_4 \) (isomer F) shows at 11.298 \( \mu \text{m} \) feature with a strength of 85.7498 \( \text{km} \cdot \text{mole}^{-1} = 0.3694 \text{cm}^2\text{g}^{-1} \), and has a potential energy of 0.4-0.6 eV above the ground state, depending on the gas conditions. The ground state of \( \text{Si}_5\text{C}_5 \) (isomer A) shows an emission at 11.298 \( \mu \text{m} \), but the IR intensity (0.2336 \( \text{km} \cdot \text{mole}^{-1} \)) is (too) low. Other \( \text{Si}_n\text{C}_n \) isomers show signatures in this wavelength range, namely, structure C (which is the minimum structure in the higher pressure cases) at 11.405 \( \mu \text{m} \) with 3.1128 \( \text{km} \cdot \text{mole}^{-1} \), D at 11.424 \( \mu \text{m} \) and 3.3497 \( \text{km} \cdot \text{mole}^{-1} \), E at 11.350 \( \mu \text{m} \) with 0.5734 \( \text{km} \cdot \text{mole}^{-1} \), and F at 11.299 \( \mu \text{m} \) with 3.5731 \( \text{km} \cdot \text{mole}^{-1} \).
km·mole$^{-1}$. Although Si$_5$C$_5$ has several low-lying candidate carriers of 11.3 $\mu$m features, the IR intensities are very low, compared with the other spectral features these isomers have. For the larger clusters, we compiled a table with vibrational intensities in the 11.2-11.5 $\mu$m range (see Table 2).

Table 2

| n | X | $\lambda$ (in $\mu$m) | I (in km·mole$^{-1}$) | I (in cm$^2$·g$^{-1}$) |
|---|---|------------------------|-----------------------|-----------------------|
| 6 | B | 11.365                 | 1.0139                | 0.4801                |
| 7 | B | 11.510                 | 14.8496               | 6.1042                |
| 8 | A | 11.449                 | 83.6211               | 29.9181               |
| 10 | A | 11.555                 | 9.9048                | 2.8365                |
| 11 | A | 11.384                 | 8.1423                | 2.1066                |
| 11 | D | 11.181                 | 5.1542                | 1.3988                |
| 12 | C | 11.424                 | 3.9820                | 0.9477                |
| 12 | D | 11.461                 | 7.4771                | 1.7853                |
| 13 | B | 11.449                 | 3.4249                | 0.7541                |
| 13 | C | 11.293                 | 0.3679                | 0.080                 |
| 13 | D | 11.219                 | 24.8402               | 4.9765                |
| 14 | C | 11.363                 | 0.8570                | 0.1739                |
| 11 | B | 11.289                 | 2.8705                | 0.5787                |
| 15 | B | 11.227                 | 7.8250                | 1.4641                |
| 15 | C | 11.213                 | 4.8333                | 0.9032                |
| 16 | C | 11.363                 | 5.7596                | 1.0226                |

For cluster size n=8,11,12,13 and 15 the ground states (or next higher lying states) emit in this wavelength regime; the intensities are (apart from 8A), however, quite low. Large abundances of a specific cluster, though, could increase the intensity significantly.

Some of the spectral peaks identified in our calculations are not explicitly reported in the literature. Nevertheless, SiC clusters may represent a key player for the onset of dust formation in carbon-rich AGB stars, albeit not directly detected.

In fact, Frenklach et al. (1989) found experimental evidence for a scenario in which SiC nucleates at higher temperatures and provides surfaces for subsequent carbon condensation in a hydrogen-rich atmosphere. Moreover, Cadwell et al. (1994) used the model of induced nucleation, where the grain growth proceeds on reactive surfaces of pre-existing seed particles, and showed that a subsequent condensation of carbonaceous material results in composite grains that are consistent with grains found in pristine meteorites. Kozasa et al. (1996) thus suggested that SiC grains form at high temperatures by homogeneous nucleation, but as soon as the temperature has decreased (i.e. at larger radii), a mantle of amorphous carbon (amc) may deposit on SiC seeds. The spectral signatures of pure SiC may thus be blended and/or suppressed by the amc mantle.

There is a series of UnIdentified Bands (UIBs) at 3.3, 6.2, 7.7, 8.6 and 12.7 $\mu$m, respectively, seen in carbon-rich AGB stars. These features are commonly attributed to Polycyclic Aromatic Hydrocarbon (PAH) emission (Beintema et al. 1996; Hron et al. 1998; Jørgensen et al. 2000; Boersma et al. 2006). As both PAHs and SiC clusters, contain aromatic C$_6$ rings and have conjugated bonds in common, they may show a remarkable spectral similarity. In the following we examine whether SiC clusters could account for the emission of UIBs or not.

Table 2 lists the IR intensities of the presented clusters (n $\geq$ 6) in the 11.2-11.5 $\mu$m wavelength range. The two columns identify cluster size n and state X, the third column displays the wavelength $\lambda$ in $\mu$m and the intensity I (in km·mole$^{-1}$ and cm$^2$·g$^{-1}$) is listed in the fourth column.

- Si + C $\rightarrow$ SiC + hν (radiative association)
- Si + CH$_2$ $\rightarrow$ SiC + CH (bimolecular collision)

whereas the bimolecular collision reaction is estimated by analogy to the reaction Si + CH$_3$ $\rightarrow$ SiCH + H$_2$ (Kunz & Roth 2001). Despite low energy barrier of 136.73 K (1.14kJ/mol) the radiative association reaction is very slow (Andreazza et al. 2009). Moreover, owing to the lack of gas phase reaction rates, isovalences of Si and C are presumed, and rates for SiC are equalized with rates for C$_2$ (see e.g. Cherchneff & Dwek (2010)). This may be adequate as a first approximation. However, the binding energy of SiC (4.71 eV) is higher by more than 1 eV compared with C$_2$ (3.6 eV). Moreover, the Si-C bonding has a small, but not negligible dipole moment of $\sim$ (1.7-1.8) Debye, due to the larger size and the higher number of electrons of the Si atom. This may have non negligible effects on the reactivity of the molecules.

Yasuda & Kozasa (2012) provide reaction enthalpies for SiC cluster growth for temperatures 1500 K and 1000 K. The enthalpies indicate that a homo-molecular cluster growth (i.e. the addition of SiC molecules to a Si$_n$C$_n$ cluster) is energetically most favourable formation route. Albeit the reaction enthalpies are approximately with that of solid SiC for n >3, they conclude that the reactions

$$S_i n C_n + SiC \rightarrow Si_{n+1}C_{n+1}$$

are the dominant processes in the formation of SiC dust grains, consistent with our findings (see Figure 22).

In the following, we list observation of silicon carbon molecules in C-rich AGB stars and compare them
with our findings. The molecular SiC radical has been detected first in CW Leo by Cernicharo et al. (1989). We find a rotational constant of 20643.1 MHz consistent with the spectroscopic constant B=20297.6 MHz. Note, that SiC is a triplet and thus the rotational level is split into three states. Our M11 calculations of SiC yield the following rotational constants A=58363.8 MHz, B=13504.6 MHz and C=10462.1 MHz, whereas the derived constants in Cernicharo et al. (2015) (S reduction) as A=64074.3, B=43957.5, C=4102.1 are slightly different, but still compatible. For SiC, we obtain the following rotational constants A=53511.7 MHz, B=13004.6 MHz and C=10462.1 which are in good agreement with the laboratory (A=53909 MHz, B=13530 MHz, C=10751 MHz) and observational data (A=52390 MHz, B=13156.2 MHz, C=10447.4 MHz) of Thaddeus et al. (1984). The most stable isomer of SiC₃ has a cyclic geometry and was detected in CW Leo (Apponi et al.1999; Cernicharo et al. (2000)). We find rotational constants of 39.962 GHz and 6.240 GHz with the M11 functional which is relatively close to the laboratory spectra of 37.9 and 5.83 GHz, respectively. Linear SiC₄ was detected by Ohishi et al. (1989) in CW Leo. With the M11 functional we obtain a rotational constant of 1549.6 MHz, close to the observed value of 1533.8 MHz.

Recent observations revealed that, among the silicon carbon molecules, SiC₃ and SiC₄ dominate the inner envelope whereas the SiC molecule is 2-3 orders of magnitude less abundant (Cernicharo et al. 2015). We conclude that the SiC molecule is rapidly converted in SiC₂, SiC₂C and SiCN clusters. The emission of SiC₃ and SiC₄ arises in the intermediate and outer envelope of CW Leo. Thus, we suggest that the latter molecules are the result of photochemistry or grain surface reactions and that they do not play a role in the nucleation of SiC dust. Assuming a dust-to-gas mass ratio of 2.5 × 10⁻³ and a fraction of 10% SiC in the dust grains results in a solid SiC abundance, (SiC)_{dust} / H₂, of 1.25 × 10⁻⁵. This is slightly less than the half of the solar Si abundance (3 × 10⁻⁵). It has been suggested that the recently discovered SiC₂ molecule plays a key role in the formation of SiC dust grains (Cernicharo et al. 2015). Although the molecules are well characterised in terms of geometry and energetics, reaction rates are lacking for SiC₂. In our study, we find that the Gibbs free energy of formation of SiC₂ is lower by at least 100 kJ/mol compared to SiC₂ for all p-T combinations listed in Table 1. In fact, the latter explains the observed higher SiC₂ abundance between 1 and 4 R, compared with SiC. In the intermediate envelope region (4-40 Rₜ), equal amounts of SiC₂ and SiC₃ are present. Further out (∼40-1000 Rₜ), again SiC₂ is favoured over SiC, before both species are essentially dissociated/depleted. These results indicate that SiC₂ is favoured over (or at least equivalent to) SiC₂C in circumstellar outflows, and agrees with our calculations, assuming a formation pathway via the SiC molecule and equal amounts of Si and C atoms. As carbon is ∼17 times more abundant than silicon, assuming scaled-solar abundances, the dominance of SiC₂ versus SiC and SiC₂C is even emphasized. Owing to the excess of carbon relative to silicon, the molecular species SiC₃ and SiC₄ are excluded from the present study. In carbon-rich atmospheres of evolved AGB stars, this (C/Si) ratio tends to be even higher and has values ∼20-30 (Cristallo et al. 2015). As can be evaluated from Table 3 cluster growth via SiC₂ is energetically unfavourable at temperatures of 1000 K and 1500 K. The formation of SiC₂ represents thus a competing branching to the synthesis of SiₙCₙ, n ≥ 3 clusters for conditions close to the star. Therefore, we conclude that SiC₂ is a by-product of Si dust formation in the inner envelope. Further away from the star, at lower temperatures and pressures, however, the cluster nucleation via SiC₂ becomes exothermic and exergonic and thus also likely to occur. A nucleation pathway involving Si₂C as intermediary is energetically thoroughly viable, also close to the star, albeit a cluster growth according to Equation 6 is expected to be faster and more efficient. Our theoretical findings thus explain and reflect the observed radial abundance profiles of the silicon carbon molecules in CW Leo.

In Table 3 we compare the energetics of the ground-state clusters derived in this study with Yasuda & Kozasa (2012). The authors evaluated the reaction enthalpies ΔH° from a data set by Deng et al. (2008) at 1000 and 1500 K. We find similar trends in the exothermicity of the reactions, though our value are systematically lower by 3-77 (16-86) kJ/mol for T=1000 K and 24-108 kJ/mol for T=1500 K.

| Reaction | our study ΔH° | Yasuda+(2012) study ΔH° |
|----------|---------------|-------------------------|
| R1 | -807.8 (-821.1) | -804.5 (-816.9) | -751.5 | -751.0 |
| R2 | -572.6 (-605.0) | -566.9 (-623.0) | -518.8 | -514.5 |
| R3 | 15.1 (9.7) | 19.57 (15.1) | 77.0 | 78.1 |
| R4 | 250.3 (225.7) | 257.2 (209.0) | 309.7 | 314.7 |
| R5 | -187.1 (-134.6) | -183.2 (-133.9) | -110.8 | -109.8 |
| R10 | 48.2 (81.5) | 54.4 (55.0) | 121.9 | 126.7 |
| R11 | 235.3 (216.1) | 237.6 (183.9) | 232.7 | 236.5 |

Further listed reactions in Yasuda & Kozasa (2012) could not be compared, as we have not investigated the species SiC₃, SiC₄, SiC₅, SiC₆, SiC₇, SiC₂, SiC₃, SiC₄ and SiC₅. The reason for the systematic offset may arise due to the use of different functions / basis sets in Deng et al. (2008) (M11/cc-pVTZ and B3LYP/cc-pVTZ vs. B3PW91/6-31G(d)), other ground state clusters and by the use of combined thermo-chemistry databases.
Another point that we aim to address is the cluster physics. Therefore, we compare our results to studies of SiO - representing a counterpart to SiC in oxygen-rich environments - and TiC, another metallic carbide.

Silicon oxide (SiO) is a key ingredient for the formation of the astronomically relevant and abundant silicates of pyroxene and olivine. Under circumstellar conditions, homogeneous SiO nucleation is limited by considerably large energy barriers of the order ~ 1 eV (Goumans & Bromley 2012; Bromley et al. 2016). Moreover, the (SiO)ₙ global minimum structures show segregations in the form of Si-Si bonds for sizes n > 5. In contrast to silicon oxide clusters, (SiO)ₙ, the most energetically favourable SiC clusters tend to have alternating Si-C bonds for sizes larger than 12 units and exhibit segregations for sizes n < 12. We thus observe opposing trends in the degree of segregation versus size for SiO and SiC clusters. Furthermore, homogeneous SiC nucleation is feasible in circumstellar environments and may occur even at elevated temperatures (T=2000K). Titium carbide (TiC) is found in the centers of pristine meteoric grains and laboratory measurements of small-sized TiC nano-crystals show a prominent spectral feature around 21 μm (von Helden et al. 2000). However, Chigai et al. (2003) demonstrated that TiC grains are improbable carriers of the observed infrared 21 μm feature around carbon-rich post-AGB stars. Recent investigations of small TiCₙ (n=6,12) clusters have shown that the lowest energy structures possess a cubic geometry with alternating Ti-C bondings (Lamiel-Garcia et al. 2014). Isomers deviating form pure alternating bonds (i.e. exhibiting C-C bonds) have potential energies slightly above the cubic forms. We thus conclude that segregation plays a negligible (or minor) role in homogeneous TiC nucleation and that the transition to the crystalline bulk material takes place at comparable small sizes.

5. SUMMARY

We have found energetically favourable clusters for (SiC)ₙ up to a size of n=16. The results are used to predict the viability of nucleation and the reaction probability in SiC cluster chemistry. Our findings show that SiC dust formation is viable in the dense cooling atmospheric gas layers by addition of single SiC gas phase molecules (homogeneous nucleation). The nucleation pathway includes waiting points, where the SiC addition may be energetically unfavourable. Nevertheless, nucleation owing to changes in gas conditions (e.g. shocks, radiation) is not unlikely. The 11.3 μm feature represents an emission which is uniquely attributable to SiC dust grains in the near infrared regime. There is a number of clusters showing emission around this feature. However, their overall intensities are rather low. We thus conclude that the major contribution to 11.3 μm emission arises from bulk SiC material. The rate enthalpies confirm qualitatively well with a previous study (Yasuda & Kozasa 2012), albeit the data derived by our study is systematically lower by ~ 3-77 (16-86) kJ/mol.

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