Dynamical Identification of a Threshold Instability in Si-Doped Heterofullerenes

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We rationalize the origins of a threshold instability and the mechanism of finite temperature fragmentation in highly Si-doped $C_{60-m}Si_m$ heterofullerenes via a first-principles approach. Cage disruption is driven by enhanced fluctuations of the most internal Si atoms. These are located within fully segregated Si regions neighboring the C-populated part of the cage. The predominance of inner Si atoms over those involved in Si-C bonds marks the transition from thermally stable to unstable $C_{60-m}Si_m$ systems at $m = 20$.

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Modifying the behavior of fullerenes via the introduction of dopant atoms allows us to tailor structural and bonding properties as a function of the impurity identity and content [1–7]. In substitutional doping, the main goal is to alter the electron distribution of the cage, thereby increasing its chemical reactivity. By selecting silicon (less electronegative than carbon) to create heterofullerenes one has to reconcile two opposite tendencies. On the one hand, it appears feasible to replace carbon by an element with the same number of valence electrons and very close to it in the periodic table. On the other hand, bonding of silicon is limited to the sp^3 single bond form, which contrasts with the chemical nature of carbon, capable of interacting via single, double and triple bonds with itself and other atoms.

Mass spectroscopy experiments gave clear evidence on the existence of stable Si-doped fullerenes with at least three Si atoms [8–12]. Less conclusive is the estimate of the largest number m of Si atoms which can replace C atoms in the network without causing its breakdown. A value lying in between $m = 7$ and $m = 12$ was extracted on the basis of combined mass spectroscopy and photofragmentation data, with $m = 12$ taken as the upper limit [13,14]. To advance toward the definition of an upper limit for Si-C replacements, a recent set of geometry optimizations within density functional theory (DFT) has proved beneficial. These calculations have unambiguously assessed the structural stability (at $T = 0$ K) of highly doped $C_{60-m}Si_m$ heterofullerenes, namely $C_{40}Si_{20}$, $C_{36}Si_{24}$ and $C_{30}Si_{30}$ [15,16]. An extended isomer search has shown that the most stable configurations are those in which the Si atoms are spatially separated from the C atoms, the two species forming two distinct homogeneous subnetworks. The resulting distorted cage structures feature the typical conjugated pattern of C-C bonds, while Si atoms cap the fullerene in a protruding fashion. Despite these advances, precise understanding of stability in Si-doped fullerenes requires the account of thermal motion. This allows us to address two key issues, (a) the determination of a threshold value m for the number of Si-C replacements and (b) the mechanism by which the doped cage becomes unstable with increasing m. In this Letter these goals are achieved by employing first-principles molecular dynamics within the DFT approach. We find that a dynamical instability is triggered by the innermost Si atoms within the Si-populated part of the cage. Accordingly, the increase in the number of Si atoms not involved in Si-C interactions (the ''inner atoms'') provides a threshold criterion for the occurrence of instability for high m.

Calculations are performed within DFT by using the framework of the first-principles molecular dynamics (FPMD) approach [17,18]. Generalized gradient approximations after Becke (B) [19] for the exchange energy and Lee, Yang and Parr (LYP) [20] for the correlation energy are employed. The core-valence interaction is described by norm-conserving pseudopotentials of the Troullier-Martins type [21]. Periodic boundary conditions are used with a face-centered cubic cell of edge of 21.17 Å, large enough to minimize interactions with periodically repeated images. Wave functions are expanded in plane waves with an energy cutoff of 40 Ry at the Γ point. For FPMD calculations, we took a fictitious mass for the electronic degrees of freedom $\mu = 300$ a.u. and a timestep $\Delta t = 3$ a.u.. Temperatures are increased every 4 ps beginning from $T = 1000$ K up to $T = 1500$ K, $T = 2000$ K, $T = 3000$ K, $T = 4000$ K, and $T = 5000$ K for a total temporal trajectory covering 24 ps. Temperature control is implemented via the Nose-Hoover thermostat [22,23]. To insure Born-Oppenheimer adiabaticity, the same approach has been used for the fictitious electronic degrees of freedom at the highest temperatures [24]. We recall that the dynamics of Si-doped heterofullerenes, limited to m not larger than 12, has been the object of recent molecular dynamics studies [25–28].

Representative optimized isomers for $C_{36}Si_{24}$ and $C_{30}Si_{30}$ are shown in Fig. 1 and are considered hereafter. For $C_{30}Si_{30}$ the three lowest energy structures are found within 0.01 eV/at and share similar morphologies [16]. Our notion of stability is inclusive of a vibrational analysis, carried out via the finite difference method implemented in the CPMD code. Accordingly, isomers featuring imaginary

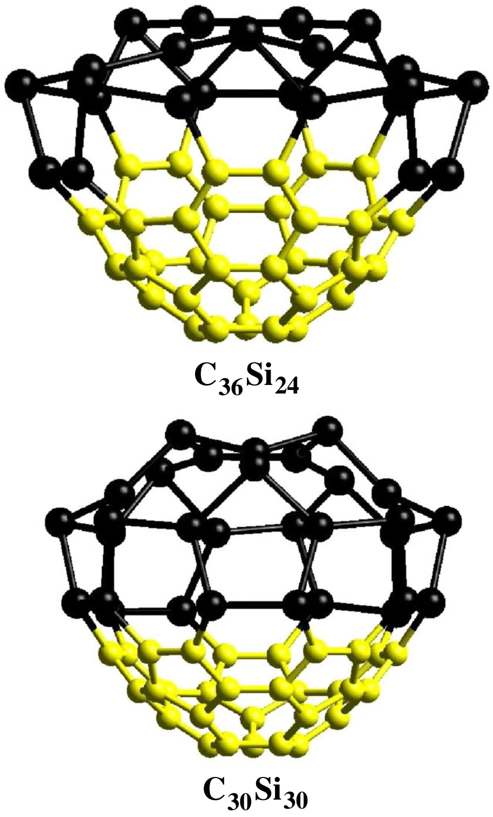

FIG. 1 (color online). Representative isomers of $C_{36}Si_{24}$ and $C_{30}Si_{30}$. Silicon atoms reside in the upper part of the cage. Interatomic and bond distances can be found in Ref. [15] and in Ref. [16].

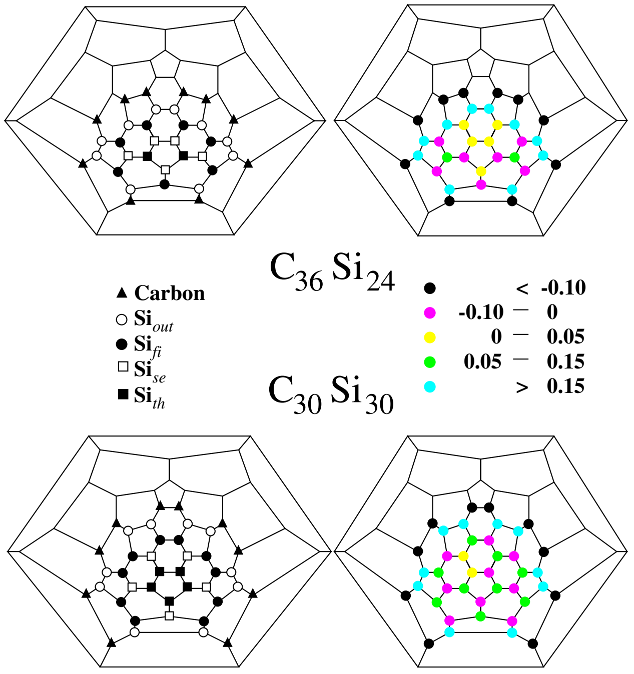

FIG. 2 (color online). A flattened view of $C_{36}Si_{24}$ and $C_{30}Si_{30}$. On the left, the symbols refer to the C atoms (first neighbors of Si atoms) and to the Si atoms. These are labeled as Si_{out} (first neighbors of C atoms) and Si_{fi}, Si_{se}, and Si_{th} (first, second, and third neighbors of Si_{out} atoms, respectively). On the right, the shading (color online) codes correspond to values of the Mulliken charge for the above C and Si atoms.

frequencies have been discarded. A detailed description of our search of equilibrium minima for $C_{60-m}Si_m$, together with essential structural data at $T = 0$ K are available elsewhere [15,27,29]. In particular, two and three dimensional views of $C_{40}Si_{20}$ isomers are provided in Ref. [15]. It is worth stressing that the binding energy is systematically increased (most stable isomers) by the separation of C and Si in two distinct networks. Moreover, any distribution of Si atoms in two or more disjointed Si regions results in a binding energy decrease of several eV. The shape of the clusters reflects the different nature of bonding in C and Si. Carbon is able to accommodate three neighbors in a sp^2 fashion, while silicon concurs to widen its portion of the cage and form Si-Si-Si triads with an average angle 109.5°, the tetrahedral value for sp^3 bonding. This is consistent with the ultimate structural evolution accompanying $C_{60-m}Si_m$ heterofullerenes when m approaches 60: the Si_{60} hollow configuration relaxes into a "puckered ball" [30–32]. A classification of Si atoms in terms of their belonging or not to the frontier with C (outer Si atoms, Si_{out} vs inner Si atoms Si_{in}) is highlighted in the flattened view of $C_{36}Si_{24}$ and $C_{30}Si_{30}$ (Fig. 2). Inner atoms can be further labeled as first (Si_{fi} hereafter), second (Si_{se}), or third (Si_{th}) neighbors of outer Si atoms. The outer Si atoms bear a substantial positive charge (0.27 average value), corresponding to highly Coulombic Si-C bonds. This interaction stabilizes the Si-C interface by compensating the unfavorable sp^2 environment of the Si atoms involved. Moving inside the Si regions, charges are considerably reduced, taking alternate signs in most sixfold rings, as an attempt to reduce repulsive effects. The latter stem from a small and yet residual positive net charge associated to the whole set of Si_{in} atoms.

Figure 3 shows the time fluctuations with respect to the initial atomic positions for the Si_{out} and the set of Si_{in} atoms in $C_{36}Si_{24}$ and $C_{30}Si_{30}$. Nearest-neighbor carbon atoms are also included. In $C_{36}Si_{24}$, fluctuations are comparable and quite limited for C, Si_{in}, and Si_{out} atoms, with the notable exception of Si_{th} neighbors, definitely more mobile. In particular, the increase of temperature to $T = 4000$ K leads to marked outward movements of the two Si_{th} atoms over the time interval 16–21 ps. This strong rearrangement allows for heat dissipation, preserving the close nature of the fullerene, at least on the time scale spanned by the simulation. These first indications of an incoming dynamical instability are confirmed by the drastic change observed at about 15 ps in the case of $C_{30}Si_{30}$. A rapid increase is noticeable, at $t \sim 15$ ps, first for Si_{th} atoms and then for all the other Si_{in} atoms, proving that the seed of thermal instability of the cage has to be localized in the innermost Si region. Note that Si_{out} and C atoms depart from their position only after irreversible diffusion

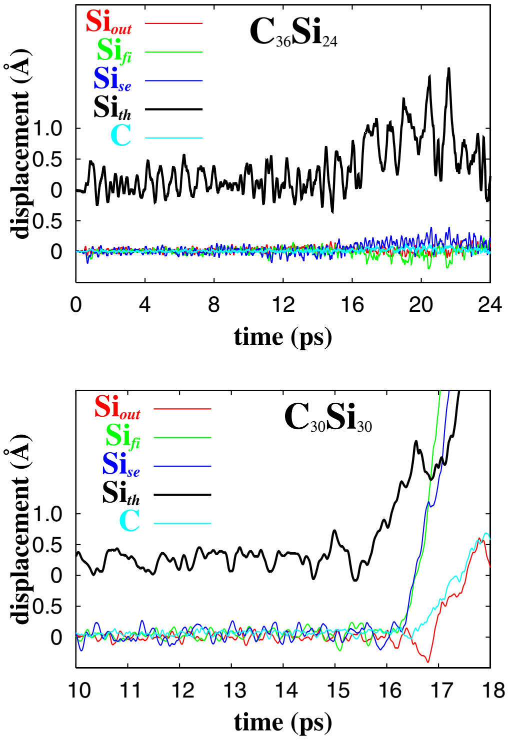

FIG. 3 (color online). Temporal evolution of the coordinates of relevant C and Si atoms for $C_{36}Si_{24}$ and $C_{30}Si_{30}$. The values are calculated with respect to the $t = 0$ positions and, in the case of the Si_{th} atoms, moved up on the y axis by 1 Å for clarity. Note that for $C_{30}Si_{30}$ the displacements along the first 10 ps are not shown to allow a better focus on the behavior during fragmentation.

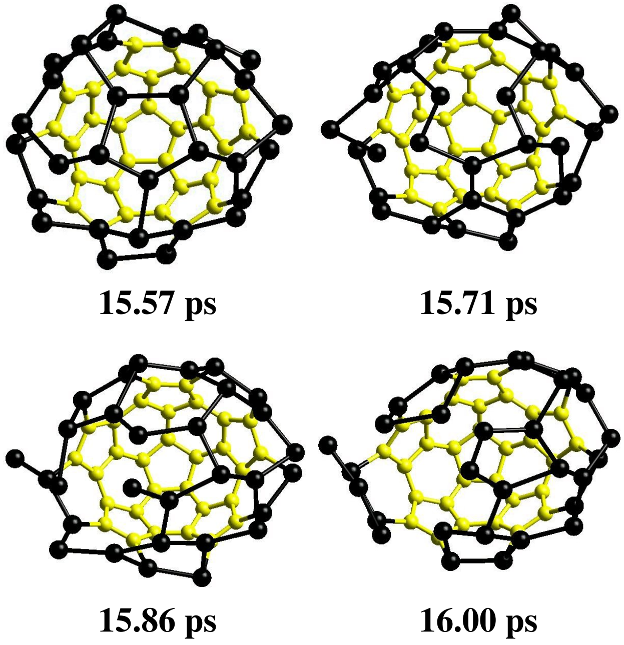

FIG. 4 (color online). Snapshot of the dynamical evolution of $C_{30}Si_{30}$ during the first stages of fragmentation at $T = 3000$ K.

of Si_{in} atoms has taken place. Cage breaking is recorded at $T = 3000$ K and proceeds along the mechanism visualized in Fig. 4, where the structure opens due to elongation of the Si_{in}-Si_{in} distances.

Our pieces of evidence allow the establishment of a sound relationship between doping content and stability. Positive charges on the Si_{out} atoms are common to all $C_{60-m}Si_m$ systems for increasing m, due to charge transfer toward the neighboring C atoms. Therefore, the propensity of Si_{out} atoms to stand an atypical sp^2 environment does not change with increased doping, being sustained by the polar Si-C interaction. Indeed, moving from $C_{40}Si_{20}$ to $C_{36}Si_{24}$ and eventually to $C_{30}Si_{30}$, the number of Si_{out} does not exceed 12 throughout all relevant isomers (10 in the isomers of Figs. 1 and 2). Given these premises, it appears that structural instability is due to the increased number of Si_{in} atoms. There are as many Si_{in} as Si_{out} atoms in $C_{40}Si_{20}$ (10) but the former become more numerous in $C_{36}Si_{24}$. In the absence of thermal motion, the overall repulsion among Si_{in} atoms results in structural distortions at the very origin of the protruding shape for the Si-made cap of the heterofullerene. Calculations of vibrational frequencies confirm that these fullerenes are stable against disruption for small displacements from the equilibrium positions. By squeezing and then stretching the Si-Si distances, temperature induces even stronger repulsive interaction among pairs of Si_{in} atoms, by causing fragmentation of the cage. This rationale shows that $C_{40}Si_{20}$, in which the number of Si_{in} atoms equals that of Si_{out} (10), stands out as the best candidate for the upper limit of structural stability in $C_{60-m}Si_m$. Any other structure with a higher Si_{in}/Si_{out} ratio is inevitably weakened by energetically unfavorable Si_{in}-Si_{in} sp^2 interactions. This argument is fully consistent with our FPMD simulations, where fragmentation becomes apparent only for $m > 20$ due to the length of our temporal trajectories.

In weakly doped Si-heterofullerenes the localization of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states on the dopant atoms exemplifies their nature of highly reactive sites [5]. Visual inspection of Kohn-Sham orbitals for the optimized $C_{30}Si_{30}$ at $T = 0$ K allows to associate the HOMO mainly to a Si_{out} atom and to a C atom at the Si-C border. The LUMO state is found on one of the five Si_{th} inner atoms (Fig. 5, top). We have selected, at the beginning of the fragmentation process of $C_{30}Si_{30}$, a configuration at $T = 3000$ K by fully relaxing the electronic degrees of freedom to the ground state. Both the HOMO and the LUMO are now localized on Si_{in} atoms (Fig. 5, bottom). This feature goes along with a substantial reduction of the gap (0.53 eV at $T = 0$ K, 0.09 eV at $T = 3000$ K). Accordingly, temperature effects induce enhanced reactivity of the inner Si atoms, leading to a radical configurational change.

We have shown that highly Si-doped $C_{60-m}Si_m$ heterofullerenes are thermally stable as long as Si atoms neighbors of C atoms in segregated regions are predominant over inner Si atoms. Due to its polar character, the Si-C inter-

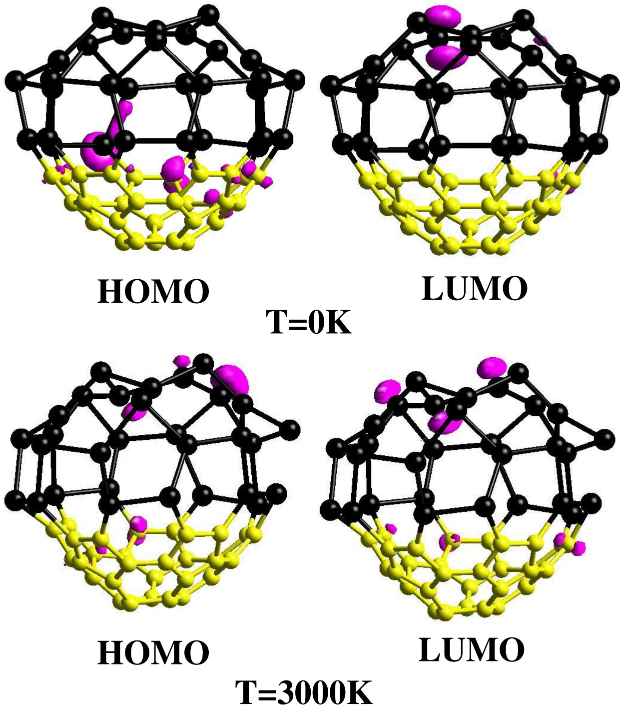

FIG. 5 (color online). Probability isodensity surfaces associated with the HOMO and the LUMO levels $[0.005e/(\text{a.u.})^3]$ of $C_{30}Si_{30}$ at $T = 0$ K and at $T = 3000$ K, shortly before fragmentation occurs.

action is able to stabilize the cage and offsets the energetic cost of sp^2 interaction for $m < 20$. Beyond this threshold, repulsive interaction among inner Si atoms cause fragmentation. HOMO localization on the inner Si atoms is the chemical bonding fingerprint of this behavior. Our results are intended to stimulate renewed experimental effort in the search of novel synthesis approaches to produce highly doped heterofullerenes.

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