Synthesis and Structure of Silicon-doped Heterofullerenes

C. Ray, M. Pellarin, J. L. Lermé, J. L. Vialle, and M. Broyer
Laboratoire de Spectrométrie Ionique et Moléculaire (UMR C.N.R.S. 5579), Université Claude Bernard-Lyon 1, Bâtiment 205,
43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cédex, France

X. Blase, P. Mélinon, P. Kéghélian, and A. Perez
Département de Physique des Matériaux (UMR C.N.R.S. 5586), Université Claude Bernard-Lyon 1, Bâtiment 203,
43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cédex, France
(Received 9 January 1998)

We report on the synthesis of $C_{2n-q}Si_q$ clusters with $2n = 32 - 100$ and $q < 4$. The analysis of the abundance distribution and photofragmentation spectra provides clear evidences that such clusters remain in the fullerene geometry and that the Si atoms are located close to each other in the fullerene network. These results are corroborated by *ab initio* calculations within the density functional theory. The stability and electronic properties of these heterofullerenes are discussed. [S0031-9007(98)06351-0]

PACS numbers: 61.48.+c, 36.40.Qv, 71.20.−b

Since the discovery of C_{60} [1,2] in 1985, considerable effort has been devoted to understanding the properties of this new molecule. Much of the incentive lies in the hope that new materials with novel properties may be synthesized with C_{60} as the building unit. For example, exohedrally and/or endohedrally doped fullerenes [3] have been produced and studied, leading in the first case to the well known superconductivity of fullerides. Another approach to creating novel fullerene-related materials consists in modifying the "functionality" of C_{60} itself by substitutional doping of carbon [4]. In particular, the synthesis of $C_{59}Si$ heterofullerenes has been recently reported [5,6]. This is a quite surprising result since silicon is known to strongly prefer sp^3-like bonding. SiC fullerenes are therefore expected to be very reactive at their Si sites, offering a path towards the polymerization of fullerenes. Further, the possibility of growing nanostructured films by low energy deposition of clusters [7] suggests that novel phases of the technologically important family of SiC compounds may be obtained. The expected transition from the fullerene to the cubic structure with increasing Si doping [8,9] offers a means to tailor the structural and electronic properties of these novel SiC compounds by tuning the Si to C ratio.

In this Letter, we report on the synthesis of silicon-doped heterofullerenes in the carbon-rich limit. SiC mixed clusters are generated in a standard laser vaporization source from rod-shaped targets of a well-defined Si:C composition [10]. The plasma produced by a Nd:YAG laser (532 nm, 10 Hz) is quenched with a high pressure helium burst in order to induce the SiC cluster growth and ejection from the source. Their average stoichiometry is then directly proportional to the target composition. The abundance distribution of clusters directly produced as ions is analyzed in a reflectron time-of-flight mass spectrometer [11]. The reflectron geometry is also suitable for the study of the photofragmentation (by an XeCl excimer laser [12]) of size selected clusters.

A first evidence for the stability of silicon doped heterofullerenes $C_{2n-q}Si_q^+$ ($2n > 32$ and $q = 1, 2$) can be found in the mass spectra of carbon rich mixed clusters cations with a target containing typically 5% of silicon [6,10]. The size abundances of pure carbon fullerenes C_{2n}^+ are exactly mirrored [10] by those of the $C_{2n-1}Si^+$ and $C_{2n-2}Si_2^+$ doped species with, in particular, common enhanced stabilities for the same total even number of atoms: $2n = 44$, 50, or 60. Besides these main peaks, all clusters are detected each eight atomic mass units (a.m.u.). This periodicity indicates that clusters with an odd number of atoms are nearly absent whatever the number of silicon atoms they may contain. This behavior and its slight dependence with cluster source settings is usually considered as the signature of the fullerene geometry [1].

Additional information can be obtained from photofragmentation spectra of size-selected heterofullerenes as shown in Fig. 1. Three different sizes are selected and photoexcited. The time-of-flight spectra are drawn on a mass scale indicating the size of the surviving ionic products. Nonevaporated parents are located on the right side of each spectrum. They are enlarged by isotopic distribution effects. The C_{68}^+ evaporation pattern consists of sequential losses of the C_2 neutral molecules which is a well-known feature of the fullerene [13,14]. The same behavior is observed for $C_{69}Si^+$ and $C_{68}Si_2^+$, except that the first evaporated dimers are those containing Si atoms: respectively, SiC and Si_2. Just after the complete elimination of silicon (producing C_{68}^+ in both cases) the continuing evaporative processes are "fullerenelike" with a fragment size distribution very similar to what is observed on native C_{68}^+. This strongly confirms the idea that these clusters are presently grown in the fullerene geometry.

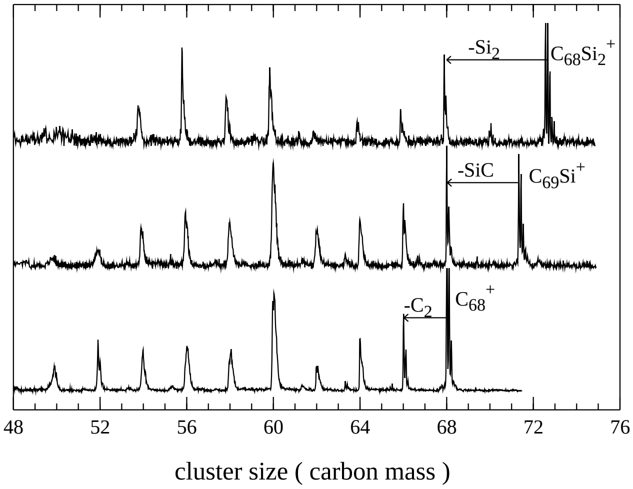

FIG. 1. Photofragmentation mass spectra of C_{68}^+, $C_{69}Si^+$, and $C_{68}Si_2^+$ selected clusters. The horizontal scale gives the size of the products in an equivalent number of C atoms. The first evaporation process is precised for each cluster size.

The next interesting stage is to check the possibility of substituting more than two silicon atoms in a stable cage structure. The equality in mass of both $C_nSi_m^+$ and $C_{n\pm 7p}Si_{m\mp 3p}^+$ (p integer) classes of isomers hinders the straightforward identification of $C_{2n-q}Si_q$ ($q \geq 3$) clusters in the mass spectra analysis. Nevertheless, the stability of more siliconized fullerenes such as $C_{2n-3}Si_3^+$ can be checked from the analysis of the photofragmentation spectra. The small extra peaks detected in Fig. 2a (marked by triangles) are indeed related to Si-doped fragments. In particular, the peak corresponding to label *A* in Fig.2b is the signature of Si_2 evaporation and indicates that $C_{59}Si_3^+$ or even more Si-rich clusters have been selected together with C_{66}^+ fullerenes. Upon lowering of the laser intensity, this peak *A* is strongly enhanced while the peaks originating from the sequential C_2 evaporations are nearly wiped out (see Fig. 2b). Correspondingly, the peak labeled B in Fig. 2b must originate mainly from the loss of Si_3C rather than C_8 fragments, as in Fig. 2a. This suggests that silicon rich clusters as $C_{59}Si_3^+$ are less stable than C_{66}^+ fullerenes and, possibly, have a higher photoabsorption cross section.

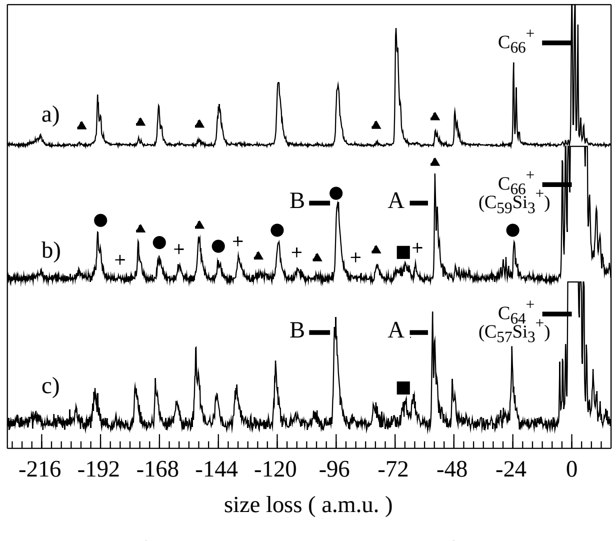

FIG. 2. Photofragmentation mass spectra of selected clusters having the C_{66}^+ mass at high (a) and low (b) laser fluence. The photofragmentation mass spectrum of C_{64}^+ at the same low fluence is given in (c). *A* and *B* indicate the global loss of Si_2 and Si_3C, respectively, and the black squares locate the Si_2C molecule evaporation. Circles, triangles, and crosses indicate fragments containing 0, 1, and 2 Si atoms.

If nonfullerene Si-rich clusters were produced and photofragmented, they would yield a large amount of Si_2C evaporation [10]. This is hardly evidenced here considering the very weak corresponding signal (black square in Figs. 2b and 2c). The photofragmentation patterns in Figs. 2b and 2c are complex but very similar even though the selected parents are different. The fragments are easily identified as heterofullerenes with 0 (circles), 1 (triangles), or even 2 (crosses) remaining silicon atoms. These fragments all have an even number of atoms and the spectra display the characteristic 8 a.m.u. periodicity of heterofullerene systems. As shown in Ref. [10], this would not have been the case with nonfullerene isomers. The complexity of the present spectra originates both from the contribution of a non-negligible amount of more Si-rich heterofullerenes as, e.g., $C_{2n-14}Si_6^+$ and from the increasing number of competing evaporation channels as the number of Si atoms increases. In this respect, the absence of SiC evaporation in Figs. 2b and 2c shows that the loss of Si_3C fragments (*B* peak) results from a direct rather than a sequential (Si_2 + SiC) process. The enhanced abundances of Si_2 (*A* peak) and Si_3C (*B* peak) evaporations is, nevertheless, consistent with the dominant yield of $C_{2n-7}Si_3^+$ species within the selected parents. From all these features, we conclude that Figs. 2b and 2c demonstrate the existence of fullerenes doped with at least three, and certainly more, Si atoms.

We note that the early ejection of siliconized dimers enlightens the dissymmetry between the involved C-C, Si-C, and Si-Si bonds. Moreover, in the case of $C_{68}Si_2^+$, the negligible weight of a sequential loss of two SiC to the benefit of a direct Si_2 evaporation is an indication that the two Si atoms are close neighbors in the heterofullerene network. This will be confirmed by the calculations detailed below. Similar conclusions can be drawn for all cluster sizes in the range studied here ($2n = 32-100$).

In order to understand the present experimental findings, and predict the electronic properties of carbon rich SiC clusters, we study within the density functional theory [15] (DFT) various isomers of $C_{2n-q}Si_q$ clusters with $2n = 28, 60$ and $q = 1, 2$. The present calculations are performed with the local density approximation [16] (LDA) and standard nonlocal pseudopotentials [17] are used for C and Si atoms. We adopt a supercell geometry in the FCC packing. Total energy differences are well converged for a typical cluster-cluster minimum distance of 7 Å. The wave functions are expanded on a plane-wave basis with kinetic energy up to 45 Ry. Since we study the carbon rich limit, we assume that the SiC clusters preserve the cage fullerenelike structure as suggested by the present experimental results. We therefore start by substituting in C_{60}, e.g., one or two C atoms by Si for various configurations and relax the atomic structure using a standard conjugate-gradient scheme [18].

We represent in Figs. 3a, 3b, and 3c the relaxed atomic geometries for, respectively, the $C_{59}Si$ cluster and two $C_{58}Si_2$ isomers with the two Si atoms neighbors (Fig. 3b) and second nearest neighbors (Fig. 3c). Besides the ortho- and meta- configurations represented in Fig. 3, we study as well a "para"-isomer as described in footnote [19]. The Si atoms are seen to "pop out" from the ideal C_{60} sphere in order for the cluster to accommodate the Si-C and Si-Si bonds [20]. We now compare the energy of the three $C_{58}Si_2$ isomers we have studied. We find the metaconfiguration to be more stable that the para one by 0.65 eV. The metaconfiguration is also more stable than the $C_{58}Si_2$-ortho configuration but the energy difference is rather small (0.15 eV). We have studied as well small $C_{26}Si_2$ clusters. We again find the metaconfiguration to be the most stable, by 0.76 and 0.26 eV, respectively, as compared to $C_{26}Si_2$-para and $C_{26}Si_2$-ortho [21]. Similar results have been obtained for $C_{25}Si_3$ clusters.

The present results strongly indicate that there exist preferred sites for the polysubstitution of C by Si. In the limit of C-rich Si doped fullerenes, Si atoms are either in a meta- or orthoconfiguration, in good agreement with the present experimental findings. We recall that in the case of the photofragmentation of C_{60}, the C_2 dimers loss has been shown to be preceded by complex multiple bond breaking and switching processes [22]. This suggests that the two atoms ejected are not necessarily neighbors in, e.g., the $C_{58}Si_2$ most stable isomer at zero temperature but are certainly close to each other due to the rather local character of these dynamical rearrangements [23].

We now study the electronic properties of the $C_{60-q}Si_q$ $(q = 1, 2)$ isomers shown in Fig. 3. The energy levels around the gap are represented in Fig. 4. In each case, the highest occupied molecular orbital (HOMO) is indicated by an arrow. For the sake of comparison, we have taken as the energy reference for each cluster the highest occupied "carbon-only" orbital [24]. The most striking result is that the energy gap between the C-HOMO and C-LUMO states is very stable from one cluster to another, and very close to the 1.68 eV gap of pure C_{60} as calculated within the same formalism. The Si-related orbitals (represented by dotted lines) can therefore be described in terms of defect levels, even though the proportion of Si to C atoms is so large that it is difficult to invoke the standard defect models in extended systems. Further, the Si orbitals in the gap are seen to be arranged as donorlike and acceptorlike levels. This can be understood from the partly ionic character of the SiC bonds.

The analysis of the Si-related orbitals provides an explanation for the relative stability of the meta-, ortho- and paraisomers. While the polarization of the SiC bonds forbids the creation of homopolar Si-Si dimers in bulk SiC, isolated Si atoms in the fullerene network are characterized by a lonely dangling bond which weakly couples to the surrounding delocalized carbon π-orbitals. The creation of Si pairs in, e.g., $C_{58}Si_2$ benefits therefore from the stabilizing hybridization between these two neighboring Si lonely orbitals. This can rationalize the greater stability of orthoisomers as compared to the paraconfigurations. We note further that the 2.79 Å for the Si-Si distance in the meta configuration of Fig. 3c is only 10 to 20% larger than typical first nearest neighbor Si-Si distances in pure Si_n clusters. The greater stability of the metaisomers indicates that such geometries offer in general the best compromise in trying to minimize the Si-Si electrostatic repulsion while still pairing the Si lonely dangling bonds.

In conclusion, we have provided experimental evidence that at least three Si atoms can be incorporated in C_{2n} carbon clusters ($2n = 32-100$) without destroying their fullerenelike structure. Further, the corresponding photofragmentation spectra show that Si atoms are close neighbors in these mixed fullerenes. These results are confirmed by *ab initio* calculations of the stability, structure and electronic properties of various $C_{2n-q}Si_q$ clusters. Si doping of fullerenes is predicted to increase their chemical reactivity, offering a path towards the polymerization of fullerenes via SiC bonds. We are

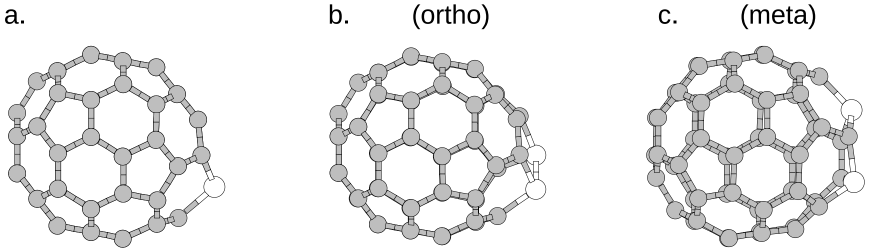

FIG. 3. Symbolic ball-and-stick representation of various $C_{60-q}Si_q$ $(q = 1, 2)$ isomers (see text). The white spheres are the Si atoms.

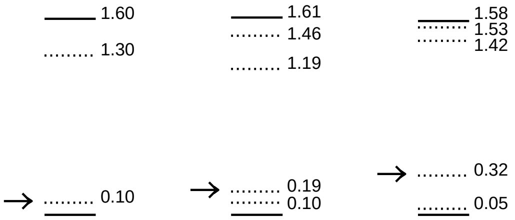

FIG. 4. Selected energy levels for (left) $C_{59}Si$, (center) $C_{58}Si_2$-ortho and (right) $C_{58}Si_2$-meta. The arrows point to the HOMO states. Full lines and doted lines indicate, respectively, the carbon- and silicon-related orbitals (see text and footnote [24]). Energies are given in eV.

presently studying the transition from fullerene to SiC bulklike clusters with increasing Si concentration.

X. B. is indebted to A. Dal Corso and S. Baroni for making available the parallelized PWSCF code used in this work (see Ref. [18]). The calculations have been performed on the Cray-T3E of the French *Commissariat à l'Energie Atomique* (CEA) in Grenoble, France.

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[2] W. A. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) **347**, 354 (1990).

[3] R. D. Johnson *et al.*, Nature (London) **355**, 239 (1992).

[4] R. Taylor and D. R. M. Walton, Nature (London) **363**, 685 (1993).

[5] J. L. Fye and M. F. Jarrold, J. Phys. Chem. A **101**, 1836 (1997).

[6] T. Kimura, T. Sugai, and H. Shinohara, Chem. Phys. Lett. **256**, 269 (1996).

[7] V. Paillard *et al.*, Phys. Rev. Lett. **71**, 4170 (1993).

[8] U. Röthlisberger, W. Andreoni, and M. Parrinello, Phys. Rev. Lett. **72**, 665 (1994).

[9] E. Kaxiras, Phys. Rev. Lett. **64**, 551 (1990).

[10] M. Pellarin *et al.*, Chem. Phys. Lett. **277**, 96 (1997).

[11] J. L. Vialle *et al.*, Rev. Sci. Instrum. **68**, 2312 (1997).

[12] S. Wei and A. W. Castleman, Jr., Int. J. Mass Spectrom. Ion Process. **131**, 233 (1994).

[13] S. C. O'Brien, J. R. Heath, R. F. Curl, and R. E. Smalley, J. Chem. Phys. **88**, 220 (1988).

[14] P. Scheier, B. Dünser, R. Wörgötter, D. Muigg, S. Matt, O. Echt, M. Foltin, and T. D. Märk, Phys. Rev. Lett. **77**, 2654 (1996).

[15] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[16] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[17] For carbon, see P. Giannozzi and S. Baroni, J. Chem. Phys. **100**, 8537 (1994); for silicon, see Ref. [8].

[18] Technical details about the formalism and algorithms can be found in A. Dal Corso, *The PWSCF Code and Some Case Studies*, in Quantum-Mechanical Ab-Initio Calculation of the Properties of Crystalline Materials, edited by C. Pisani (Springer, Heidelberg, 1996).

[19] The $C_{58}Si_2$ isomers are said to be in a para-, ortho- or metaconfiguration if the two Si atoms are located at opposite sites with respect to the C_{60} molecule, are first nearest neighbors, or second nearest neighbors, respectively. The paraconfiguration we study can be obtained by "symmetrizing" the $C_{59}Si$ cluster represented in Fig. 3a. The same notations are used for the $C_{26}Si_2$ isomers.

[20] The Si-C bond lengths are found to range from 1.75 Å to 1.84 Å, while the Si-Si bond length in Fig. 3b is equal to 2.19 Å. This can be compared to the two nonequivalent C-C bond lengths in pure C_{60} which are calculated to be 1.39 and 1.45 Å.

[21] In the case of C_{28}, there are two types of nonequivalent carbon atoms which display a very different chemical reactivity [see, e.g., A. Canning, G. Galli, and J. Kim, Phys. Rev. Lett. **78**, 4442 (1997)]. However, we have calculated the energy difference between the two possible $C_{27}Si$ isomers to be smaller than 0.1 eV.

[22] C. Xu and G. E. Scuseria, Phys. Rev. Lett. **72**, 669 (1994).

[23] We note that these results contrast significantly with those of previous semiempirical calculations performed at the AM1 level which predict that $C_{58}Si_2$ meta- and paraconfigurations have the same energy and are more stable than the orthoisomer. Such results would not allow one to understand the preferential evaporation of Si_2 dimers. See D. A. Jelski *et al.*, J. Cluster Sci. **4**, 173 (1993).

[24] The carbon-related orbitals (noted C-MO) and the Si-related orbitals (noted Si-MO) are easily recognizable if we plot the corresponding charge density distribution. In particular, the highest carbon-related occupied state (C-HOMO) and the lowest carbon-related unoccupied state (C-LUMO), represented by full lines in Fig. 4, hardly show any weight on the Si atoms. On the contrary, the Si-MO orbitals are seen to be bonding or antibonding states localized in Si-C or Si-Si bonds depending on the isomer.