Molecular dynamics study of the fragmentation of silicon doped fullerenes

Chu-Chun Fu*, Javier Fava, Ruben Weht, M. Weissmann
Departamento de Física, Comisión Nacional de Energía Atómica,
Avda. del Libertador 8250, 1429 Buenos Aires, Argentina

Tight binding molecular dynamics simulations, with a non orthogonal basis set, are performed to
study the fragmentation of carbon fullerenes doped with up to six silicon atoms. Both substitutional
and adsorbed cases are considered. The fragmentation process is simulated starting from the equi-
librium configuration in each case and imposing a high initial temperature to the atoms. Kinetic
energy quickly converts into potential energy, so that the system oscillates for some picoseconds and
eventually breaks up. The most probable first event for substituted fullerenes is the ejection of a C2
molecule, another very frequent event being that one Si atom goes to an adsorbed position. Ad-
sorbed Si clusters tend to desorb as a whole when they have four or more atoms, while the smaller
ones tend to dissociate and sometimes interchange positions with the C atoms. These results are
compared with experimental information from mass abundance spectroscopy and the products of
photofragmentation.

I. INTRODUCTION

Since the discovery of C60 in 1985 \(^1\) and the following
large scale synthesis of fullerenes, considerable effort has
been devoted to use these molecules as building blocks
for novel and more interesting materials. One of the
most important attempts is to try to change their elec-
tronic and mechanical properties through doping. In re-
cent years exohedrally and endohedrally doped fullerenes
have been produced, with a variety of doping atoms and
even small molecules. In the exohedral case, the for-
ever atoms (or groups of atoms) are outside, attached
to the fullerene, as in the case of the superconducting
fullerides. In the endohedral case the molecule encloses
the strange element, isolating it from the outside. Many
possible applications, specially in medicine, have been
envisaged using these new systems. A third approach
to create fullerene-related compounds is to modify the
fullerene itself through substitutional doping. This is
expected to be easier if the dopant atom has a similar
electronic configuration to that of carbon, but has been
successfully performed with several elements, such as B,
N, O and some transition metal atoms as Fe, Co, Ni,
Rh and Ir. At first glance, substitutional doping with
silicon should be also easy due to the similar electronic
configuration of carbon and silicon. However, both atoms
should be able to form different kinds of bonding. While carbon can
form \(sp^1\), \(sp^2\), and \(sp^3\) bonds, silicon strongly prefers the
\(sp^3\) configuration, making silicon clusters to be generally
in a three dimensional arrangement. Silicon doped and
silicon coated fullerenes have been produced only very
recently \(^2\), \(^3\), \(^4\) starting either from an initially doped
carbon-based material or from precursor pure carbon
fullerenes interacting with a vapor of the doping element.
Both mass abundance spectroscopy and the analysis of the
photofragmentation products of selected species show
clearly that several carbon atoms can be substituted in
the cage structure and also that silicon clusters can be
adsorbed on its surface.

From the theoretical side, some semiempirical \(^5\) and ab-
initio calculations \(^6\), \(^7\), \(^8\) have been performed to study
the structure, stability and electronic properties of these
new molecules. Up to now the main way to infer the
structure of the doped systems is through the study of
their fragmentation and the analysis of the residual clus-
ters with different compositions. For this reason, in the
present work we attempt to model those fragmentation
processes, using molecular dynamics simulations within
a density functional based tight-binding model \(^9\). This
seems to be an adequate choice, as it takes into account
the bonding characteristics of the two elements, carbon
and silicon, being less time consuming than full ab-initio
simulations.

This paper is organized as follows: In section II we
present the method used in the calculations, putting spe-
cial emphasis on the different approximations used. In
section III we analyze the results, first for substitutional
doping and then for coated fullerenes. Finally in section
IV are our conclusions and comments.

II. METHOD OF CALCULATION

Along this work we use a density functional based non
orthogonal tight binding hamiltonian, that was devel-
oped and tried for different systems containing carbon
and silicon atoms \(^10\), \(^11\).

In this method the hamiltonian and overlap matrix el-
ements were obtained from pseudo-atomic orbitals as a
function of distance, in a parameter free way. In this
sense it seems more satisfactory than the orthogonal
tight-binding parametrization we previously developed
for mixed systems \(^12\). Although only a minimal basis set
is used, the method has been proved to be transferable,
giving good results for clusters, surfaces and solids \(^12\). It
gives also a good description of some non-trivial low di-
ensional systems, for example the reconstructed Si
and \(\beta\)-SiC surfaces \(^13\), which is an indication that a rea-
nsonable description of the fullerenes when bonds break
up should be obtained.

The method uses only two center integrals and the to-
tal energy is written as the sum of a band-structure term and a repulsive term, this last one being parametrized also with experimental information. When performing the dynamical simulations at finite temperatures or obtaining the relaxed equilibrium structures, the atoms are moved according to the Hellmann-Feynmann forces and the equations of motion are integrated using Verlet’s algorithm.

The approach used here does not consider charge self-consistency to avoid unreasonably large simulation times and the introduction of a new set of parameters (a Hubbard type U and a Madelung correction). The effect of this approximation is that charge transfers may be rather large and the fragments carry incorrect amount of net charges. Semiempirical methods, like this one, should be used instead of an ab-initio calculation when this one makes the simulation too lengthy.

It is worth mentioning that experiments are performed on single positively charged clusters, however the fragmentation of non-doped fullerenes, the successive emission of $C_2$ molecules is correctly described by simulations with neutral molecules. For this reason we have used the same approximation in this case. Nevertheless, we have also proved with a few examples that there is no statistical difference when using positive ions instead of neutral fullerenes if the same parameters are used. Our previous ab-initio calculations also show that even in the case of Si substituted ions, where the original fullerene cage is far more strongly perturbed than in the adsorbed case, we do not find very different geometries or energy gaps. We therefore do not expect the fragmentation results to differ in any important way between the neutral molecules and the positive ions, in both substitutional and coated cases.

Before starting the simulations we checked that the structure, stability and electronic properties of the substituted fullerenes, that we studied previously with an ab-initio procedure, are correctly reproduced. In fact, the substituted fullerenes are also stable in this case and the energy ordering of the different isomers containing 2, 3 and 6 carbon atoms substituted by silicon atoms is well reproduced, giving energy differences of the same order of magnitude. The energy differences obtained by the tight-binding method are not consistently higher or lower than the corresponding ab-initio ones. The two characteristic $C-C$ bond lengths in the fullerene cage are maintained in the relaxed substituted molecules and the lowest energy, when more than two silicon atoms are in the cage, is when they are nearest neighbors, so as to reduce the number of $Si-C$ bonds. As in the ab-initio calculations, sometimes lower energy configurations present some weak bonds that could indicate the possible fragmentation paths. In the case of adsorbed silicon atoms, they form weakly bound clusters of silicon atoms on the surface of the fullerene molecule, with silicon atoms locating preferentially in front of a hh (hexagon-hexagon) $C-C$ bonds and close to each other for cases with more than two adsorbed silicon atoms.

With respect to the electronic properties the tight-binding calculations give very similar values for the band-gaps but, as expected for a non self-consistent calculation, the charge transfers between different atoms are rather large, about double those of the ab-initio calculations, and the bond orders somewhat smaller.

To simulate the fragmentation process we start from a relaxed molecule at 0 K and attribute a random velocity to each atom, with a maxwellian distribution corresponding to a high temperature. It assumes a very fast energy interchange between electronic and ionic degrees of freedom. This high initial ionic temperature approximation has been used previously to simulate the excitation produced by a femtosecond laser pulse. In these experiments, after being photoexcited the molecules do not collide before dissociation, so that it is quite reasonable to assume energy conservation during the fragmentation process. For pure fullerenes a kinetic energy corresponding to an initial temperature of about 12000 K was needed to produce the first breakup, that is, the first emission of a $C_2$ molecule, in a reasonable simulation time of tens of picoseconds. This time is of course much smaller than the experimental time of flight, but the experimental facts are correctly reproduced and the energies involved in reasonable agreement. The occupation of the electronic energy levels is time dependent, in each simulation step it corresponds to the Fermi function of the corresponding instantaneous ionic temperature. However, due to the large energy gap of the fullerene molecule, this only allows for a small amount of electronic excitation to the antibonding states. The microcanonical molecular dynamics interchanges kinetic and potential energy so that after a few time steps the system equilibrates at about 3000 K in the silicon substituted cases and it vibrates for some picoseconds before breaking up, the initial energy converts quickly into molecular vibrations.

Substituted fullerenes need lower initial temperatures to break up, and coated ones even lower, but the contribution of excited states is always quite small, especially once the systems achieve a stable temperature of 3000K or less. According to our previous ab-initio calculations and also to the present tight binding ones the Si doped fullerenes do not have a much smaller energy gap than the unsubstituted molecule. For example it is 1.32 eV for $C_{59}Si$ and around 1 eV for the different isomers of $C_{57}Si_3$.

Each simulation run in this work lasted between 20 and 30 ps, the time step being either 0.5 fs or 1 fs. This assures a reasonable energy conservation for the whole simulation. Due to the random nature of the initial conditions, several examples were performed for each type of molecule and each initial temperature.
III. RESULTS

A. Substituted Fullerenes

The tight binding approximation is only valid when the leaving fragment is at a smaller distance than the cut off from the remaining molecule. We therefore report here only the first event observed in each simulation run, and attribute significance to the results up to that fragmentation instant. Once the system separates into fragments, they do not interact with each other and therefore the tight-binding wavefunction does not make sense.

After the high initial temperature is applied, between 6000 and 9000 K, the system achieves in less than one picosecond a temperature of around 3000 K due to the fast interconversion between kinetic and potential energy.

When more than one silicon atom is present, the results may differ for the different isomers. In some cases it is particularly easy for one silicon atom to become adsorbed outside of the carbon cage, in others it is not.

The dynamics of three different isomers is studied for two substituted atoms, two different isomers in the case of three substitutions and only the lowest energy isomer is studied in the case of six substitutions. Table 1 shows the results from all the simulations, totalling about 3300 ps, and the following general features can be observed:

1) The most frequent first event is the ejection of a $C_2$ molecule, usually located near a silicon atom. The first bond to break is one between a $Si$ and a $C$ atom, which left an open chain of carbon atoms from which $C_2$ is removed. The $Si$ atom rebonds quickly, as it strongly prefers tetrahedral coordination, while the carbon atoms are quite comfortable in the chain structure $sp^1$ (see Fig. 1).

2) Another very frequent first event is that a $Si$ substituted atom moves to an adsorbed position, from which it orbits around the fullerene cage. This adsorbed atom easily leaves the molecule, alone. (see Fig. 2)

3) Odd numbered molecules, for example those that remain after one $Si$ atom leaves, seem to be as stable as even numbered ones within our simulation time, although the calculated binding energy is smaller for the odd molecules. However, the surviving ionic products in the mass spectra show very few molecules with an odd number of atoms.

4) Small clusters containing both $Si$ and $C$ atoms are ejected in a few cases but again there is no significative preference for even numbers.

FIG. 1: Selected instantaneous intermediate structures, leading to the fragmentation of $C_{59}Si$

FIG. 2: Same as Fig. 1, for one of the observed paths leading to the fragmentation of $C_{59}Si_3$
TABLE I: First events observed in the fragmentation of Si substituted fullerenes. The maximum simulation time is 30 ps for each run and between 10 and 20 simulations were run for each system. The more stable isomers are indicated with an asterisk, and *nn* indicates that the Si atoms are nearest neighbors.

| System | Initial Temp. | Freq. | Event description |
|--------|---------------|-------|-------------------|
| $C_{59}Si$ | 9000 K | 0.82 | $C_2$ ejected |
|         |               | 0.06 | $SiC_2$ ejected |
|         |               | 0.12 | no frag. observed |
| $C_{59}Si$ | 8000 K | 0.50 | $C_2$ ejected |
|         |               | 0.08 | $Si$ ejected |
|         |               | 0.08 | $C_4$ ejected |
|         |               | 0.34 | no frag. observed |
| $C_{58}Si_2$ | 8000 K | 0.10 | $C_2$ ejected |
| $Si$ in a pentagon |       | 0.10 | $Si$ ejected |
| (nn) |       | 0.60 | became adsorbed |
|       |               | 0.20 | no frag. observed |
| $C_{58}Si_2$ | 8000 K | 0.90 | $C_2$ ejected |
| $Si$ in a pentagon |       | 0.05 | $SiC_2$ ejected |
| (not nn) |       | 0.05 | no frag. observed |
| $C_{58}Si_2$ | 8000 K | 0.67 | $C_2$ ejected |
| $Si$ in a hexagon |       | 0.33 | no frag. observed |
| (opposite) * |       |       | |
| $C_{57}Si_3$ | 6500 K | 0.30 | $C_2$ ejected |
| $Si$ in a hexagon |       | 0.50 | adsorbed $Si$ ejected |
| (nn) * |       | 0.20 | no frag. observed |
| $C_{57}Si_3$ | 6500 K | 0.20 | $C_2$ ejected |
| $Si$ in a pentagon |       | 0.10 | $SiC_2$ ejected |
| (not nn) * |       | 0.10 | $Si$ became adsorbed |
|       |               | 0.60 | no frag. observed |
| $C_{54}Si_6$ | 6000 K | 0.50 | $C_2$ ejected |
| $Si$ in a hexagon |       | 0.10 | $Si_2C$ ejected |
|       |               | 0.10 | $Si$ ejected |
|       |               | 0.05 | $Si_2$ ejected |
|       |               | 0.25 | no frag. observed |

The lack of self-consistency may be one reason for not finding the molecule SiC as a result of fragmentation, as it appears in the experimental results. Other possible explanations for the above mentioned discrepancy between experimental and simulation results can be suggested. For example, the experimental laser excitation lasts nanoseconds, therefore allowing for sequential absorption of several photons, while the simulations only study fast femtosecond laser induced fragmentations. Different time scale excitations could produce different fragments.

Also, the simulations study essentially the dynamics of the first fragmentation event but the experimental spectra may be more related to the energies of the final products. For example, starting from $C_{59}Si$ one may end up with $C_{58} + SiC$ or with $C_{57}Si + C_2$. The first system is energetically favorable, but there possibly is high activation energy for that fragmentation process that does not allow us to see it within our simulation time and statistics.

A few examples were tried in which some excited (antibonding) states of the molecule were artificially populated, so as to simulate the laser excitation in a different way, as proposed by other authors to study non-thermal fragmentation. However, no qualitatively different results were obtained if the excitation energy was small, although after conversion of the electronic energy to phonons, the activated phonons are those in which the silicon atoms vibrate more than the carbons, as both the HOMO and the LUMO have large contributions from the silicon atoms. Of course, when all the antibonding states are populated a spherically symmetric explosion occurs.

Singly substituted $C_{70}$ systems were also studied in some cases, but again no new fragmentation processes were evident.

B. Coated fullerenes

We have also investigated the stable geometries and the dynamical behavior of $C_{60}$ coated with a small number (1, 2, 3, 4, and 6) of Si atoms. In the equilibrium configurations our results show that the Si atoms are weakly bound to the fullerene surface, each Si atom being located in front of a hh $C – C$ bond and therefore bonded to two $C$ atoms, if the number of adsorbed Si atoms is less than three. For three adsorbed Si atoms, they are arranged as a regular triangle in front of a hexagon. For four adsorbed Si atoms, one of them has two $C$ neighbors, of a hh $C – C$ bond, and the other three have only one $C$ neighbor. For 6 adsorbed Si atoms, two of them have two $C$ neighbors, two have only one, and the other two have no $C$ neighbors. Table 2 shows the average $Si – Si$ and $Si – C$ bond lengths for the lowest energy isomers. In the case of $C_{60}Si_2$ the Si atoms prefer to be far away from each other but in systems containing more than two $Si$ atoms they prefer to be close to each other and located in front of a hexagon. These results are in
TABLE II: Average $Si-Si$ and $Si-C$ bond lengths for the lowest energy isomers of fullerenes with adsorbed $Si$ atoms.

|      | $Si-Si$ (/Å) | $Si-C$ (/Å) |
|------|--------------|-------------|
| $C_{60}Si_1$ | 2.11 | 2.11 |
| $C_{60}Si_2$ | 8.01 | 2.11 |
| $C_{60}Si_3$ | 2.65 | 2.27 |
| $C_{60}Si_4$ | 2.63 | 2.23 |
| $C_{60}Si_6$ | 2.62 | 2.26 |

In order to study the dynamical behavior of these $Si$ coated molecules we performed finite temperature molecular dynamics simulations with initial temperatures of 5000, 4000 and 3000 K. Ten different runs were performed for each system, with different initial maxwellian velocity distributions. Due to the fast interconversion between initial kinetic and potential energies, temperatures of around 2300, 1900 and 1400 K respectively were achieved in less than a picosecond. At these temperatures no desorption is observed in systems with one or two $Si$ atoms, but the adsorbed atoms move on the fullerene surface. In $C_{60}Si_2$ the two $Si$ atoms move independently and if by chance they collide and form a dimer, they easily separate again. As the number of adsorbed $Si$ atoms increases, the desorption probability also increases.

In Table 3 we see that $C_{60}Si_3$ is more stable than $C_{60}Si_4$. The silicon atoms desorb easily from $C_{60}Si_6$ as a tridimensional cluster, at even lower temperatures. Fig. 3 shows the average number of neighbors of an adsorbed silicon atom during the whole simulation time, as a function of the total number of adsorbed atoms. If it is less than three they tend to have more carbon than silicon neighbors, while for larger groups they form clusters and the number of neighbors of the same kind increases.

Our simulation results agree with the experimental mass abundance results, that show a much larger probability of finding molecules with one, two or three adsorbed $Si$ atoms than with four or more. Another interesting result also shown in Table 3 is that smaller adsorbed groups have a higher probability to dissociate and then desorb separately while four adsorbed $Si$ atoms or more, tend to desorb as a unit (see Fig. 4). Fig. 5 shows $Si_3$ first dissociating into $Si_2$ and $Si$, later $Si_2$ desorbing and the remaining $Si$ adsorbed atom orbiting on the fullerene surface. In Fig. 6 another possibility is shown, two $Si$ atoms from $C_{60}Si_3$ exchange their positions with two $C$ atoms and as a result they are incorporated into the fullerene cage. The two $C$ atoms evaporate and therefore the final system consists of $C_{58}Si_2$ plus an adsorbed $Si$ atom moving on the surface. This suggests that $Si$ substituted and adsorbed fullerenes may be interchangeable cases, with a greater possibility of substituted $Si$ atoms becoming adsorbed ones.

IV. DISCUSSION AND CONCLUSIONS

Non orthogonal tight-binding calculations are found to reproduce quite well the ab-initio static structural and electronic results for $Si$ doped fullerenes and for this reason the method seems adequate to study the fragmentation of these molecules by molecular dynamics simulations. We have used this method in the microcanonical ensemble and simulated the initial excitation by giving a high initial ionic temperature to the atoms.

The first fragmentation event in $Si$ substituted fullerenes shows, as expected, that the molecules break in those places where the bond orders are smaller, that
is, in some $\text{Si} - \text{Si}$ or $\text{Si} - \text{C}$ bonds. However, the most frequent first event is the ejection of a $\text{C}_2$ molecule and the second most probable event is that of a $\text{Si}$ substituted atom going to an adsorbed position.

For $\text{Si}$ coated fullerenes we show that adsorbed $\text{Si}$ clusters containing more than three $\text{Si}$ atoms are less stable and tend to desorb as a whole while smaller clusters may break into even smaller groups, remain adsorbed or exchange with $\text{C}$ atoms and become substituted fullerenes.

Comparison with experimental results shows several points of agreement, such as the stability of substituted and coated fullerenes and the successive ejection of $\text{C}_2$ molecules when excited. The difference in abundance between adsorbed clusters with three or more silicon atoms is also well reproduced by the simulations.

The agreements obtained between experiments and the results of past and also of the present calculations suggest that they must contain some real information about the very beginning of the fragmentation process, on a very local scale where the total charge and the charge transfers are not the deciding factor. However, the stability of odd numbered molecules and fragments, and the fact that the $\text{SiC}$ molecule was never found as an ejected fragment in the simulations are differences with the experiments that remain to be understood. We plan to continue investigating the reasons for the discrepancies.

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| System Initial Temperature | Frequency | Event description |
|-----------------------------|-----------|------------------|
| $C_{60}Si_3$ 5000 K         | 0.2       | no desorption within 20 ps |
|                             | 0.2       | $Si_3$ ejected between 10 and 20 ps |
|                             | 0.1       | $Si_3$ ejected within 10 ps |
|                             | 0.3       | $Si_3 \rightarrow Si_2 + Si$ |
|                             | 0.2       | exchange of $Si$ with $C$ atom, $Si$ in the cage |
| $C_{60}Si_4$ 5000 K         | 0.1       | no desorption within 20 ps |
|                             | 0.8       | $Si_4$ ejected within 10 ps |
|                             | 0.1       | $Si_4 \rightarrow Si_3 + Si$ |
| $C_{60}Si_3$ 4000 K         | 1.0       | no desorption within 20 ps |
| $C_{60}Si_4$ 4000 K         | 0.4       | no desorption within 20 ps |
|                             | 0.4       | $Si_4$ ejected within 10 and 20 ps |
|                             | 0.2       | $Si_4$ ejected within 10 ps |

**TABLE III:** Desorption events observed in 20 ps simulation time when clusters of three or four $Si$ atoms are adsorbed on the fullerene cage. 10 simulations were ran in each case.

*Present Address:
1. H. W. Kroto, J. R. Heath, S. C. O’Brien, R. F. Curl and R. E. Smalley, Nature (London) 318, 162 (1985)
2. T. Kimura, T. Sugai and H. Shinohara, Chem. Phys. Lett. 256, 269 (1996)
3. J. Fye and M. Jarrold, J.Phys.Chem.A 101, 1836 (1997)
4. C. Ray, M. Pellarin, J. Lermé, J. L. Vialle, M. Broyer, X. Blase, P. Mélinon, P. Kéghélian and A. Perez, Phys.Rev.Lett 80, 5365 (1998)
5. M. Pellarin, C. Ray, J. Lermé, J. L. Vialle, M. Broyer, X. Blase, P. Kéghélian, P. Mélinon and A. Perez, J.Chem.Phys. 110, 6927 (1999)
6. M. Pellarin, C. Ray, J. Lermé, J. L. Vialle, M. Broyer and P. Mélinon, J.Chem.Phys. 112, 8436 (2000)
7. M. Menon, J.Chem.Phys. 114, 7731 (2001)
8. I. M. L. Billas, C. Massobrio, M. Boero, M. Parrinello, W. Branz, F. Tast, N. Malinowski, M. Heinemrodt and T. P. Martin, J.Chem.Phys. 111 6787 (1999)
9. J. Lu, Y. Zhou, Y. Luo, Y. Huang, X. Zhang and X. Zhao, Mol. Phys. 99, 1203 (2001)
10. H. Tanaka, S. Osawa, J. Onoe and K. Takeuchi, J.Phys.Chem.B 103, 5939 (1999)
11. Chu-Chun Fu, M. Weissmann, M. Machado and P. Ordejon, Phys.Rev.B 63 085411 (2001)
12. D. Porezag, Th. Frauenheim, T. Kohler, G. Seifert, F. Weich and S. Uhlmann, Phys.Rev.B 52, 492 (1995)
13. R. Gutierrez, T. Frauenheim, T. Kohler and G. Seifert, J.Mater.Chem. 6, 1657 (1996)
14. Chu-Chun Fu and M. Weissmann, Phys.Rev.B 60, 2762 (1999)
15. S.A. Shevlin, A.J. Fisher and E. Hernández, Phys.Rev.B 63 195306 (2001)
16. C. Xu and G. Scuseria, Phys.Rev.Lett. 72, 669 (1994)
17. S. Tomita, J. U. Andersen, C. Gottrup, P. Hvelplund and U. V. Petersen, Phys.Rev.Lett. 87, 073401 (2001)
18. H. O. Jeschke, M. E. Garcia and J. A. Alonso cond-mat /0104036
19. B. Torralva, T. A. Niehaus, M. Elsner, S. Suhai, Th. Frauenheim and R. E. Allen, Phys.Rev.B 64, 153105 (2001)
20. A. Gambirasio, M. Bernasconi, G. Benedek and P. L. Silvestrelli, Phys.Rev.B 62, 12644 (2000)