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Stability and electronic properties of Si-doped carbon fullerenes

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The electronic structure and stability of several Si-doped C_{60} and C_{70} fullerenes (endohedral, exohedral, and substitutional) are investigated within the framework of both semiempirical modified-neglect-of-diatomic-overlap (to determine the most stable geometrical arrangements) and *ab initio* density-functional theory (calculation of the electronic structure and total energies). For endohedral species, the equilibrium configurations show a tendency of the Si atoms to move from the center of the molecule toward the cage, producing sizable expansions of the carbon bonds closer to the encapsulated atoms. Exohedrally doped structures exhibit similar geometrical deformations, being localized (also around the impurity) and relatively large (expansions in the C—C bond lengths as large as 12%), while minor changes in the C—C distances of the cage are obtained in fullerenes with substitutional Si. In agreement with relative abundance spectra, the endohedral silicon-doped carbon fullerenes are found to be less stable when compared to the hollow structures (C_{60} and C_{70}), with configurations in which the Si atoms are attached to the outside of the cage, and also with arrangements in which carbon atoms of the fullerene are replaced by silicon atoms. The small energy difference between the highest occupied molecular orbital and lowest unoccupied molecular orbital obtained with the inclusion of Si atoms into the fullerene cage as well as the weak Si—C bonds formed in these kind of arrangements seems to be at the origin of this behavior. On the other hand, substitutionally doped molecules are the ground-state configurations since Si atoms can be viewed as carbonlike atoms in the fullerene network, also due to its four valence electrons, binding thus more strongly to the carbon units of the structure. For some particular cases we analyze the influence of oxygen chemisorption on the electronic spectrum and stability of our Si-doped carbon molecules, and finally we give a qualitative estimation of the energy-barrier height for Si^{+} penetration into a C_{60} fullerene.

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I. INTRODUCTION

One interesting aspect of fullerene cages is the existence of an endohedral cavity large enough to contain an atom or a small molecule. In the last years, an increasing variety of species have been encapsulated in fullerenes,[1] being interesting candidates for the constructing unit of new materials. From the point of view of theory, there are several *ab initio* calculations involving endohedral rare gas (e.g., He and Ne) (Ref. 2) as well as metal (e.g., La, Ni, Na, K, Rb, and Cs) (Refs. 3–5) atoms and in all cases, by analogy with alkali-doped fullerides, the electronic properties have been found to depend sensitively on the internal dopant. This is actually due to the significant charge transfer between the fullerene cage and the interstitial (or trapped) metal atoms occurring in both type of systems, a fact that can change considerably their electronic structure, chemical behavior, and solid-state properties.

As is well known, the implementation of the Krätschmer-Huffman method[6] for the production of bulk quantities of fullerenes led to an adaption for the production of macroscopic amounts of endohedral fullerenes such as $La@C_{82}$.[7] Furthermore, the availability of bulk quantities of C_{60} allowed also the preparation of exohedrally doped fullerenes in the solid phase,[8] and finally the replacing of a fullerene atom with a heteroatom by means of gas phase experiments was archived, being transition-metal atoms as well as lanthanide metals,[9] boron and nitrogen[10] of primary interest.

Of particular importance are also silicon-doped fullerenes, considering the large effort devoted to the technology of silicon carbide (SiC). At this respect, recent laser vaporization experiments on a silicon-graphite target[11] have provided experimental evidence for the existence of closed-cage carbon clusters with two types of doped fullerenes: (a) fullerenes with Si atoms attached to the outer surface of the cage and (b) fullerenes with substitutional Si. Actually, fullerenes with Si atoms attached to the outer surface could be good precursors for the endohedral formation since, at high temperatures, the breaking of a bond between two carbon atoms is highly probable, a fact that could allow the inclusion of the Si atoms into the cage. However, despite the possibility of a penetration mechanism, both mass-spectrometric studies as well as gas phase ion mobility measurements of these samples concluded that the presence of fullerenes with silicon atoms inside the cage was very unlikely.

In this work, we report on semiempirical (modified-neglect-of-diatomic-overlap) [MNDO] and *ab initio* density-functional (DF) calculations of endohedral, exohedral, and substitutionally Si-doped C_{60} and C_{70} fullerenes, in order to shed some light in to their electronic properties and structural stability. The rest of the paper is organized as follows. In Sec. II, we discuss briefly the theoretical methods used for the calculations. In Sec. III, we present our results and finally in Sec. IV the summary and the conclusions are given.

II. METHOD OF CALCULATION

In all cases we will consider that up to three silicon atoms can be encapsulated as small clusters [single Si atom, Si_2, and Si_3 (equilateral triangle)] and also attached (outside the surface) or substituted as individual atoms in the carbon cage. The preference of Si atoms to reside outside the surface or as a substitutional impurity, but not in the endohedral state, must be of course related to precise electronic and geometrical features present in the particles and as a consequence, we have decided to perform a systematic study by combining two different theoretical approaches. In a first step, we have fully optimized the considered structures using the semiempirical MNDO level of theory[12] and then, in a second step, we have used these MNDO geometries to perform single-point DF calculations considering the Becke exchange functional and the Lee-Yang-Parr correlation.[13] This procedure could be justified since the accuracy of the MNDO method has been proved in several calculations of fullerenes and fullerene-derived materials. For example, for the C_{60} molecule MNDO finds bond lengths of 1.474 and 1.400 Å,[14] for single and double bonds respectively, in good agreement with gas phase electron studies (1.458 ± 0.006 Å and 1.401 ± 0.010 Å) (Ref. 15) and *ab initio* calculations (1.446 Å and 1.406 Å).[16] MNDO calculates the ionization potential of C_{60} to 8.95 eV,[14] slightly larger than the values obtained from *ab initio* calculations (7.92 eV)(Ref. 17) and experiment (7.56–7.62 eV) (Ref. 18), and finally doped fullerenes [e.g., Li_xC_{60} ($x = 0 \ldots 14$)] (Ref. 19) and large carbon clusters[14,20] have also been successfully studied using the MNDO approximation.

The key issues we want to focus on are the evolution of the electronic and geometrical structure as well as of the atomization energy (defined as the energy difference between a molecule and its components atoms) as a function of the number and position of the Si atoms, as well as on the effect of different fullerene cavities. As is well known, MNDO is a method that requires a parametrization of the elements, and thus sacrifices some of the accuracy of *ab initio* calculations for a significant gain in computation speed. However, we expect that reoptimization of all geometries at the DFT level will have only a very small effect on the calculated relative energies of the different structures.

The electronic structure and total energy of the molecules are obtained by means of the GAUSSIAN98 software[21] where the molecular orbitals are expanded as a combination of Gaussian functions centered at the atomic sites, and the exchange-correlation effects can be treated within the density-functional scheme. In particular, the Kohn-Sham equations are solved by considering the nonlocal Becke exchange functional and the Lee-Yang-Parr correlation (BLYP).[13] We use the STO-3*G* basis[22] (Slater-type orbital) that is a minimal set that is formed by fixed-size atomic-type orbital. The STO-3*G* considers three Gaussians per basis function, for example, in a carbon atom we have three Gaussians that are a least-square fit to a Slater $1s$ orbital, and we have also another three Gaussians that are a least-square fit to Slater $2s$ and $2p$ orbitals. Obviously, larger basis sets approximate more accurately the orbitals by imposing fewer restrictions on the location of electrons in space. As a consequence, in order to illustrate the dependence of results on the choice of basis functions, we have done some calculations by using a more extended set, 6-311*G*. The calculations, which involved a higher numerical effort, are found to lead essentially to the same conclusions.

The numerical accuracy of the method is tested by calculating some well-known properties of the C_{60} molecule. We obtain that the occupied electronic states fall within a range of 19.2 eV and that the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is of 1.45 eV, both results being in good agreement with the experimental measurements.[23,24] We obtain also an atomization energy of 10.04 eV/atom, which is overestimated with respect to the reported values in the literature, however, as clearly stated by other authors,[25] this corresponds to a basis set effect. Actually, the calculation using the 6-311*G* basis gives an atomization energy of 8.5 eV/atom, which is closer to the estimated experimental value of 7.25 eV/atom.[26] Therefore, in the following, only relative values are important.

Our results can be also compared with similar or more elaborated methods. Guo *et al.*[27] obtained by means of the self-consistent field discrete variational method an HOMO-LUMO energy gap of 1.68 eV and that the occupied states fall in an energy range of 20 eV. The electronic spectrum obtained by Saito and Oshiyama[28] using the local-density approximation to density-functional theory shows a valence bandwidth of 21 eV and a band gap of 1.9 eV. Finally, a pseudopotential based local-density-approximation calculation[23] yields states up to 23 eV below the highest occupied state.

III. RESULTS AND DISCUSSION

In the following, we present results for the structural and electronic properties of several Si-doped C_{60} and C_{70} fullerenes.

A. Structural properties

In Fig. 1, we show as representative examples the most stable atomic configurations obtained for the $(Si,Si_2)@C_{60}$ [Figs. 1(a) and 1(b)] and $(Si_2,Si_3)@C_{70}$ [Figs. 1(c) and 1(d)] molecules. We also show the lowest energy arrangements for exohedral SiC_{60} [Fig. 1(e)] and Si_2C_{60} [Fig. 1(f)] as well as for substitutional SiC_{59} [Fig. 1(g)] and Si_2C_{58} [Fig. 1(h)] fullerenes. These equilibrium structures were calculated by computing the force at each atomic site and relaxing the geometry, without symmetry constraints, by the method of steepest descent. Different starting configurations were used to ensure that the geometry of the molecule corresponds to the global minimum. From the figure we note that, in both C_{60} and C_{70}, the cage center is an unstable position for the encapsulated Si atoms and that their relaxed positions are close to the carbon structure. Actually, the nearest-neighbor Si-C distances vary from $1.93-2.10$ Å, being slightly larger than the Si—C bond lengths found in organic molecules ($1.83-1.90$ Å).[29] It is important to remark that, in general, the presence of the endohedral silicon atoms has little effect on the global shape of the carbon clusters, however we find sizable Si-induced modifications on the C—C bond lengths of the carbon cage in the proximity of the Si atoms. The nearest-neighbor distances in the carbon surface vary be-

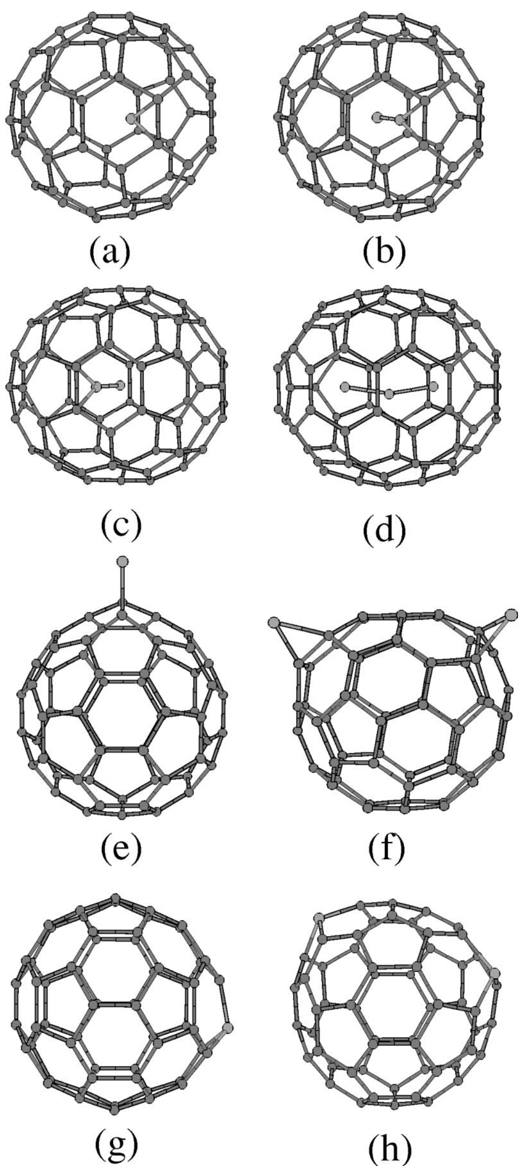

FIG. 1. Calculated (MNDO) lowest energy structures for (a) Si@C_{60}, (b) Si_2@C_{60}, (c) Si_2@C_{70}, (d) Si_3@C_{70}, (e) SiC_{60}, (f) (Si,Si)C_{60}, (g) SiC_{59}, and (h) Si_2C_{58} fullerenes.

tween 1.40−1.54 Å for the C_{60} molecule and from 1.38 −1.51 Å for C_{70}, the largest expansions (∼14%) being at the C—C bonds closer to the Si_N clusters. Note that, for the C_{60} molecule, the trapped silicon atoms are always attached to a double bond between two fused six-membered rings, which are the electron-rich regions acting normally as the attraction centers for the encapsulated atoms. However, we observe that for the C_{70} fullerene, which has a more complex nearest-neighbor bond-length distribution,[9] bridging of Si across the bond between five- and six-membered rings is also possible [see the results for Si_2@C_{70} in Fig. 1(c)]. In general, we must say that depending on the charge, the size, and the propensity to form a directional bond with the carbon atoms, the guest molecule will position itself more or less away from the center of the fullerenes, surrounding the double bonds of the cage.

It is important to comment also about the significant structural transformations present in endohedral Si_2 and Si_3 clusters. For the silicon dimer trapped inside the C_{60} molecule [Fig. 1(b)] we found a 20% of contraction in the nearest-neighbor distance with respect to the bulk value (2.35 Å, diamond structure), while inside the C_{70} cavity [Fig. 1(c)] a 19% of reduction is obtained. These values are considerably larger than the one corresponding to the free Si_2 cluster in which the nearest-neighbor bond length is equal to 2.23 Å.[30] For the silicon trimer we have found almost linear arrangements in both encapsulating cavities, the three silicon atoms forming an angle of 145° inside C_{60} and of 163° inside C_{70} [Fig. 1(d)], and having Si—Si bond lengths of approximately 1.7−1.8 Å . At this respect, we must comment that tight-binding molecular-dynamics calculations by Khan and Broughton[31] have found a ground state for the free Si_3 cluster in which the three atoms lie on the vertices of an isosceles triangle, characterized by an angle of 82° between the Si atoms, and a nearest-neighbor Si-Si distance of 2.26 Å . When comparing the calculations for free Si_N clusters with the results obtained in our work we can conclude that significant structural transformations are induced on small silicon clusters when encapsulated in fullerene structures. This result could be of fundamental importance in the case of magnetic guests for which modifications in the geometrical arrangement could be at the origin of strong variations in their magnetic properties.

Figure 1 shows also the most stable atomic configurations for exohedrally doped fullerenes [Figs. 1(e) and 1(f)] as well as for the most stable arrangements when up to two carbon atoms of the fullerene network are replaced by Si atoms [Figs. 1(g) and 1(h)]. Notice that, as in the endohedral molecules, the silicon atoms attached to the outside of the cage always bridges over a double bond of the carbon structure. Moreover, shorter Si—C nearest-neighbor distances are obtained, being now of the order of 1.8 Å , which reveals that stronger Si-C bonds are formed in these kind of arrangements. As in previous cases we also find that, upon adsorption of a single Si atom, there are no noticeable changes in the C-C bond lengths except for those bonds neighboring the silicon atom. However, as the number of Si atoms increases, appreciable variations in the general morphology of the C_{60} cage are observed [compare Figs. 1(e) and 1(f)] due to the more sizable geometrical perturbation that extends over a wider region of the cage.

The silicon-substituted fullerene geometries [Figs. 1(g) and 1(h)] exhibit also similar features. However, in these cases, the typically larger Si—C bond lengths ($1.8 \leqslant R_{\text{Si-C}} \leqslant 2.1$ Å) do not easily fit into the C_{60} cage structure ($R_{\text{C-C}} = 1.40$ and 1.46 Å), producing thus an outward relaxation on the Si atom. Actually, increasing the concentration of the dopant atom results in a puckered type of structure that is expected to have unique reactive properties. We must emphasize that, despite the substitution of a carbon atom for a silicon atom in the fullerene cage introduces a chemically distinct site in the surface, and perturbs the electronic and geometrical structure in the vicinity of the dopant atoms, it preserves the bond-length alternation pattern of the un-

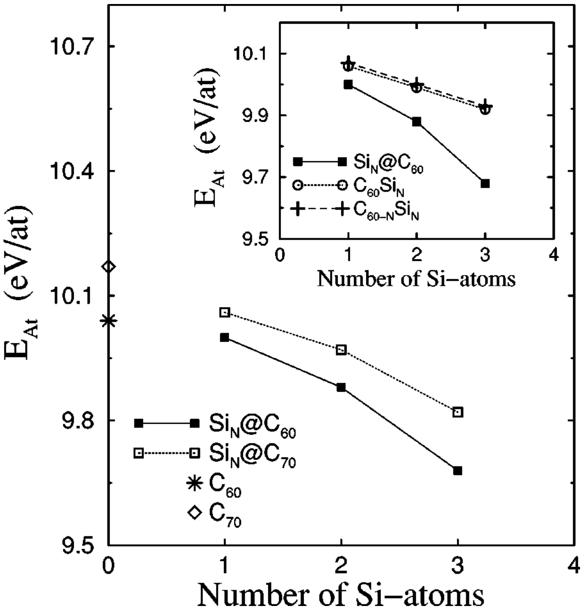

FIG. 2. The atomization energy E_{At} for $\mathrm{Si}_N@\mathrm{C}_{60}$ and $\mathrm{Si}_N@\mathrm{C}_{70}$ fullerenes as a function of the number of trapped Si atoms N. The isolated points correspond to hollow C_{60} and C_{70}. In the inset, we show a comparison of E_{At} found for $\mathrm{Si}_N@\mathrm{C}_{60}$ arrangements, with the values obtained for exohedral ($\mathrm{C}_{60}\mathrm{Si}_N$) and substitutional ($\mathrm{C}_{60\text{-}N}\mathrm{Si}_N$) configurations.

dopped C_{60}. Around each Si atom we can distinguish also two single (1.73 Å) and one double (1.66 Å) bond.

We would like to emphasize that, in all cases, the Si-C orbital mixing is not negligible and this causes strong variations in the charge transfer between the silicon $3s$ and $3p$ and carbon $2p$ orbitals. For example, in the endohedral fullerenes, we have found that up to 1.3 electrons are donated to the carbon cage, a fact that produces substantial deviations from the normal electron occupancy ($N_i = 4$) at some sites of the structure. Obviously, larger guests (such as transition metals) (Ref. 33) will exhibit much more chemical interaction between the valence orbitals of the guest and the HOMO of the cage, a fact that could lead to a wide variety of behaviors. We must emphasize that also for the exohedral configurations and even when substituting Si atoms for C atoms in the cage, the carbon atoms always act as an electron acceptor. This excess of charge at the surface strongly modifies the chemical reactivity of the molecules since some of the carbon atoms near the adsorption site will now have a tendency to donate electrons to form bonds with electropositive reactants, a fact that could be used to identify the presence of this kind of compounds.

B. Stability and electronic spectra

In Fig. 2, we present results for the atomization energy E_{At} of a single silicon atom as well as for the Si_2 and Si_3 clusters placed inside the C_{60} and C_{70} cages. We also show in the inset the calculated energies of configurations in which the same number of Si atoms (up to three) are bonded outside the C_{60} cage (exohedral configurations), together with the values obtained when the Si atoms are considered as substitutional impurities in the carbon network. In these configurations, distinct atomic arrangements are possible, however, we have considered only those in which the distance between the silicon atoms is large enough ($R_{\text{Si-Si}} \gtrsim 5$ Å) in order to minimize the stress induced by the inclusion of the bigger Si dopant [see for example Figs. 1(e)-1(h)]. From the figure we note that all $\mathrm{Si}_N@\mathrm{C}_{60}$ and $\mathrm{Si}_N@\mathrm{C}_{70}$ fullerenes are stable, however, they are less favorable as compared to hollow C_{60} and C_{70}, and to both exohedral and substitutional arrangements. The results shown in Fig. 2 are in agreement with the lower relative abundance spectra obtained for the silicon-containing fullerenes as compared to the pure carbon clusters reported by Fye and Jarrold.[11] Moreover, they also agree with inverse mobility measurements performed on free Si-doped carbon fullerenes by the same group, from which the presence of carbon cages with a silicon atom incorporated only as an exohedral or subtitutional impurity has been inferred. Finally, it is important to note that increasing the number of Si atoms in both C_{60} and C_{70} cages (either as an endohedral, exohedral or substitutional dopants) always decreases the energy of the molecules, and as a consequence, it will be interesting to know the number of Si atoms that can be added to these carbon structures without modifying the geometry of the cage.

As is well known, the structural rearrangements and energetics presented in Figs. 1 and 2 result from a delicate balance between the electronic and geometrical details present in the particles. Consequently, in the following we analyze various of these factors that could be at the origin of the observed relative stability between the different configurations. First, when we discussed the equilibrium geometries in Fig. 1 we found sizable differences in the way silicon atoms are bonded to the carbon cages. As previously stated, the calculated Si—C bond lengths range from 1.66 to 2.10 Å, the largest values (1.93−2.10 Å) corresponding to Si atoms attached to the internal surface of the carbon structure. This result already implies that the relative bonding between Si and C in endohedral fullerenes is weak and that the stability of these compounds could be enhanced by promoting a different type of doping. Actually, reduced $R_{\text{Si-C}}$ distances are obtained (∼1.8 Å) when Si atoms are attached to the outer surface, accompanied by considerable energy gains (see inset of Fig. 2), while for substitutional impurities (which are the ground-state arrangements) the smallest values are found, the single and double Si—C bonds being equal to 1.73 and 1.66 Å, respectively. It is important to note that, even if the various Si—C bond lengths in all configurations are relatively close to each other, we can see that there are more sizable differences between the various calculations of the atomization energy per atom (see Fig. 2). However, it is important to remark that, as a general trend, structures with the more robust Si—C bonds (i.e., those with the shortest Si—C distances) correspond in all cases to the most stable arrangements.

Local electron occupancies are also of fundamental importance in determining the global properties of a system. In situations, where there is a redistribution of valence electrons and/or charge transfer, analysis of the occupations in each one of the orbitals involved in the bonding can provide us

TABLE I. On-site orbital occupancy ($n_{i\alpha}, \alpha = s, p_x, p_y$, and p_z) and the total number of on-site electrons (N_i) for a single Si atom in C_{60} as an endohedral, exohedral, and substitutional impurity.

	n_s	n_{p_x}	n_{p_y}	n_{p_z}	N_{Si}
Si@C_{60}	1.92	0.56	0.22	0.48	3.18
SiC_{60}	1.84	0.08	0.68	0.64	3.24
SiC_{59}	1.16	0.80	0.65	0.65	3.26

also with relevant information concerning the local electronic structure and energetics. For example, in carbon atoms, it is well known that the deviation from planar character is archived by forming C-C bonds with hybridization intermediate between sp^3 (diamond) and sp^2p (graphite), as discussed by Haddon[34] for C_{60} and other higher fullerenes. As a consequence, it is important to analyze also the on-site orbital electron occupancy $n_{i\alpha}$ ($\alpha = s, p_x, p_y$, and p_z) in our Si-doped carbon fullerenes, specially at the Si atoms that are the ones with the largest deviations from their bulk valence state ($N_i = 4$). Actually, it will be interesting to see if the local geometrical arrangements obtained around the dopant atoms (see Fig. 1) are favorable (or not) to the preferred sp^3 hybridization of bulk Si, a fact that could play also an important role in the relative stability observed in Fig. 2.

In Table I, we show the on-site orbital occupancy $n_{i\alpha}$ as well as the total number of on-site electrons N_i for a silicon atom in an endohedral, exohedral, and substitutional arrangement. From the table we observe that considerable redistributions of charge are obtained on the silicon atom as a function of the local atomic environment. We note that, for the endohedral species, the electron occupancy in the p orbitals is highly nonuniform and that a relatively large number of electrons ($0.82e$) are transferred to the carbon cage. For exohedral molecules, the anisotropy in the redistribution of charge is considerably reduced, while for the substitutionally doped structures the p_y and p_z orbitals have the same number of electrons, a fact that indicates the formation of an sp^2p type of hybridization. Furthermore, small differences are obtained when compared with the occupancy of the p_x orbital ($n_{p_x} - n_{p_{y(z)}} = 0.15e$), leading thus to a more spherical distribution of charge and being also very close to the sp^3 configuration obtained at the bulk diamond structure. Actually, for substitutional impurities we can see the formation of almost two tetrahedral C-Si-C angles (110.4°) and a third one with a value of 98.4°.

Further insight into the relative stability observed in Fig. 2 can be also gained by looking at the electronic spectrum of our silicon-doped carbon fullerenes. In Fig. 3, we show as a representative example a comparison of the eigenvalues for the hollow C_{60} with the energy-level distribution obtained when a Si_2 cluster is trapped inside the cage [Fig. 1(b)] as well as with the case in which two Si atoms are incorporated as substitutional impurities [Fig. 1(h)] in the carbon structure. The x axis shows the number of the eigenvalue (the core states have been excluded from the figure) and the y axis shows the corresponding eigenvalue. The horizontal lines define the Fermi level (the highest occupied state) in each case.

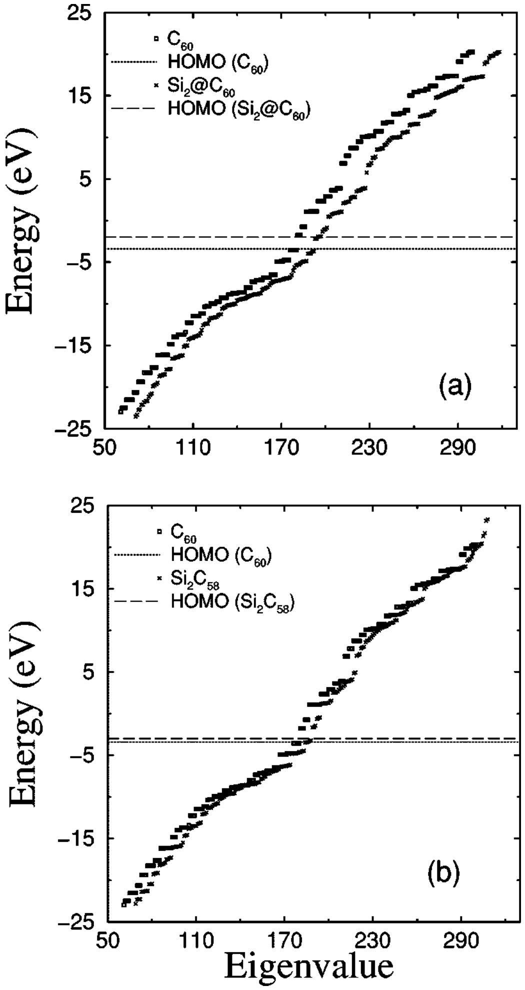

FIG. 3. Eigenvalues vs eigenvalue number for (a) hollow C_{60} (squares) and Si_2@C_{60} (crosses) and (b) hollow C_{60} (squares) and Si_2C_{58} (crosses) fullerenes.

From Fig. 3(a), we observe that the degeneracy of the spectrum for the hollow structures is considerably modified upon inclusion of the Si_2 cluster and that the HOMO is now placed in a region with a different distribution of energy states. As stated before, the hollow structures show a considerable energy gap ($\Delta_{\mathrm{HL}} = 1.45$ eV) between the occupied and unoccupied states. However, we can see that this gap is strongly reduced when the Si_2 cluster is inside the molecule ($\Delta_{\mathrm{HL}} = 0.34$ eV). On the contrary notice that, for the Si_2C_{58} structure [Fig. 3(b)], less dramatic changes are observed all along the energy-level distribution, being the HOMO-LUMO energy gap now increased to 1.7 eV. It is important to emphasize that these values for Δ_{HL} in the Si-doped fullerenes can be correlated with the energy ordering observed in Fig. 2. As is well known, previous studies[32] have shown that, for C_{60} and C_{70}, large fragmentation energies are accompanied by large HOMO-LUMO gaps, both quantities being strongly correlated to the extraordinary abundance of these two fullerenes. The Si-doped carbon fullerenes follow this simple electronic arguments, all the exohedral and substitutionally doped structures having HOMO-LUMO energy gaps of the order of 1.7 eV. These values are considerably larger than the

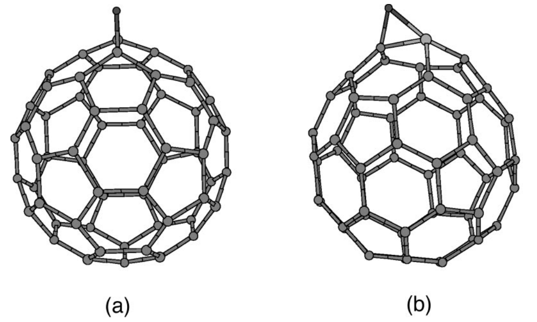

FIG. 4. Calculated (MNDO) lowest energy structures for (a) $C_{60}O$ and (b) $SiC_{59}O$ fullerenes.

ones obtained for the endohedral molecules, an energy ordering that agrees with the one found for the atomization energies in Fig. 2. Obviously, the observed changes in the electronic structure as well as on the position of the Fermi level are a direct consequence of a lowering in the symmetry of the system due to the inclusion of the silicon atoms (see Fig. 1), as well as of the redistribution of valence electrons among the orbitals (see Table I).

C. Oxygen adsorption

We would like to comment also about the influence of the presence of Si atoms on the chemical reactivity of fullerene cages. To see this, we have studied the reaction of oxygen with the external surface of both C_{60} and substitutionally SiC_{59} [Fig. 1(g)] fullerenes, the latter corresponding to the ground-state configuration in our single Si-doped carbon structures (see Fig. 2). Starting with the C_{60} and SiC_{59} lowest energy arrangements, we allowed the O atom to interact and varied the various bonds and bond angles until the forces at each site vanish. The corresponding lowest energy structures are shown in Fig. 4. From Fig. 4(a), we can see that the most stable $C_{60}O$ fullerene is formed by the oxygen atom bridging the bond between two fused six-membered rings in C_{60}. However, we have found a second configuration (not shown), close in energy but less stable, in which the O atom is attached to a bond between five- and six-membered rings, a bond that actually breaks to lead to an open form. As in the case of Si doping, oxygen absorption deforms also the cage locally in a sizable manner, modifying the length of the single and double bonds present in the structure. In this case we have found expansions in the C—C bond lengths as large as 20%, most of these changes being localized within the first- and second-nearest neighbors around the absorption site. On the other hand, the C—O bond length is equal to 1.40 Å.

Oxygen adsorption in substitutionally Si-doped structures is also interesting to analyze since, even if incorporating a Si atom on the carbon network has little effect on the general shape of the cage [see Fig. 1(g)], the induced changes in the eigenvalue spectra around the Fermi level [see for example the results for Si_2C_{58} in Fig. 3(b) where, when compared with the C_{60} cage, the degeneracy of the HOMO and LUMO as well as their energy separation are considerably modified] should strongly affect their adsorption properties. It is important to comment also that, for substitutionally doped structures, several adsorption sites are possible, however, we are going to consider only the most representative initial configurations namely: O directly on top of the Si impurity (C1), around the adsorption site (C2), and far enough from the substituted Si atom (C3) in order to minimize the Si-O interaction. To illustrate this facts we are going to consider the particular case of the SiC_{59} fullerene [Fig. 1(g)].

From our calculations we have noted that, for O on top of Si (C1), the redistribution of charge leads to both negatively charged Si and O atoms (-0.56 and -1.86, respectively), a fact that originates a clear repulsive interaction between both species, considerably increasing the total energy of the system. Actually, as we show in Fig. 4(b), the most stable atomic arrangement for the SiC_{59}-O molecule corresponds to the case in which the oxygen atom is laterally displaced with respect to the C1 configuration, the adsorption site taking place over a Si—C bond (C2), which are the electron-rich regions normally acting as attraction centers. Finally, for the case in which both Si and O are considerably spaced in the cage (~ 7 Å) (C3) a less stable configuration is found ($|E(\mathrm{C1})|<|E(\mathrm{C3})|<|E(\mathrm{C2})|$), which obviously reproduces the well-known isolated impurity limits, namely: small charge transfer ($\sim 0.73e$) from Si to C (see Table I), leading to a positively charge Si atom, and a small gain of electronic charge for the O atom ($\sim 0.13e$). In view of these results it is reasonable to expect that, for substitutionally Si-doped fullerenes, a highly nonuniform oxygen accommodation on the surface (around the impurity) should be obtained, a fact that can considerably influence the ion mobility spectra of the particles.

We must say that despite the oxygen bonding has little effect on the global structure of the cage, the atomization energy of the $C_{60}O$ ($E_{\mathrm{At}}=10.07$ eV/atom) is larger than the value obtained for the $SiC_{59}O$ ($E_{\mathrm{At}}=10.03$ eV/atom) molecule, which actually implies that the latter is less sensitive to oxygen atoms than the pure carbon structures. As in previous cases, we found that this relative stability can be also correlated with the HOMO-LUMO energy separation of the structures. Actually, the HOMO-LUMO gap for the $C_{60}O$ molecule is equal to 2.02 eV while a value of 1.8 eV is obtained for the the $SiC_{59}O$ fullerene, a result that is in agreement with the energy ordering obtained between these molecules.

D. Insertion mechanism and energy-barrier height

Finally, we would like to say that, despite our total-energy calculations (see Fig. 2) and the laser vaporization experiments performed by Fye and Jarrold[11] have demonstrated that endohedral silicon fullerenes will be difficult to isolate, it could be possible that, by performing low-energy Si ion bombardment on a C_{60} sample (in a solid or gas phase), silicon atoms may get trapped in the fullerene cage. At this respect, it is important to comment that previous experimental studies considering interactions between Li^+, Na^+, and K^+ with C_{60} molecules[35] have revealed that insertion of the alkali atoms is possible, leading to sizable amounts of $[(\mathrm{Li,Na,K})@C_{60}]^+$ complexes. Despite the insertion mecha-

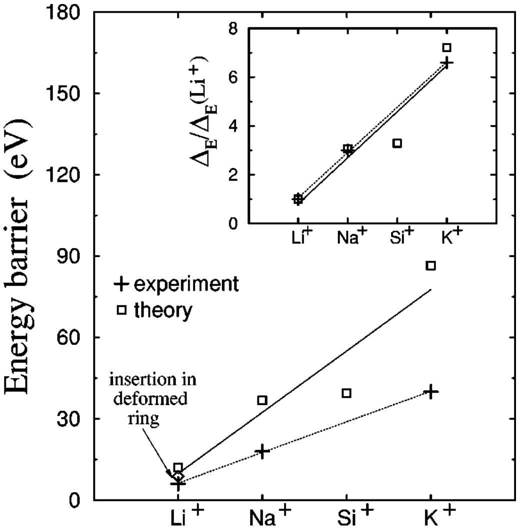

FIG. 5. Energy-barrier heights Δ_E for Li^+, Na^+, Si^+, and K^+ penetrating into a C_{60} fullerene. Open squares correspond to our calculated values by assuming a projectile insertion trough the center of a rigid hexagonal ring. The crosses indicate the experimental results of Wan *et al.* (Ref. 35). The isolated diamond refers to Li^+ insertion into a deformed ring. The continuous and doted lines correspond to a linear fit of the data. In the inset we show the same results, the experimental and theoretical values being now normalized to $\Delta_E^{\mathrm{exp}}(\mathrm{Li}^+)$ and $\Delta_E^{\mathrm{theo}}(\mathrm{Li}^+)$, respectively.

nism is a very complicated dynamical process, some qualitative estimation of the magnitude of the energy barrier Δ_E for a Si ion to be inserted into a C_{60} cavity can be obtained by simulating the penetration mechanism by a series of static total-energy calculations. In this case, we are going to assume that the Si ion follows a linear trajectory and that actually slips through the center of a rigid hexagonal ring of the C_{60} surface. This is, in principle, not obvious since it has been found that the inclusion mechanism changes with the projectile size and actually, for bigger ions (such as Na^+ and K^+), significant deformations on the carbon bonds around the insertion point can be induced. In fact, as we will see in the following, Li^+ insertion on deformed rings will reduced the height of the energy barrier, being more in agreement with the experimental measurements.[35]

In Fig. 5, we present results for the energy-barrier height Δ_E as the Si ion passes through a rigid hexagonal ring of the C_{60} fullerene. We also show the experimental results (Δ_E^{exp}) of Wan *et al.*[35] for Li^+, Na^+, and K^+ insertion into C_{60} cages, together with our estimated theoretical energy barriers (Δ_E^{theo}) for the same ions (Li^+, Na^+, and K^+) in a static picture (see discussion above). At this point it is important to comment that, despite these two set of values are not strictly comparable, we believe that both results should be very helpful in evaluating the possible formation of $[\mathrm{Si}@C_{60}]^+$ compounds. From the figure we note that, in general, our calculated energy barriers are overestimated with respect to the experimental measurements (by a factor of ~ 2 eV), however, we note that the same behavior for Δ_E as a function of the projectile size is observed. Actually, if we normalized both sequences to their respective smallest Δ_E (i.e., using Δ_E^{exp} and Δ_E^{theo} for Li^+), we obtain the same linear dependence (see inset of Fig. 5), the largest deviations being for K^+ for which (contrary to our assumption) an insertion mechanism that breaks C—C bonds has been proposed.

It is clear that in an experimental setup where high kinetic energies and elevated temperature are present, a considerable amount of energy is transferred to the carbon cage causing sizable relaxations of the carbon rings. This must decrease the ring-ion repulsion at the insertion point, lowering as a consequence the height of the energy barriers. This fact is clearly illustrated in Fig. 5 where the value of Δ_E for Li^+ penetration into a deformed hexagonal ring is also shown (see the isolated point). In this case, we have increased the area at the insertion point by performing reasonable expansions in the various C—C bonds up to an average bond length of 1.51 Å between the carbon atoms forming the hexagonal ring. Notice that Δ_E decreases with respect to the unperturbed structure, being now our energy barrier $[\Delta_E^{\mathrm{theo}}(\mathrm{Li}^+ = 8.8\ \mathrm{eV})]$ more in agreement with the experimental measurement of Ref. 35. Note also that our calculated Δ_E for Si^+ is located between $\Delta_E(\mathrm{Na}^+)$ and $\Delta_E(\mathrm{K}^+)$, which indicates that some trapping of Si^+ within the C_{60} cage should be possible, probably involving a penetration mechanism in which bond breakage of the fullerene network could be necessary.

IV. CONCLUSIONS

In this work, we have investigated by means of semiempirical (MNDO) and density-functional methods the stability and electronic properties of Si-doped C_{60} and C_{70} fullerenes. In agreement with relative abundant spectra, we have found that endohedral, exohedral, and substitutional Si-doped configurations are less stable when compared to the undoped carbon fullerenes. The present results are also in good agreement with inverse mobility measurements, from which the presence of Si-doped fullerenes with silicon atoms only in exohedral or substitutional arrangements has been inferred. In all cases, the structure of the fullerenes has been found to be modified only in the vicinity of the dopant atoms, producing sizable expansions in the C-C distances. Significant structural transformations have also been obtained for encapsulated Si clusters when compared to their free ground states, consisting of larger contractions in their bond lengths as well as considerable angular distortions. These results should be taking into account when encapsulating magnetic guest (for which applications in magnetic recording technology are being envisioned), since it is well known that small changes in their local atomic environment can lead to sizable variations in their magnetic properties.

Our results have revealed that, when compared to pure carbon cages, Si-doped carbon fullerenes exhibit profound changes in their electronic spectrum (which can be detected by photoemission experiments) and that have important implications in the conducting character, chemical reactivity, and stability of the molecules. We have found that charge transfer operates, in all cases, from Si to C; however, it is well known that C_{60} possesses a great ability to adapt itself to various environments, being able to act either as an electron donor or as an electron acceptor. Finally, within our theoretical scheme, we have been able to elucidate the electronic and geometrical features responsible for the observed relative stability in this kind of compounds as well as some qualitative estimation of the energy-barrier height necessary for Si^+ insertion into the C_{60} molecule.

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[1] T. Weiske, T. Wong, W. Krätschmer, J.K. Terlouw, and H. Schwarz, Angew. Chem. Int. Ed. Engl. **31**, 183 (1992); K.A. Caldwell, D.E. Giblin, C.S. Hsu, D. Cox, and M.L. Gros, J. Am. Chem. Soc. **113**, 8519 (1991); M.M. Ross and J.H. Callahan, J. Phys. Chem. **95**, 5720 (1990); Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.C. Chibante, J. Fure, L. Wang, J.M. Alford, and R.E. Smalley, *ibid.* **95**, 7564 (1991).

[2] M. Saunders, H.A. Jiménez-Vázquez, R.J. Cross, and R. Poreda, Science **259**, 1428 (1993).

[3] B. Dunlap, O.D. Häberlen, and N. Rösch, J. Phys. Chem. **96**, 9095 (1992).

[4] O.D. Häberlen, N. Rösch, and B. Dunlap, Chem. Phys. Lett. **200**, 418 (1992).

[5] T. Guo, R. Smalley, and G.E. Scuseria, J. Chem. Phys. **99**, 352 (1993).

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

[7] Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford, and R.E. Smalley, J. Phys. Chem. **95**, 7564 (1991).

[8] A.R. Kortan, N. Kopylov, E. Ozdas, A.P. Ramirez, R.M. Fleming, and R.C. Haddon, Chem. Phys. Lett. **223**, 501 (1994).

[9] W. Andreoni, F. Gygi, and M. Parrinello, Chem. Phys. Lett. **190**, 159 (1992).

[10] D.E. Clemmer, J.M. Hunter, K.B. Shelimov, and M.F. Jarrold, Nature (London) **372**, 248 (1994).

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

[12] M.J.S. Dewar and W. Thiel, J. Am. Chem. Soc. **99**, 4899 (1977); **99**, 4907 (1977).

[13] A. Becke, Phys. Rev. A **38**, 3098 (1988); C. Lee, W. Yang, and R.G. Parr, Phys. Rev. B **36**, 785 (1988).

[14] D. Bakowies and W. Thiel, J. Am. Chem. Soc. **113**, 3704 (1991).

[15] K. Hedberg, L. Hedberg, D.S. Bethune, C.A. Brown, H.C. Dorn, R.D. Johnson, and M. de Vries, Science **254**, 410 (1991).

[16] M. Häser, J. Almlöf, and G.E. Scuseria, Chem. Phys. Lett. **181**, 497 (1991).

[17] H.P. Lüthi and J. Almlöf, Chem. Phys. Lett. **135**, 357 (1987).

[18] J. de Vries, H. Steger, B. Kanke, C. Manzel, B. Weisser, W. Kamke, and I.V. Hertel, Chem. Phys. Lett. **188**, 159 (1992).

[19] U. Zimmermann, A. Burkhardt, N. Malinowsky, U. Näher, and T.P. Martin, J. Chem. Phys. **101**, 2244 (1994).

[20] D.L. Strout, R.L. Murry, C. Xu, W.C. Eckhoff, G.K. Odom, and G.E. Scuseria, Chem. Phys. Lett. **214**, 576 (1993).

[21] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, and J.A. Pople, GAUSSIAN 98, Revision A. 9, Gaussian, Inc., Pittsburgh PA, 1998.

[22] W.J. Hehre, R.F. Stewart, and J.A. Pople, J. Chem. Phys. **51**, 2657 (1969); J.B. Collins, P.V.R. Schleyer, J.S. Binkley, and J.A. Pople, *ibid.* **64**, 5142 (1976).

[23] J.H. Weaver, J.L. Martins, T. Komeda, Y. Chen, T.R. Ohno, G.H. Kroll, N. Troullier, R.E. Haufler, and R.E. Smalley, Phys. Rev. Lett. **66**, 1741 (1991).

[24] R. Haufler, L.S. Wang, L.P.F. Chibante, C. Jin, J. Conceicao, Y. Chai, and R.E. Smalley, Chem. Phys. Lett. **179**, 449 (1991).

[25] B.V. Reddy, S.N. Khanna, and B.I. Dunlap, Phys. Rev. Lett. **70**, 3323 (1993).

[26] M. Pederson, K.A. Jackson, and L.L. Boyer, Phys. Rev. B **45**, 6919 (1992).

[27] J. Guo, D.E. Ellis, and D.J. Lam, Chem. Phys. Lett. **184**, 418 (1991).

[28] S. Saito and A. Oshiyama, Phys. Rev. B **44**, 11 532 (1991).

[29] J.H. Callomon, *et al.*, *In Structure Data of Free Polyatomic Molecules*, edited by K.H. Hellwege and A.M. Hellwege, Landolt-Börnstein, New Series, Group II, Vol. 15 (Springer-Verlag, Berlin, 1987).

[30] K. Raghavachari and V. Logovinsky, Phys. Rev. Lett. **55**, 2853 (1985).

[31] F.S. Khan and J.Q. Broughton, Phys. Rev. B **39**, 3688 (1989).

[32] C.Z. Wang, B.L. Zhang, C.H. Xu, C.T. Chan, and K.M. Ho, Int. J. Mod. Phys. A **6**, 3833 (1992).

[33] D.M. Poirier, M. Knupfer, J.H. Weaver, W. Andreoni, K. Laasonen, M. Parrinello, D.S. Bethune, K. Kikuchi, and Y. Achiba, Phys. Rev. B **49**, 17 403 (1994).

[34] R.C. Haddon, Acc. Chem. Res. **25**, 127 (1992).

[35] Z. Wan, J.F. Christian, and S.L. Anderson, Phys. Rev. Lett. **69**, 1352 (1992); Z. Wan, J.F. Christian, Y. Basir, and S.L. Anderson, J. Chem. Phys. **99**, 5858 (1993).