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Ab initio study of silicon-multisubstituted neutral and charged fullerenes

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The electronic and structural properties of Si-doped fullerenes, obtained from C_{60} by replacing up to 12 C atoms with Si atoms, are studied by means of first-principles density-functional theory calculations using numerical atomic orbitals as basis sets. We have analyzed the relative stability of several $C_{60-x}Si_x$ isomers, with $x=1$, 2, 3, 6, and 12. We find that, for $x=3$ and 6, the Si atoms strongly ''prefer'' to be first neighbors of each other, in order to minimize the number of Si-C bonds. However, these configurations of lower energy present a few relatively weak Si-C and Si-Si bonds that could indicate possible breaking paths. For a better comparison with the experimental measurements, we have also considered some positively charged ions, and report the differences between properties of these ions and the corresponding neutral molecules.

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I. INTRODUCTION

In recent years many experimental and theoretical efforts have been devoted to the study of endohedrally,[1] exohedrally,[2] and substitutionally[3] doped fullerenes, due to the interest in synthesizing fullerene-based materials with specific physical and chemical properties. In the case of substitutional doping, many transition-metal atoms, such as Fe, Ni, Co, Rh, and Ir, have been successfully incorporated into the fullerenes.[3] There is also a strong experimental indication for the existence of lanthanum and niobium substituted heterofullerenes.[4] Experimental and theoretical[5,6] works also provided evidence of the incorporation of nitrogen and up to six boron atoms.

Besides the previously mentioned atoms, silicon seems to be a good candidate to consider for substitutional doping, as it is in the same group of carbon in the Periodic Table. But the fact that Si strongly ''prefers'' to form tetrahedral bonds should cause the Si-doped fullerenes to become unstable as the number of Si atoms is increased. However, ion mobility and mass spectroscopy[7,8] experiments revealed evidence of heterofullerenes containing one or two Si atoms, and recently photofragmentation[9] results indicated the presence of at least seven Si atoms in fullerene molecules. Therefore, it seems very interesting to do a first-principles study of these Si-doped fullerenes with more than one or two Si atoms to study the stability, structure, and electronic properties. The purpose of this work is to address theoretically, using density-functional electronic structure calculations with numerical atomic orbitals, the following issues.

(1) As mass spectroscopy and photofragmentation experiments[8,9] observe positively charged fullerene ions but almost all theoretical approaches deal with neutral Si-doped molecules,[8,10] we ask whether there is any relevant difference between the neutral molecule and the charged one.

(2) According to photofragmentation experiments, Si_3C evaporating clusters are abundantly detected.[9] Therefore, heterofullerenes with three or more Si atoms must be present. This fact motivated us to investigate the stability of several isomers of $C_{57}Si_3$. Which is the energetically most favorable way to arrange three Si atoms in a fullerene cage? And what are the atomic-scale and electronic origin of its stability?

(3) Based on our study of $C_{60-x}Si_x$, with $x<4$, we try to answer the following question: Is it possible to find a large number of Si atoms ($x>4$) substituting in the carbon fullerene structure? And in which way is the original cage structure affected?

This paper is organized as follows: Section II gives a brief description of the method of calculation used and the approximations made. Section III shows the results, and it is divided into three subsections: In Sec. III A we report our results for nine isomers of $C_{58}Si_2$ which are in excellent agreement with those of other first-principles studies.[8,10] Similarities and differences between neutral and positively charged molecules are described. Section III B gives the relative stability, structural, and electronic properties of some $C_{57}Si_3$ molecules. Section III C provides theoretical evidence for the possibility to substitute up to 12 Si atoms in the carbon fullerene cage. In Sec. IV the final conclusions are presented.

II. METHOD OF CALCULATION

Ab initio calculations were performed using a numerical-atomic-orbital density-functional-theory method described in detail elsewhere,[11] and implemented in the SIESTA code. It has already been applied to large fullerene molecules and nanotubes[12] and many other systems.[13] The calculations are done using the local-density approximation for the exchange correlation, as parametrized by Perdew and Zunger.[14] Core electrons are replaced by nonlocal, norm-conserving pseudopotentials[15] factorized in the Kleinman-Bylander form,[16] whereas valence electrons are described using linear combinations of numerical pseudoatomic orbitals, of the Sankey-Niklewski type,[17] but generalized for mutiple-ζ and polarization functions.[18] In this work we have used a split-valence triple-ζ basis set[18] (that is, three orbitals with different radial form for each s and p orbital of both Si and C atoms). These pseudoatomic orbitals are calculated with the boundary condition that they vanish outside a given r_c, and are therefore slightly excited. The cutoff is fixed by the ''energy shift'' parameter (the change in the eigenstate in the free atom due to the confinement), which we took in this work as 0.2 eV.[18] For a calculation of the self-consistent Hamiltonian matrix elements, the charge density is represented in a regular real space grid of 0.15 Å, equivalent to a cutoff of 100 Ry using a plane-wave basis.

The Hamiltonian matrix is solved by straight diagonalization, and the relaxed atomic structures of the molecules are obtained by a minimization of the total energy by means of the Hellman-Feynman forces, including Pulay-like corrections (to account for the incompleteness of the basis set and the fact that the orbitals move with the atoms). Structural optimizations were performed using the conjugate gradient algorithm until the residual forces in the optimization are smaller than 0.04 eV/Å. Periodic boundary conditions have

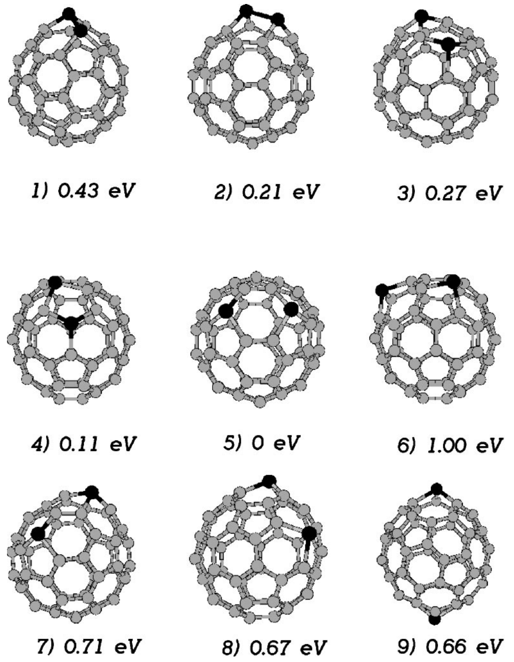

FIG. 1. Isomers of $C_{58}Si_2$ studied. The total energies are given relative to the lowest-energy isomer.

TABLE I. Calculated structural properties of neutral and single positively charged C_{60}, $C_{59}Si$, and $C_{58}Si_2$. First neighbor distances Si-Si, Si-C, and C-C are given in Å; in each case minimum and maximum values are shown. R(Si) indicates the distance of the Si atoms to the original C_{60} molecule center.

		Neutral				Charged		
	Si-Si	Si-C	C-C	R(Si)	Si-Si	Si-C	C-C	R(Si)
C_{60}			1.45 ph				1.45 ph	
			1.40 hh				1.40 hh	
$C_{59}Si$		1.85 ph	1.44–1.48 ph	4.27		1.84 ph	1.44–1.49 ph	4.23
		1.79 hh	1.40–1.42 hh			1.79 hh	1.40–1.43 hh	
$C_{58}Si_2$								
(1)	2.18 hh	1.84 ph	1.46 ph	4.45	2.22 hh	1.84 ph	1.44–1.51 ph	4.45
			1.40–1.41 hh				1.40–1.41 hh	
(2)	2.24 ph	1.87 ph	1.44–1.47 ph	4.47	2.26 ph	1.86 ph	1.44–1.48 ph	4.48
		1.80 hh	1.40–1.41 hh			1.80 hh	1.40–1.42 hh	
(3)		1.83–1.88 ph	1.43–1.45 ph	4.27		1.81–1.88 ph	1.43–1.50 ph	4.24
		1.78–1.81 hh	1.40–1.41 hh			1.78–1.82 hh	1.40–1.43 hh	
(4)		1.84–1.88 ph	1.44–1.48 ph	4.25		1.83–1.88 ph	1.44–1.48 ph	4.23
		1.77 hh	1.40–1.41 hh			1.78 hh	1.40–1.42 hh	
(5)		1.84–1.87 ph	1.43–1.45 ph	4.23		1.83–1.87 ph	1.43–1.48 ph	4.18
		1.81 hh	1.40–1.41 hh			1.81 hh	1.39–1.42 hh	
(6)		1.83–1.84 ph	1.44–1.47 ph	4.26		1.83–1.84 ph	1.45–1.50 ph	4.24
		1.79 hh	1.40–1.41 hh			1.79 hh	1.39–1.44 hh	
(7)		1.84–1.85 ph	1.45–1.47 ph	4.27		1.84–1.86 ph	1.45–1.49 ph	4.25
		1.78–1.80 hh	1.40–1.42 hh			1.79–1.80 hh	1.40–1.44 hh	
(8)		1.84–1.85 ph	1.44–1.48 ph	4.25		1.84 ph	1.45–1.48 ph	4.22
		1.79 hh	1.40–1.42 hh			1.79 hh	1.40–1.42 hh	
(9)		1.85 ph	1.44–1.48 ph	4.30		1.84 ph	1.45–1.49 ph	4.26
		1.79 hh	1.40–1.42 hh			1.79 hh	1.40–1.42 hh	

TABLE II. Electronic properties of neutral and single positively charged C_{60}, $C_{59}Si$, and $C_{58}Si_2$ molecules. $q(\mathrm{Si})$, and $q(\mathrm{C})$ are the net charges of Si atoms and their first C neighbors, respectively; in each case maximum and minimum values are given. P is the electric dipole in atomic units, e*bohr

			Neutral				Charged		
	$q(\mathrm{Si})$	$q(\mathrm{C})$	Bond order	Gap (eV)	P (a.u.)	$q(\mathrm{Si})$	$q(\mathrm{C})$	Bond order	Gap (eV)
C_{60}			0.46 C-C ph 0.52 C-C hh	1.78	0			0.46 C-C ph 0.52 C-C hh	1.78
$C_{59}Si$	0.23	-0.11	0.38 Si-C ph 0.46 Si-C hh	1.32	0.25	0.35	-0.10	0.38 Si-C ph 0.43 Si-C hh	1.27
$C_{58}Si_2$									
(1)	0.16	-0.11	0.46 Si-Si hh 0.39 Si-C ph	0.63	0.69	0.28	-0.12	0.41 Si-Si hh 0.39 Si-C ph	0.52
(2)	0.14	-0.12	0.38 Si-Si ph 0.38 Si-C ph 0.45 Si-C hh	1.07	0.49	0.25	-0.12	0.36 Si-Si ph 0.38 Si-C ph 0.43 Si-C hh	0.98
(3)	0.23	$-0.10, -0.21$	0.39 Si-C ph 0.44 Si-C hh	1.21	0.49	0.33	$-0.14, -0.21$	0.35–0.40 Si-C ph 0.41–0.44 Si-C hh	1.18
(4)	0.23	$-0.11, -0.23$	0.38 Si-C ph 0.47 Si-C hh	1.28	0.54	0.33	$-0.09, -0.23$	0.36–0.40 Si-C ph 0.45 Si-C hh	1.29
(5)	0.22	-0.10	0.38 Si-C ph 0.44 Si-C hh	0.83	0.49	0.33	-0.11	0.37–0.40 Si-C ph 0.42 Si-C hh	0.80
(6)	0.23	-0.11	0.38 Si-C ph 0.45 Si-C hh	1.09	0.39	0.33	-0.10	0.38 Si-C ph 0.44 Si-C hh	1.10
(7)	0.24	-0.11	0.38 Si-C ph 0.45 Si-C hh	1.25	0.42	0.33	-0.10	0.38 Si-C ph 0.44 Si-C hh	1.23
(8)	0.23	-0.12	0.38 Si-C ph 0.45 Si-C hh	1.16	0.39	0.33	-0.10	0.38 Si-C ph 0.44 Si-C hh	1.14
(9)	0.23	-0.11	0.38 Si-C ph 0.45 Si-C hh	1.15	0	0.33	-0.11	0.38 Si-C ph 0.44 Si-C hh	1.17

been adopted, using a simple cubic cell of 20 Å, that is large enough so that no significant spurious interactions with periodically repeated images are present.

For charged molecules, special consideration must be given to obtaining the correct value for the total energy, as the energy of a periodically repeated system with a net charge diverges. To solve this problem, we use the procedure proposed by Makov and Payne,[19] introducing a uniform background charge in the cell in order to make the total charge zero. In the limit of a very large cell, this approach would produce the same energy as an isolated system, but the convergence with cell size is slow. Introducing analytical correction terms for finite-size scaling[19] accelerates this convergence dramatically, and therefore we have used these corrections in this work.

III. RESULTS

A. $C_{58}Si_2$ and the corresponding positive ions

The first step of our calculations was to obtain the optimal structures of molecules C_{60}, $C_{59}Si$, and the same nine isomers of $C_{58}Si_2$ studied by Billas *et al.*[10] (see Fig. 1). We found our results to be in very good agreement with previous *ab initio* studies,[8,10] and therefore report only briefly some of the calculated properties.

The total binding energy of the molecules $C_{59}Si$ and $C_{58}Si_2$ is smaller than that of C_{60} by 5.77 eV and around 11.14 eV, respectively. The relative energy of the different $C_{58}Si_2$ isomers is indicated in Fig. 1, the most stable isomer (5) being the one having two Si atoms located as third neighbors in a hexagon.

The bond lengths of nearest-neighbor atoms for ph (pentagon-hexagon) and hh (hexagon-hexagon) bonds are given in Table I, as well as $R(\mathrm{Si})$, the distance of the Si atoms to the center of the cubic unit cell, where the original C_{60} molecule before doping was centered. This is to be compared with 3.55 Å, the radius of C_{60}, and it is clear that in all cases the Si atoms tend to ‘‘pop out’’ from the original molecule. The bond lengths of ph bonds deviate more from the original values (approximately 2%) than those of the stronger hh bonds, but in all cases the conjugation pattern of C-C bonds is preserved.

In Table II we show the net Mulliken charge of the Si atoms and their nearest-neighbor C atoms. There is a clear charge transfer from Si to C, and charge rearrangement among the C atoms. In the case of $C_{59}Si$ the group of Si and its three first C neighbors has a total net charge of $-0.1e$. Therefore, a charge of $0.1e$ is uniformly distributed among the rest of the C atoms. This polar character of the Si-C

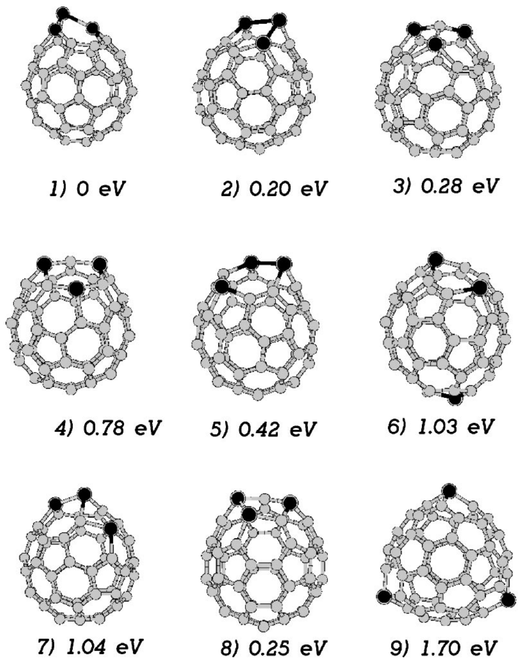
1) 0 eV
2) 0.20 eV
3) 0.28 eV
4) 0.78 eV
5) 0.42 eV
6) 1.03 eV
7) 1.04 eV
8) 0.25 eV
9) 1.70 eV

FIG. 2. Isomers of $C_{57}Si_3$ studied.

bonds produces an electric dipole (P) in the silicon-doped fullerenes which amounts to 0.25 a.u. in $C_{59}Si$, and it is maximum (0.69 a.u.) for configuration (1) of $C_{58}Si_2$, where the Si atoms are close together.

Also shown in Table II are the bond orders, or off-diagonal elements, of the Mulliken overlap population matrix, which are proportional to the bond strength between different atoms.[20] For C_{60} we have obtained bond orders of 0.46 for ph and 0.52 for hh bonds. These values are in between those of the single bond in the diamond structure (0.37) and the double bond in the molecule C_3 (0.82). Isomers (1) and (2) are the only ones containing Si-Si bonds for $C_{58}Si_2$. The bond order is 0.38 for the ph bond in isomer (2) (slightly larger than the value of 0.32 in bulk Si), and 0.46 for the hh bond in isomer (1) (in between that of bulk Si and the Si_2 molecule, of 0.62). For Si-C bonds, as indicated in Table II, we obtain 0.38 for ph bonds, and about 0.46 for hh bonds (equal to those in Si-Si bonds), to be compared to the values of 0.33 in crystalline SiC with zinc-blende structure, and 0.74 in the SiC molecule. All the results quoted were obtained with the same method and basis set. By a more careful examination of isomer (5), the most stable $C_{58}Si_2$ configuration, we observe that it has a Si-C hh bond length (1.81 Å) longer than average and closer to the Si-C single bond length of 1.83-1.90 Å.[21] The release of stress by local deformation is also revealed by the smaller value of $R(\mathrm{Si})$. This does not happen in isomers (1) and (2), because in those cases there is a strong Si-Si repulsion giving bond lengths of 2.18 and 2.24 Å, respectively: quite small values compared to the bonding distance in bulk Si, of 2.345 Å. We observe similarities in many properties like bond length, net charge, and bond orders between $C_{58}Si_2$ isomers (6), (7), (8), and (9) and $C_{59}Si$, which implies that the influence of the substitutional Si atoms in the fullerene network is quite local, not exceeding a shell of fourth neighbors.

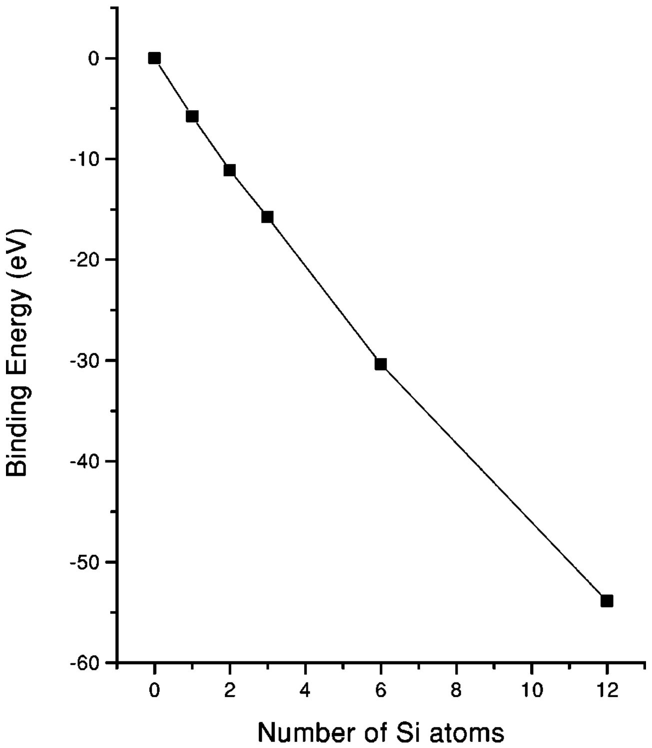

FIG. 3. Total binding energy of $C_{60-x}Si_x$ as function of the number of Si atoms in the fullerene x, minus the total binding energy of a fullerene molecule C_{60}.

It is interesting to compare the neutral fullerenes considered above with their corresponding single-positively charged ions (Tables I and II). In $C_{60}{}^+$ the single charge is uniformly distributed among 60 C atoms, and there is no appreciable Jahn-Teller distortion detected. In $C_{59}Si^+$ a positive charge of 0.1e is concentrated in the Si atom, while 0.9e is distributed in the other C atoms (0.015e each). This induces a change of distance between positive and negative charge centers in the molecule, and causes an increase of electric dipole. The net charge of the C atoms that are first neighbors of Si remain the same. The Si to molecule center distance $R(\mathrm{Si})$ decreases, and this is also seen in all $C_{58}Si_2{}^+$ isomers except (1) and (2). This effect can be explained as a global decrease in bond strength, revealed by a general decrease of the bond orders, especially of hh bond orders in charged fullerenes (Table II), that allows the Si atoms to accommodate better in the C network.

The relative energies (in eV) of the nine $C_{58}Si_2{}^+$ isomers from (1) to (9) are 0.48, 0.39, 0.43, 0.21, 0.00, 1.17, 0.95, 0.90, and 0.84, having the same ordering of their neutral partners, but presenting greater differences among them. There is more dispersion in Si-C and C-C bond lengths and bond orders; the Si-Si bonds are longer, in agreement with the decrease of Si-Si bond orders.

The calculated highest-occupied–lowest-unoccupied molecular-orbital(HOMO-LUMO) gap for C_{60} is 1.78 eV, in good agreement with the experimental value of 1.9–2.5 eV.[22] The HOMO and LUMO energy levels are strongly localized in the Si atoms due to the partially ionic character

TABLE III. Calculated structural and electronic properties of neutral and single positively charged $C_{57}Si_3$. First-neighbor distances Si-Si, Si-C, and C-C are given in Å, and $R(\mathrm{Si})$ indicates the distance of the Si atoms to the original C_{60} molecule center. $q(\mathrm{Si})$ and $q(\mathrm{C})$ are the net charges of Si atoms and their first C neighbor, respectively, and P is the molecular electric dipole in atomic units. In all cases minimum and maximum values are given.

	Si-Si	Si-C	C-C	$R(\mathrm{Si})$	$q(\mathrm{Si})$	$q(\mathrm{C})$	Bond order	Gap (eV)	P (a.u.)
$C_{57}Si_3$									
(1)	2.37 ph	1.84–2.04 ph	1.44—1.49 ph	5.18	0.26	−0.10, −0.26	0.32 Si-Si ph	0.73	0.65
	2.30 hh	1.80 hh	1.40—1.41 hh	4.28	0.07		0.39 Si-Si hh		
				4.11	0.16		0.31–0.39 Si-C ph		
							0.43 Si-C hh		
(2)	2.29 ph	1.87 ph	1.44—1.48 ph	4.30(2)	0.10(2)	−0.07, −0.15	0.39 Si-Si ph	0.60	0.70
		1.77—1.87 hh	1.40—1.41 hh	4.88	0.14		0.36 Si-C ph		
							0.40–0.46 Si-C hh		
(3)		1.82—1.86 ph	1.44–1.46 ph	4.25(2)	0.25(2)	−0.09, −0.29	0.37–0.41 Si-C ph	1.25	0.95
		1.76–1.79 hh	1.40–1.42 hh	4.19	0.26		0.46 Si-C hh		
(4)		1.82–1.85 ph	1.44–1.49 ph	4.28(3)	0.25(3)	−0.12, −0.20	0.38–0.40 Si-C ph	1.28	0.87
		1.79 hh	1.40–1.43 hh				0.45 Si-C hh		
(5)	2.26 hh	1.81–1.94 ph	1.45–1.49 ph	4.24	0.19	−0.12, −0.21	0.41 Si-Si hh	0.83	0.76
		1.79 hh	1.40–1.41 hh	4.71	0.22		0.35–0.39 Si-C ph		
				4.16	0.26		0.44 Si-C hh		
(6)		1.84–1.87 ph	1.43–1.47 ph	4.25(2)	0.22(2)	−0.08, −0.12	0.37–0.40 Si-C ph	0.77	0.28
		1.79–1.81 hh	1.40–1.42 hh	4.32	0.23		0.44–0.45 Si-C hh		
(7)	2.21 hh	1.82–1.98 ph	1.44–1.51 ph	4.21	0.22	−0.10, −0.32	0.45 Si-Si hh	0.91	0.53
		1.76 hh	1.40–1.42 hh	4.80	0.24		0.33–0.39 Si-C ph		
				4.20	0.21		0.47 Si-C hh		
(8)	2.30 ph	1.85–1.86 ph	1.44–1.48 ph	4.24	0.24	−0.11, −0.22	0.37 Si-Si ph	0.99	0.80
		1.77–1.79 hh	1.40–1.41 hh	4.47(2)	0.15(2)		0.38–0.39 Si-C ph		
							0.46-0.47 Si-C hh		
(9)		1.85 ph	1.44–1.48 ph	4.31(3)	0.23(3)	−0.12	0.38 Si-C ph	1.25	
		1.79 hh	1.40–1.42				0.46 Si-C hh		
$C_{57}Si_3^+$									
(1)	2.36 ph	1.83–2.03 ph	1.44–1.48 ph	5.22	0.37	−0.10, −0.27	0.33 Si-Si ph	0.71	
	2.32 hh	1.82 hh	1.40–1.41 hh	4.22	0.15		0.36 Si-Si hh		
				4.14	0.19		0.30–0.37 Si-C ph		
							0.39 Si-C hh		

of Si-C bonds. The first ionization energies calculated for C_{60}, $C_{59}Si$, and $C_{58}Si_2$ are 7.24, 6.93, and 6.85 eV, respectively, to be related to the laser power used in mass spectroscopy and photofragmentation experiments to ionize the samples, 6.4 eV.[9]

B. $C_{57}Si_3$

Here we report an *ab initio* study of different $C_{57}Si_3$ isomers, shown in Fig. 2. In configurations (1) and (2) the three Si atoms are arranged as first neighbors in a hexagon and a pentagon, respectively. In cases (3) and (4) they are second neighbors, and in cases (5) and (6) the optimal configuration of two substitutional Si atoms is used and the other Si atom is either a first neighbor or occupies the opposite position. In cases (7) and (8) the second, more stable, configuration of $C_{58}Si_2$ is used and the other Si is a first neighbor in a hh or ph bond, respectively. Finally in case (9) we have the three Si atoms distributed as far away as possible from each other. The relative energies are indicated in the figure. The energetically more favorable isomer is (1), and the highest energy isomer is (9), their energy difference being 1.71 eV. The total binding energy of these isomers is about 15.75 eV smaller than that of C_{60} (Fig. 3). Because the deformation introduced by the dopant Si atoms is local, we have not considered isomers with Si atoms beyond third neighbors of each other: we expect their properties to be quite similar to those of paraisomer (9).

In Table III we show some structural and electronic properties. We see that the Si-Si bond lengths are larger than those in $C_{58}Si_2$, especially in the most stable isomer (1). They are 2.37 Å in the ph bond and 2.30 Å in the hh bond, very close to the value of 2.35 Å in bulk Si single bonds. This case also presents longer Si-C bonds, of 1.84–2.04 Å in the ph bond and 1.80 Å in the hh bond. Clearly the stronger single bond character of Si-Si and Si-C is one of the reasons for its stability. However, it is interesting to point out that, in spite of being energetically favorable, it shows a weak bond order of 0.32 in the Si-Si ph bond, and one of 0.31 in the Si-C ph bond, suggesting the possibility of evaporating Si_3C or Si_2C_2 clusters, as detected in recent photofragmentation experiments.[9]

There is charge transfer from Si to its first C neighbors, but there is also a charge redistribution among the Si atoms when they are nearest neighbors, as in cases (1) and (2). In all cases except (4) and (9) the Si net charge $q(\mathrm{Si})$ and the distance $R(\mathrm{Si})$ are different for each Si atom, because of the lack of third-order symmetry and consequent environmental differences.

These molecules have a band gap ranging from 0.60 to 1.28 eV. The two lowest-energy configurations (1) and (2) have rather small gaps, of 0.73 and 0.60 eV, respectively. Considering the different isomers studied, we do not find the gap to be a parameter directly related to the molecular stability.

In these Si-doped fullerenes the original fivefold and threefold degeneracies present in the C_{60} HOMO and LUMO are generally removed, with a greater splitting in the LUMO. One level is shifted down in most cases, and a maximum separation of 0.7 eV is found in isomer (2). However, isomers that preserve C_3 symmetry like (3), (4), and (9) present larger gaps of 1.25, 1.28, and 1.28 eV, respectively. In all cases energy levels around the HOMO and LUMO are strongly localized in Si and their C neighbor atoms.

The $C_{57}Si_3{}^+$ ion is studied only in the most favorable configuration (1). There is an increase of Si-Si and Si-C hh bond lengths when compared with the neutral molecule, and a decrease of about 8% in the corresponding bond orders (see Table III). The total net charge of the three Si atoms is $0.71e$ instead of $0.49e$ in the neutral case; therefore, a charge of $0.22e$ is concentrated in the Si atoms. The net charges of C atoms remain almost the same, so that the amount of charge transferred from Si to neighbor C atoms is identical to that in the neutral molecule. The ionization energy is 6.60 eV.

In conclusion, we note a strong tendency of Si atoms to be located as closely together as possible. This is due to several reasons: (a) Si atoms that are close to each other may create a local quasitetrahedral environment, showing longer bond lengths as in Si bulk structure. (b) The total number of Si-Si and Si-C bonds is smaller, which implies fewer C atoms perturbed by the presence of Si atoms. For example, in (1) there are two Si-Si bonds and five Si-C bonds, while in (9), the highest-energy isomer, there are nine Si-C bonds and the molecule is globally more deformed than in (1). As C-C bonds are much stronger than C-Si and Si-Si bonds, there is an important energy gain.

C. $C_{60-x}Si_x$ with $x>3$

Motivated by the possible existence, confirmed by recent experimental data,[9] of $C_{60-x}Si_x$ with x as large as 7, we have investigated some selected $C_{54}Si_6$ isomers based on our experiences with $C_{58}Si_2$ and $C_{57}Si_3$. We have studied the six configurations shown in Fig. 4. In isomers (1) and (2) the Si atoms are first neighbors in a hexagon and in a pentagon with another Si nearest neighbor, respectively. Configurations (3) and (4) have the Si atoms arranged in two groups of three atoms each, in the optimal configuration of $C_{57}Si_3$. In (5) there are three groups of two Si atoms in the optimal configuration of two substitutional Si atoms, and (6) is a paraisomer with six Si atoms distributed as far as possible (fifth neighbors) from each other. The total binding energy of these fullerenes is about 30.37 eV smaller (Fig. 3) than that of C_{60}. The relative energies (in eV) are 0.00, 0.50, 2.28, 3.51, 3.55, and 6.54, respectively. Isomer (1) is the lowest-energy configuration, and isomer (9) is the highest one, separated by 6.54 eV.

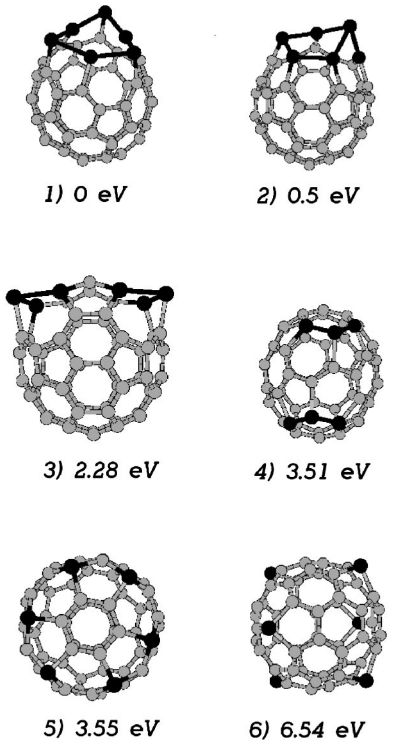
1) 0 eV
2) 0.5 eV
3) 2.28 eV
4) 3.51 eV
5) 3.55 eV
6) 6.54 eV

FIG. 4. Isomers of $C_{48}Si_{12}$ studied.

The lowest-energy isomer has Si-Si and Si-C bonds with a clear single bond character (2.32–2.34 and 1.86–1.94 Å, respectively). The conjugate pattern of C-C bonds is preserved, with two well-defined ph and hh bond lengths, which is a sign of relatively small cage deformation, and contributes to its stability. However, the hexagon of Si atoms is quite distorted, almost forming a triangle but conserving the C_3 symmetry. The Si atoms are arranged in an alternating up-down pattern with $R(\mathrm{Si})$ of 5.05 and 4.30 Å. In this way they accommodate themselves in order to achieve ideal Si-Si bond lengths. There is charge transfer from Si to C as in other cases, but also a charge transfer from up Si atoms to down Si atoms. The Si-Si 0.35–0.38 bond order and Si-C 0.35 bond order are close to those in tetrahedral structures (0.32–0.33). If we assume that the molecule breaks up where the bond order is 0.35 and not where it is 0.38 (Table IV), this fullerene may evaporate Si_2C_2 or Si_3C small clusters, as suggested by the experiments.[9] There are six bond Si-Si and six Si-C bonds in this configuration, in contrast to 18 Si-C bonds in the highest-energy isomer (6). Again the smaller number of Si-Si and Si-C bonds favor the energetic stability.

TABLE IV. Same as Table III for $C_{54}Si_6$ and $C_{48}Si_{12}$.

	Si-Si	Si-C	C-C	R(Si)	q(Si)	q(C)	Bond order	Gap (eV)	P (a.u.)
$C_{54}Si_6$									
(1)	2.34 ph	1.86–1.94 ph	1.44–1.47 ph	5.05(3)	0.21(3)	−0.10, −0.22	0.35 Si-Si ph	1.07	0.33
	2.32 hh		1.40–1.41 hh	4.30(3)	0.01(3)		0.38 Si-Si hh		
							0.35 Si-C ph		
(2)	2.29–2.45 ph	1.86 ph	1.44–1.48 ph	5.63	0.21	−0.11	0.30−0.39 Si-Si ph	0.64	1.00
	2.32 hh	1.80 hh	1.40–1.43 hh	4.45(2)	−0.06(2)		0.40 Si-Si hh		
				4.72(2)	0.06(2)		0.35 Si-C ph		
				4.14	0.11		0.43–0.45 Si-C hh		
(3)	2.35 ph	1.83–2.00 ph	1.44–1.51 ph	4.08(2)	0.14(2)	−0.10, −0.23	0.33 Si-Si ph	0.61	0.93
	2.31 hh	1.80 hh	1.40–1.44 hh	5.14(2)	0.25(2)		0.39 Si-Si hh		
				4.22(2)	0.10(2)		0.34–0.39 Si-C ph		
							0.42 Si-C hh		
(4)	2.36 ph	1.82–2.04 ph	1.45–1.52 ph	4.10(2)	0.27(2)	−0.11, −0.25	0.32 Si-Si ph	0.67	1.00
	2.30 hh	1.80 hh	1.40–1.42 hh	4.29(2)	0.08(2)		0.38 Si-Si hh		
				5.18(2)	0.14(2)		0.31–0.36 Si-C ph		
							0.42 Si-C hh		
(5)		1.83–1.90 ph	1.41–1.46 ph	4.20(6)	0.21(6)	−0.07, −0.23	0.36–0.41 Si-C ph	0.63	1.19
		1.79 hh	1.39–1.42 hh				0.45 Si-C hh		
(6)		1.84 ph	1.44–1.48 ph	4.27(6)	0.23(6)	−0.12	0.38 Si-C ph	0.74	0
		1.79 hh	1.39–1.44 hh				0.44 Si-C hh		
$C_{54}Si_6^+$									
(1)	2.34 ph	1.86–1.93 ph	1.44–1.49 ph	5.05(3)	0.04(3)	−0.10, −0.22	0.34 Si-Si ph	1.07	
	2.32 hh		1.40–1.41 hh	4.32(3)	0.29(3)		0.37 Si-Si hh		
							0.34–0.36 Si-C ph		
$C_{48}Si_{12}$									
(1)	2.31–2.38 ph	1.87 ph	1.44–1.45 ph	5.50(3)	0.16(3)	−0.05, −0.21	0.36–0.40 Si-Si ph	0.56	1.32
	2.34 hh	1.80–1.82 hh	1.39–1.41 hh	4.70(3)	0.08(3)		0.37 Si-Si hh		
				4.48(3)	−0.11(3)		0.38 Si-C ph		
				4.25(3)	0.15(3)		0.43 Si-C hh		
$C_{48}Si_{12}^+$									
(1)	2.31–2.40 ph	1.84–1.85 ph	1.44–1.47 ph	5.54(3)	0.22(3)	−0.05, −0.21	0.34–0.40 Si-Si ph	0.48	
	2.34 hh	1.81–1.82 hh	1.39–1.42 hh	4.74(3)	−0.11(3)		0.36 Si-Si hh		
				4.40(3)	0.21(3)		0.38 Si-C ph		
				4.24(3)	0.12(3)		0.42 Si-C hh		

The HOMO is twofold degenerate, and is localized in C atoms near the Si atoms and to a lesser extent in the up Si atoms, the HOMO-1 level has only carbon character, and the HOMO-2 level is concentrated in the up Si atoms. On the other hand, the LUMO level is localized in the down Si atoms; and in a smaller proportion in the up Si atoms (Fig. 5). Its ionization energy is 6.83 eV.

The second most favorable configuration (2) is 0.5 eV above isomer (1), and also shows an up-down alternating pattern in the Si pentagon, but this oscillation pattern is frustrated. There is one up Si atom, two down atoms, and two intermediate atoms with net charges of $0.21e$, $-0.06e$, and $0.06e$, respectively. There is again not only a charge transfer from Si to C atoms, but also among Si atoms. In this configuration the Si-Si and Si-C bonds also have a strong single bond character, but the frustrated arrangement is a possible reason for the instability compared to isomer (1). The bond orders suggest evaporation of Si_2C_2 as follows: two Si atoms hh-bind with their C first neighbors, and two groups each containing two ph-bound Si atoms (bond order of 0.39) and their C neighbors, weakly bonded with each other (the bond order is 0.34).

The charged partner of isomer (1) $C_{54}Si_6{}^+$ has similar structural properties to those of the neutral molecule (see Table IV). The group of six Si atoms has a total net charge of $0.99e$ instead of $0.66e$, while there is the same amount of charge transferred from the Si atoms to their C neighbors.

Unlike $C_{58}Si_2$ and $C_{57}Si_3$, the two characteristic ph and hh C-C bonds are no longer well defined, except in isomer (1) where the Si atoms are close enough to each other, as

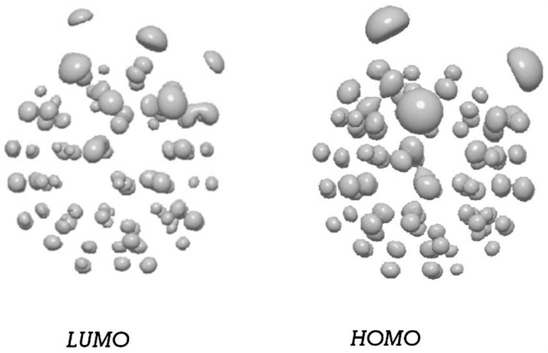

FIG. 5. Isosurfaces for the density of states in the proximity of the Fermi energy.

indicated in Table IV. This fact suggests that six Si dopant atoms may cause considerable deformation in the fullerene cage, except when they are located close enough.

To consider an extreme case of a large number of substitutional Si atoms, we have studied one isomer of $C_{48}Si_{12}$ and its positively charged ion, whose existence is suggested by photofragmentation experiments.[9] This isomer has six Si atoms arranged in a hexagon as in the lowest-energy configuration of $C_{54}Si_6$, and the other six Si atoms as their first neighbors in an outer shell (Fig. 6).

This structure is surprisingly stable, with the C-C bond lengths only slightly perturbed, as shown in Table IV. The Si atoms accommodate so as to form nearly tetrahedral bonds, presenting, in the first shell of six atoms (originally a hexagon), a triangular geometry similar to that of the $C_{54}Si_6$ case. The total Si net charge is $0.84e$, and the C first neighbors have a net charge of opposite sign (-0.05 to $-0.21e$) because of the Si to C charge transfer. The net charges of the different Si atoms are very different from each other. In the hexagon the up and down Si atoms have net charges of $0.15e$ and $-0.11e$, respectively; in the outer shell the first neighbor of up and down atoms have $0.08e$ and $0.16e$, respectively. According to bond order analysis there are only three strong ph Si-Si bonds, with a bond order of 0.40; the other ph or hh Si-Si bonds have bond orders around 0.36. A possible means of fragmentation would be by groups containing two Si atoms. This molecule shows a small gap of 0.56 eV; its total binding energy is 53.87 eV smaller than that of C_{60}, and the ionization energy is 6.00 eV. The most relevant difference between neutral and charged $C_{48}Si_{12}$ is the change in total net charge in the Si group from $0.84e$ in the neutral case to $1.32e$ in the positively charged one. It follows that $0.48e$ are in the Si atoms.

IV. CONCLUSIONS

We find that it is possible to substitute up to 12 Si atoms in the fullerene cage without deforming the original structure too much, in the sense that the two characteristic ph and hh C-C bond lengths are maintained. This surprising result corroborates the recent photofragmentation experimental evidences.

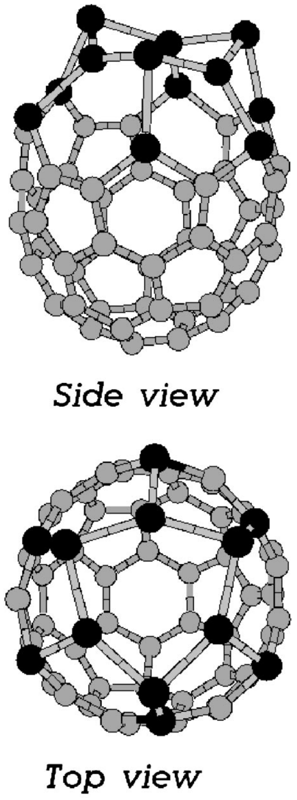

FIG. 6. Isomer of $C_{48}Si_{12}$ studied.

The best way to arrange the Si substitutional atoms is to have them as first neighbors, for cases having more than two Si atoms. In this way the Si atoms accommodate themselves to achieve desirable bond lengths, while the perturbation to the C atoms is minimized as the number of Si-C bonds is reduced. These configurations usually show some weaker bonds as, for example, in the $C_{57}Si_3$ isomer (1) and the $C_{54}Si_6$ isomer (2), indicating possible photofragmentation paths. Further finite-temperature molecular-dynamics simulations may be very useful to confirm these predictions from the bond order analysis.

Comparing neutral and positively charged molecules, no significant differences in structure or in the relative energy ordering between isomers is observed. Therefore, neutral fullerene studies are good aproximations to mass spectroscopy and photofragmentation results. Experiments using the molecular-beam deflection technique[23] can be used to compare the calculated and measured dipole moments. The present calculations give the dipole moment for the neutral molcules, and estimate that it will be larger in the positive ions, as they have a greater amount of charge localized in the Si atoms; therefore, the negative charge center will be at a longer distance from the positive one.

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