First principles study of the adsorption of C\textsubscript{60} on Si(111)

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The adsorption of C\textsubscript{60} on Si(111) has been studied by means of first-principles density functional calculations. A 2x2 adatom surface reconstruction was used to simulate the terraces of the 7\times7 reconstruction. The structure of several possible adsorption configurations was optimized using the \textit{ab initio} atomic forces, finding good candidates for two different adsorption states observed experimentally. While the C\textsubscript{60} molecule remains closely spherical, the silicon substrate appears quite soft, especially the adatoms, which move substantially to form extra C-Si bonds, at the expense of breaking Si-Si bonds. The structural relaxation has a much larger effect on the adsorption energies, which strongly depend on the adsorption configuration, than on the charge transfer.

Keywords: Density functional calculations, Fullerenes, Chemisorption

Recent studies using scanning tunneling microscopy (STM) have reported images that reveal intra-molecular features of C\textsubscript{60} molecules deposited, at very low coverages, on Si(100)-(2\times1)\textsuperscript{1} and Si(111)-(7\times7)\textsuperscript{2,3}. These observations are very interesting as they might be used to infer the orientation of the molecules 2, and other details of the bonding configuration. They also confirm the strong interaction of the fullerenes with these surfaces. Furthermore, in the images reported by Pascual et al.\textsuperscript{3} it is clear that there exist two types of molecules: “large” atomic forces with an apparent height of \approx 0.6 nm and width of \approx 2.0 nm, which appear more round and fuzzy in the constant current STM images, and “small” molecules with a height of \approx 0.5 nm and width of \approx 1.5 nm, which present a more clearly discernible internal structure and a larger variety of shapes. A similar observation of two different adsorption states has also been done by Yao et al\textsuperscript{1} on the Si(100)-(2\times1) substrate. Interestingly enough, after annealing at 870 K the “large” molecules evolve to “small” ones, indicating that they were probably in a weaker adsorption state.

In this paper we apply first-principles electronic structure methods to study the adsorption of fullerenes on the terraces of the Si(111)-(7\times7) reconstruction, identifying candidates for the two adsorption states observed. There are some previous electronic structure calculations of fullerenes over silicon substrates\textsuperscript{1,2,4,5}. However, in the sole case where a structural optimization was performed\textsuperscript{5}, a semi-empirical force field was used. Therefore, to the best of our knowledge this is the first systematic study of the adsorption geometry of C\textsubscript{60} on a silicon surface using \textit{ab initio} atomic forces.

The calculations have been performed with the SIESTA program\textsuperscript{6,7}, which allows standard calculations within density functional theory\textsuperscript{8} (DFT) for systems with hundreds of atoms. It uses norm-conserving pseudopotentials\textsuperscript{9}, and a basis set of numerical atomic orbitals, obtained from the solution of the atomic pseudopotentials at a slightly excited energy\textsuperscript{10}. In this work we have used the local density approximation to DFT\textsuperscript{11} and a minimal \textit{sp}\textsuperscript{3} basis set for both C and Si. With this basis, the Si-Si and C-C bond lengths differ only 1% and 2% from experiment, respectively. Our method also uses a real-space grid to compute the Hartree and the exchange correlation contributions to the self-consistent potential and the Hamiltonian matrix. Real and reciprocal-space integrations were performed with a 70 Ry-cutoff grid and with 2 inequivalent k-points. For a given basis set, these meshes guarantee a convergence better than \approx 1 meV/atom for the total energies and of \approx 0.1 eV for the C\textsubscript{60} binding energies\textsuperscript{12}.

The terraces of the Si(111)-(7\times7) surface have been modeled by slabs of two double layers, covered with a 2\times2 adatom reconstruction on one face, and saturated with hydrogen on the other face. The C\textsubscript{60} molecules are arranged in a \textit{2}\sqrt{3} \times \textit{2}\sqrt{3} periodic supercell, big enough to avoid strong interactions between them. First, we relax the structure of the clean surface with the lattice constant parallel to the surface fixed at the calculated bulk value, to avoid artificial stresses. The relaxed structure is similar to that of other authors\textsuperscript{13}. The distance between the pedestal atoms (restatoms bound to the adatoms) is reduced, and a strong downward relax-
reproduce the main features of the electronic structure of
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rest atom lies
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rest atom lies ∼0.4 Å higher than the ideal bulk height.
The main discrepancy with the results of Ref. [14] is that
the position of the adatoms is approximately 9% higher
in our case. This difference may be due to the use of
a minimal basis. However, this is not crucial, since we
are interested in the changes induced by the adsorption of
the C60, rather than in the surface itself. Our results also
reproduce the main features of the electronic structure of
the surface.

First we place the C60 molecule on top of one of the
rest atoms, with different orientations, suggested by the
STM images of Pascual et al. [3]. In one of them (labelled
Si) the molecule is oriented with an hexagon on top, to
preserve the threefold symmetry of the substrate. In the
other orientation, a C60 double-bond (DB) is placed
directly over the rest atom. Fig 2(a), shows the binding
energy as a function of the height of the center of mass
of the fullerene relative to the initial position of the rest
atom. If no internal relaxation of the molecule or the
surface are allowed, the binding energies are 0.64 eV and
1.47 eV for the S3 and DB configurations, respectively.
The DB molecule is more bound because it is lower and
closer to the rest atom.

We then investigate the structural changes, shown in
Fig 3, in both the surface and the molecule after the
adsorption, relaxing the atomic positions according to the
ab initio forces. The carbon atoms move very little
from their ideal positions, the molecule remains almost
spherical, and its height over the substrate decreases from
∼5.9 to 5.35 Å. In contrast, the three nearest adatoms
to the S3 molecule move substantially, approaching the
closest carbon atoms from ∼3.0 Å to 2.02 Å. The rest
atom below the molecule relaxes downward 0.61 Å, while
the pedestal atoms closer to the molecule relax upwards
0.08 Å, and their bond distance to the adatom decreases
from 2.57 Å to 2.51 Å. The pedestal atoms more distant
to the molecule relax upwards 0.24 Å, and their bond
length to the adatoms becomes 2.75 Å. The relaxation
energy is large, increasing the binding energy to 3.96 eV.

The case of the DB molecule in rather different. It
rotates during the relaxation, binding to the rest atom
and to two adatoms. The bond length with the adatoms is
2.01 Å, while the bond with the rest atom is a little
shorter (1.98 Å) and stronger (larger bond charges). The
relaxation of these atoms, and those bound to them, is
similar to that for the S3 molecule, but the displacements
are somewhat smaller. The deformation of the molecule
is again very small. The third adatom is largely displaced
towards the C60, but the large distance to the molecule
(2.63 Å), and the very low bond charge do not indicate
the formation of covalent bonding. Its displacement is
probably driven by the movement of the pedestal atoms,
and the ionic interaction with the negatively charged
molecule. The equilibrium height is reduced from ∼5.5 to
5.39 Å. The DB molecule has a binding energy of 5.96 eV,
quite larger than the S3 molecule. This difference is due
to the stronger bonds formed and to the somewhat less
strained surface.

Fig 4 shows data for two other relaxed structures.
The structure labelled as SB (not shown) has initially
a single-bond pointing towards the rest atom. Like the
DB structure, it forms, after the relaxation, a strong
covalent bond with the rest atom. However, in this
case the adatom more distant to the molecule suffers a
larger displacement, breaking its bond with one of the
pedestal atoms, and forming another covalent bond with
the fullerene. This fourth bond is longer (2.31 Å)
and weaker than the other three. In fact, in spite of the
formation of this extra-bond, the binding energy (5.93 eV)
and its height (5.41 Å) are almost identical to those of
the DB molecule. This indicates that the adatom most
loosely bound to the molecule can probably oscillate be-
tween two positions with the same energy: one where it
is covalently bound to the fullerene, and another where
the interaction with the molecule is mainly ionic.

The S3 configuration might be a good candidate for
the “large” (less stable) molecules observed by STM [3],
whose resolved internal structure present a triangular
shape [3], consistent with the threefold symmetry. The
DB and SB configurations are more bound to the sub-
strate, but their height is almost identical to that of S3.
Although STM does not directly measure the atomic
positions, our estimations, using the Tersoff-Hamann [13]
theory, also indicate a similar “electronic height” for the
DB and S3 configurations (∼6.8Å). A reasonable candi-
date for the “small” molecules should have a higher bind-
ing energy and a lower heigh over the substrate than
the structures studied to this point. The relaxed struc-
ture labelled L, which fulfills these conditions, is shown
in Fig. 3. This is just an example of the several config-
urations, with different molecular orientations, that can

FIG. 1. a) Binding energies of the C60 molecule on
Si(111)-(2×2), for different orientations, as a function of
the height of the molecular center of mass over the initial
position of the rest atom. b) Like (a), but for the charge trans-
fer. Open squares stand for the threefold-oriented unrelaxed
structure, and filled circles for the bond-oriented unrelaxed
configuration. The relaxed structures are labelled following
the text.
be obtained by allowing a larger rearrangement of the substrate than the structures previously studied. These new structures are characterized by a lower height, and the formation of more bonds between the molecule and the surface atoms. The L configuration has a binding energy of 6.36 eV (0.4 eV larger than the DB), its height is 4.56 Å (~0.8 Å lower than the other configurations). The molecule presents an hexagon on the top and occupies almost a “bridge” position between two adatoms. Each of these adatoms has a broken bond with the substrate, allowing for the formation of an extra-bond with the molecule (the new bonds have been highlighted in Fig. 3). The molecule has five bonds with the substrate, two with the adatoms (2.13 Å), two with the freed pedestal atoms (1.98 and 2.01 Å), and one with the rest atom (1.96 Å).

Our findings indicate that adsorption states like S$_3$, DB, or SB, can be accessed without overcoming any energetic barrier, in other words we have not found any physisorbed precursor for the adsorption of C$_{60}$ over Si(111). However, it must exist an energetic barrier between the “large” and “small” molecules observed experimentally, so both can be simultaneously visualized at room temperature. The nature of the barrier has been clarified by our calculations: some of the bonds of the adatoms with the substrate have to be broken to allow the formation of extra-bonds with the molecule. Only after annealing the sample the majority of the molecules are found in the lower configuration. It is also worth noting here that some recent evidence supports a strong rearrangement of the Si(111) surface upon the adsorption of C$_{60}$ [7]. In these experiments, after annealing one monolayer of C$_{60}$ at 670 K, the (7$x$7) diffraction pattern is lost and a (1$x$1) pattern appears in its place. This transition is accompanied by a change to a more strongly bound adsorption state of the molecules.

The values of the charge transfer, from the Si(111)-(7$x$7) substrate to the C$_{60}$, deduced from different experiment...
imental techniques, oscillate between $3\pm 1$ electrons [16], and $\sim 0.21$ electrons [17]. The theoretical calculations might be important to understand this discrepancy. The charge transfers reported here are obtained by Mulliken analysis [18]. Fig. 1(b) shows the evolution of the charge transferred to the molecule versus the distance to the rest atom. The charging of the molecule increases rapidly as the molecule approaches the surface. For the relaxed structures the charge transfers are: 1.00 electrons for the $S_3$, 0.94 and 0.97 for the DB and SB molecules, and 1.13 for the L configuration. Most of the transferred charge is in the atoms directly bound to the surface: 0.16-0.17 electrons in the carbon atoms bound to the rest atom, 0.12-0.14 electrons in those bound to the adatoms, and 0.16 in those bound to the pedestal atoms in the L molecule. The rest of the charge, $\sim 0.5$ electrons in all the cases, is mainly in the atoms closer to the surface, rather than uniformly distributed. This is an indication of the nature of the charge transfer. The charging of the molecule does not come through the occupation of the initially unoccupied states of the fullerene, but through the hybridization with the surface states. This result agrees with recent experimental reports of the transport through $C_{60}$ on Si(111) [3].

A previous calculation with the DV-Xα-LCAO method [6], has reported a considerably larger charge transfer of 3.35 electrons. We believe that this discrepancy stems from the inherent arbitrariness of the Mulliken analysis to split the charge to covalently bound atoms, which makes the results strongly dependent on the basis set used. However, we stress that both calculations agree on the general pattern of the charge transfer.

In conclusion, the adsorption of $C_{60}$ on Si(111)-(7×7) has been studied by ab initio density functional calculations. Different adsorption configurations have been explored, finding good candidates for the two adsorption states experimentally observed. The adsorption energies range between 4 and 6.5 eV, while the charge transfer is always very close to one electron and mainly localized on the carbon atoms bound to the substrate. Work is in progress to simulate the STM images of the different adsorption structure described in this paper. We hope this will allow a detailed comparison with the experiments. Molecular dynamics simulations are also in progress to explore the mechanism, and energetic barriers for the transition between different adsorption configurations.

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