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This is an **author produced version** of a paper published in:

Surface science 482 (2001): 39-43

[http://dx.doi.org/10.1016/S0039-6028\(00\)01008-6](http://dx.doi.org/10.1016/S0039-6028(00)01008-6)

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First principles study of the adsorption of C₆₀ on Si(111)

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The adsorption of C₆₀ 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 7x7 reconstruction. The structure of several possible adsorption configurations was optimized using the *ab initio* atomic forces, finding good candidates for two different adsorption states observed experimentally. While the C₆₀ 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 C₆₀ molecules deposited, at very low coverages, on Si(100)-(2×1) [1], and Si(111)-(7×7) [2–4]. 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.* [3] it is clear that there exist two types of molecules: “large” molecules with an apparent height of ~0.6 nm and width of ~2.0 nm, which appear more round and fuzzy in the constant current STM images, and “small” molecules with a height of ~0.5 nm and width of ~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.* [1] on the Si(100)-(2×1) 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)-(7×7) reconstruction, identifying candidates for the two adsorption states observed. There are some previous electronic structure calculations of fullerenes over silicon substrates [5,6,2]. However, in the sole case where a structural optimization was performed [6], 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 C₆₀ on a silicon surface using *ab initio* atomic forces.

The calculations have been performed with the SIESTA program [7,8], which allows standard calculations within density functional theory [9] (DFT) for systems with hundreds of atoms. It uses norm-conserving

pseudopotentials [10], and a basis set of numerical atomic orbitals, obtained from the solution of the atomic pseudopotentials at a slightly excited energy [8,11].* In this work we have used the local density approximation to DFT [12] and a minimal *sp*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 ~ 1 meV/atom for the total energies and of ~0.1 eV for the C₆₀ binding energies[†]

The terraces of the Si(111)-(7×7) surface have been modeled by slabs of two double layers, covered with a 2×2 adatom reconstruction on one face, and saturated with hydrogen on the other face. The C₆₀ molecules are arranged in a $2\sqrt{3} \times 2\sqrt{3}$ 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 [14]. The distance between the pedestal atoms (restatoms bound to the adatoms) is reduced, and a strong downward relax-

* We have used here an ‘energy shift’ of 0.5 eV. The corresponding radii are 4.65 and 5.73 a.u. for the *s* and *p* orbitals of Si, 3.79 and 4.41 in the case of C, and 4.26 for the *s* states of H.

[†] The binding energies have been corrected for the basis set superposition error as described, for example, in Ref. [13]

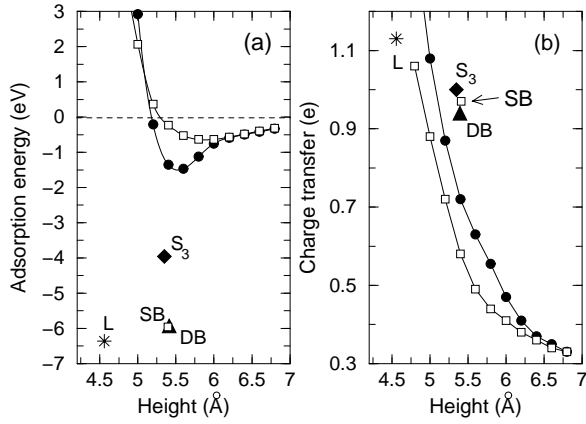


FIG. 1. a) Binding energies of the C₆₀ molecule on Si(111)-(2×2), for different orientations, as a function of the height of the molecular center of mass over the initial position of the rest atom. b) Like (a), but for the charge transfer. Open squares stand for the threefold-oriented unrelaxed structure, and filled circles for the bond-oriented unrelaxed configuration. The relaxed structures are labelled following the text.

ation for the atoms beneath the adatom is observed. The 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 S₃) 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 1(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 2, 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 is 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. 1 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 between 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 substrate, 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 [15] theory, also indicate a similar “electronic height” for the DB and S₃ configurations (~ 6.8 Å). A reasonable candidate for the “small” molecules should have a higher binding energy and a lower height over the substrate than the structures studied to this point. The relaxed structure labelled L, which fulfills these conditions, is shown in Fig. 3. This is just an example of the several configurations, with different molecular orientations, that can

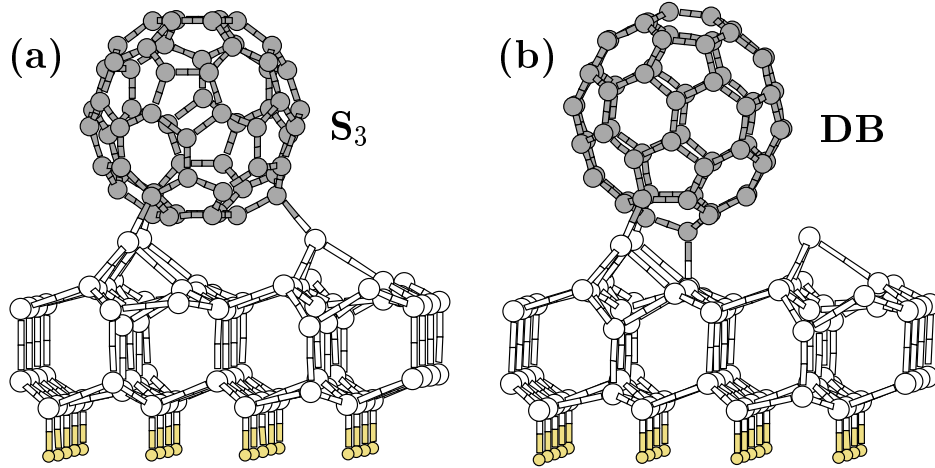


FIG. 2. Two different configurations of the C_{60} molecule adsorbed on the Si(111)-(2 \times 2) surface. a) Structure labelled as S_3 in the text, the molecule preserves the three fold symmetry of the substrate, presenting an hexagon on the top. b) DB structure which, after the relaxation, has formed a bond with the rest atom.

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} [17]. In these experiments, after annealing one monolayer of C_{60} at 670 K, the (7 \times 7) diffraction pattern is lost and a (1 \times 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 \times 7) substrate to the C_{60} , deduced from different exper-

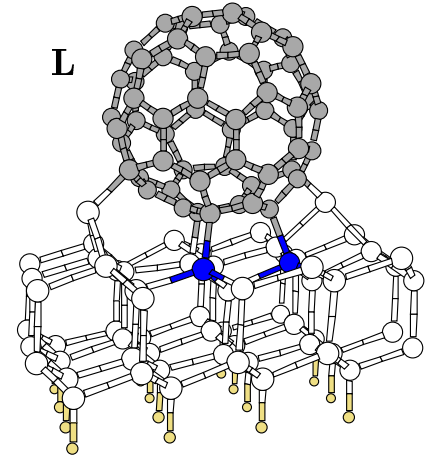


FIG. 3. Structure of the most stable adsorption configuration found in our calculations (labelled L). Two of the adatoms have broken their bonds with the corresponding pedestal atom (highlighted in the figure), allowing the formation of two extra bonds with the C_{60} molecule.

imental techniques, oscillate between 3 ± 1 electrons [16], and ~ 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, ~ 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- X_α -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 \times 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.

This work was supported by Grants No. DOE 8371494, and No. DEFG 02/96/ER 45439.

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