The bonding sites and structure of C_{60} on the Si(1 0 0) surface

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Abstract

The possible structures of C_{60} on the Si(1 0 0) surface have been investigated using ab initio total energy minimisations. The results show that fullerenes bond to the silicon surface by breaking carbon–carbon double bonds. One electron from the broken bond is contributed to the carbon–silicon bond. The second electron is generally involved in forming a new π-bond within the fullerene cage, or, for the less energetically favourable structures, is delocalised over the surrounding bonds. The carbon–silicon bond formed is primarily covalent with some charge transfer.
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1. Introduction

Buckminster fullerene, C_{60}, adsorbed on substrates is of interest both because of the fundamental science involved and because of possible applications of the system. One such potential application is a spin-based solid-state quantum computer. It has been proposed that such a device could be constructed from endohedrally doped fullerenes, the endohedral atom, the carrier of the qubit, coupling with adjacent endohedral atoms through hyperfine interactions. The fullerene would be positioned on the silicon surface over gates to read and input the quantum states and control the coupling [1].

A number of experimental studies have been carried out to determine the nature of the bonding between the C_{60} molecule and the Si(1 0 0) surface with contradictory results. Some workers in this field have obtained results which imply that the molecule is physisorbed [2–4] whilst the results of others show chemisorption [5–10]. A few ab initio theoretical calculations have been carried out [11–13] but these have all used pre-assumed structures, created by placing fullerenes above the substrate and ignoring any structural rearrangement caused by the interaction between the fullerene and the silicon surface. Earlier work by us using the classical many body potentials of the Brenner/Tersoff form [14–16] also predicted that a Van der Waals attraction rather than a covalent bond would prevail. The silicon–carbon interactions in this formalism were fitted to the bulk SiC structure and may well not transfer correctly to the C_{60} cage on the silicon surface. However these calculations did give the site between the four surface dimers as the favoured position for the fullerene to adsorb. At room temperature it is found experimentally that the majority of C_{60} molecules are situated over the

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silicon surface dimer trench, with the centre of the molecule sited between four dimers, [4,8,17] C_{60}'s are observed on top of the dimer rows only after heating the substrate.

2. Computational method

In order to accurately model the complex interactions of the fullerene molecule with the surface we have employed an ab initio density-functional-theory description. The simulation cell that we used to describe isolated fullerenes on Si(1 0 0) consisted of six Si layers with the surface containing two rows of four dimers. The Si surface was 2×1 tilted dimer reconstructed; tests show that the 2×1 and 2×2 reconstructed surfaces give essentially the same results for the binding of C_{60}'s to the surface. The bottom two layers of the silicon were frozen in their bulk positions with the bottom layer terminated with hydrogen atoms. Periodic boundary conditions were imposed in all three directions with a vacuum layer of >19 Å between the top of the C_{60} molecule and the bottom of the Si slab; this was found to give well converged results. The calculations were carried out using the Γ-point for k-point sampling due to the size of the system.

The calculations on this system were carried out using the localised orbital code PLATO [18]. This approach uses numerical atomic-like localised orbitals as a basis set. We used basis sets containing two s and p functions and one d function for both the Si and C atoms. The H atoms are described using a single s function; as the aim is not to provide an accurate description of the H atoms but to saturate the Si dangling bonds. All other calculation details are as in Ref. [21]. We have previously shown that this method gives a good description of the Si system, the C_{60} molecule and the binding of Si and C [18,21].

3. Results

Our results clearly show covalent bonding between the Si dimers and the C atoms in the cage of the fullerene in all cases. The C–Si bond lengths are in the main about 0.1 Å longer than those found in bulk SiC. Mulliken population analysis shows only a small charge on the atoms in the bonds, with at most 0.1 electrons transferred onto the C atom. For the C_{60} above the trench, there are unpaired electrons on the Si dimer atoms at the opposite end to which the C_{60} is bonded to. In the C_{60} molecule we see no significant spin with Mulliken spin analysis. We do, however, see significant rebonding taking place within the molecule.

As is well known there are two types of carbon–carbon bonds alternating in isolated C_{60}'s. The shorter bond is the common bond between adjacent hexagons and corresponds to a nominally double bond, while the longer bond is between adjacent hexagons and pentagons and corresponds to a nominally single bond. With PLATO we find these bond lengths to be 1.39 and 1.44 Å respectively. However the nominal single bond length is shorter than that of a pure single bond as in ethane (1.51 Å) and the double bond is longer than that of a pure double bond as in ethene (1.33 Å), indicating that partial delocalisation is present [19,20]. The two types of bond can clearly be distinguished by both their bond lengths and bond energies and for simplicity we shall refer to them as single and double bonds. The carbon atoms to which the silicon atoms bond were originally double bonded to one of their neighbours. This π-bond is broken, but the π-radicals formed within the fullerene molecule are absorbed by rebonding taking place within the fullerene molecule. This can clearly be observed both through changes in the bond lengths and the bond energies of these bonds.

3.1. Trench 4

With the fullerene molecule placed over the dimer trench centred between four dimers, we found four distinct structures. Pictures and diagrams of the four distinct structures are shown in Fig. 1. The diagrams show only the lower atoms of the fullerene molecule and the four dimers to which it is bonded. The four structures will hereinafter be referred to as structure (a), structure (b), etc. The trench 4 sites allow four strong Si–C bonds to be formed which is the major reason why these sites are the most stable. The binding energies for the
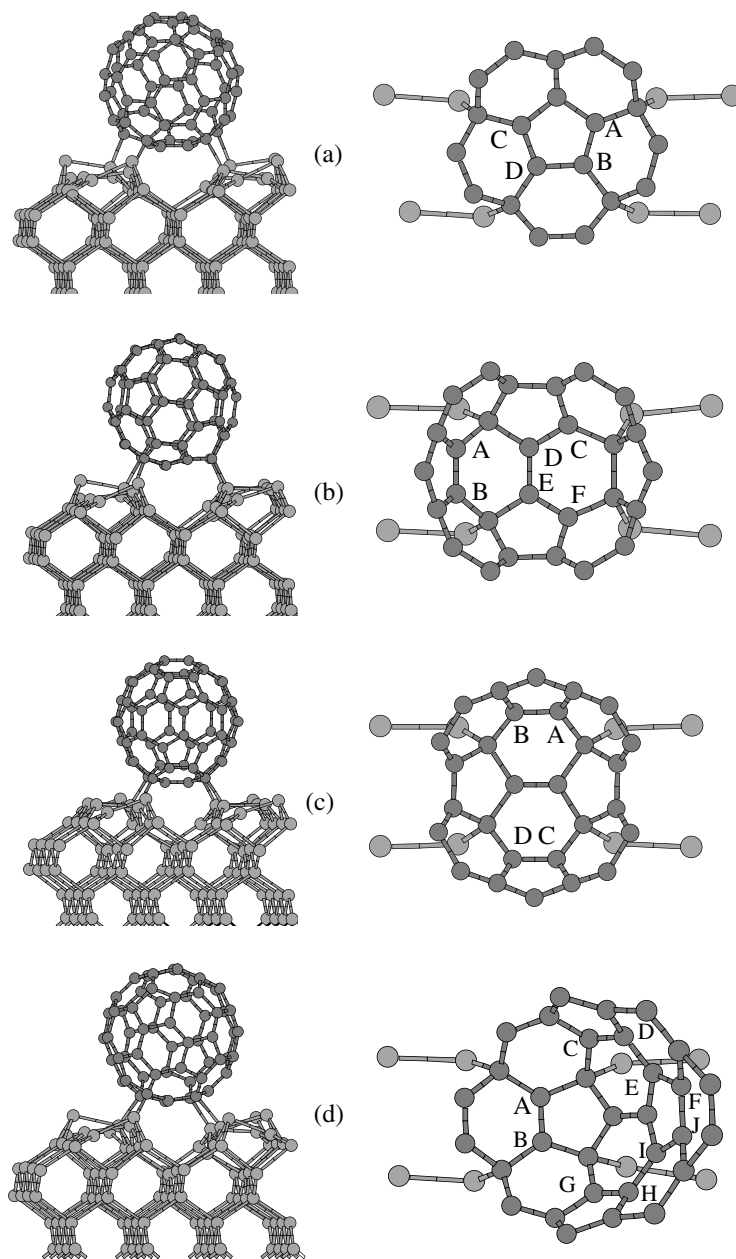
Fig. 1. Views and diagrams of a fullerene bonded to the silicon surface, with the fullerene over the dimer trench centred between four dimers.

different sites are given in Table 1 along with the Si–C bond lengths.

Examining each structure and referring to Fig. 1, in structure (a) the breaking of π-bonds would leave π-radicals on atoms A, B, C and D. Two new

π-bonds are then formed, one between atoms A and B and one between atoms C and D, these bonds are shorter and stronger than the typical double bond found in an isolated C_{60}. In structure (b), the Si–C bonds that are formed are slightly

Table 1
The binding energies and Si–C bond lengths for the stable sites of C_{60} on Si(1 0 0)

Site	Binding energy (eV)	Si–C bond lengths (Å)
Trench 4		
(a)	−5.71	1.93, 1.94, 1.95, 1.98
(b)	−5.31	1.95, 1.96, 1.98, 1.98
(c)	−4.96	1.96, 1.96, 1.96, 1.98
(d)	−4.85	1.97, 1.97, 2.03, 2.19
Trench 2		
(a)	−4.78	2.02, 2.07, 2.10, 2.11
(b)	−4.40	1.92, 2.07, 2.14, 2.47
(c)	−3.08	2.03, 2.03
Row 2		
(a)	−4.83	1.96, 1.97, 1.98, 1.98
(b)	−4.33	1.97, 1.98, 2.02, 2.02
(c)	−4.15	2.01, 2.02, 2.03, 2.07
(d)	−2.69	2.00, 2.01, 2.01, 2.02
(e)	−3.94	1.99, 1.99, 1.99, 1.99
(f)	−4.10	1.97, 1.99, 2.02, 2.04
(g)	−3.13	2.03, 2.03, 2.03, 2.07
Row 1		
(a)	−3.57	1.99, 1.99
(b)	−3.28	1.98, 1.98
(c)	−2.90	1.99, 2.00

weaker. The same rebonding takes place between atoms A and B forming a strong double bond. The situation is a little different for the other bonds. Atoms C and F have π-radicals, but there is also a double bond between atoms D and E. This π-bond is also broken and two new π-bonds are formed, one between atoms C and D and one between atoms E and F. There is some delocalisation between atoms D and E, with the bond energy being greater than for the normal fullerene single bond. In structure (c) atoms A, B, C and D have π-radicals and two new π-bonds are formed, one between atoms A and B and the other between atoms C and D. These two new double bonds formed are not as strong as was the case for (a) and (b) with the bond lengths also being longer. In structure (d) atoms A, B, C and G have π-radicals. A new π-bond is formed between atoms A and B. Atom C has π-radical and there is a double bond between atoms D and E, this π-bond is broken and a new double bond is formed between atoms C and D. Atom E now has a π-radical, and what now occurs is a delocalisation of this electron across bonds D–

E and E–F, these bonds having energies intermediate between C_{60} single and double bonds. The symmetrically equivalent rebonding takes place between atoms G, H, I and J. The fact that such complex rebonding is necessary would explain why the carbon–silicon bonds are longer, and weaker, see Table 1. We also find that the three carbon–carbon bonds surrounding the carbon atoms which are bonded to the silicon dimers are a little longer and have smaller bond energies [22] than the usual C_{60} single bond. They are similar to the carbon–carbon single bond in ethane. Clearly the partial delocalisation of the fullerene molecule is disrupted at these sites.

3.2. Trench 2

With the fullerene placed over the dimer trench and centred between two dimers, we found three stable configurations, which are shown in Fig. 2. In two of these cases four Si–C bonds form and these are the most stable structures. In the third only two Si–C bonds form and this configuration has an appreciably higher energy. The binding energies of the three sites along with the Si–C bond lengths are given in Table 1. Referring to Fig. 2, in structure (a) the π-bond between atoms A and B is broken, allowing the bonding of two dimers. The configuration of the atoms to which the other two dimers are bonded does not allow for simple rebonding. The unpaired electrons are situated on atoms C and F, and there is delocalisation across the neighbouring bonds to atoms D and E, and atoms G and H. These atoms are at the ends of double bonds. The situation is similar in structure (b), with four bonds from the Si surface to the C_{60}. The π-bond between atoms A and B is broken, allowing the bonding to the other two dimers. In the case of the other two interactions these both originate from the same Si atom making one of these very weak, as can be seen from the fact that one of the Si–C bond lengths is much longer. This arrangement with five bonds originating from a Si atom is the only such instance we observe in these systems, but similar arrangements have been observed in high pressure phases of Si [23]. The re-arrangement due to the double bonds breaking is spread out across atoms C, D, E and F. This
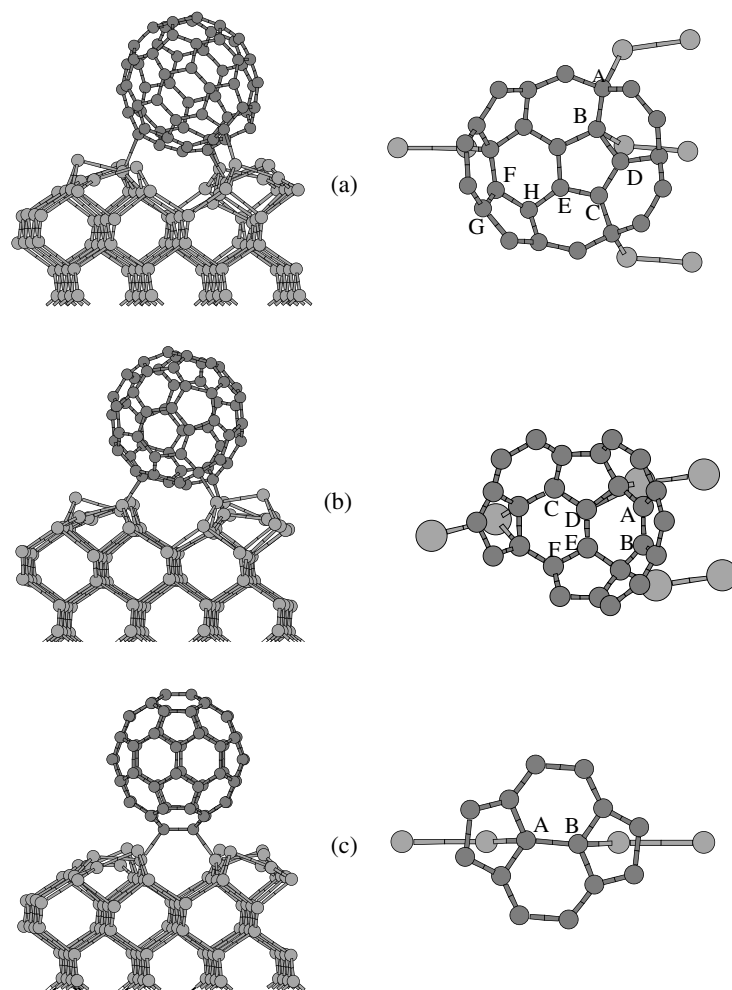
Fig. 2. Views and diagrams of a fullerene bonded to the silicon surface, with the fullerene over the dimer trench centred between two dimers.

inconjunction with one of the Si–C bonds being weak makes this a higher energy structure than (a). For structure (c) the situation is simpler, with the π-bond between atoms A and B being broken and allowing the bonding of the two dimers. Due to the fact that in this configuration only two Si–C bonds are formed, this structure is higher in energy than the previous two.

3.3. Row 2

With the fullerene over the dimer row centred between two dimers, we find all seven possible

configurations are stable. Four of these configurations are shown in Fig. 3. The other three configurations correspond to the first three structures of Fig. 3 with the molecule rotated by 90° about the vertical axis and are shown in the corresponding order in Fig. 4. The most energetically favourable of each pair is shown in Fig. 3.

The binding energies for these structures and their Si–C bond lengths can be found in Table 1. In structure (a) the rebonding is simple; four π-bonds are broken leaving a π-radical on atoms A and B which then form a new π-bond. The symmetrically equivalent bond breaking and rebonding happens
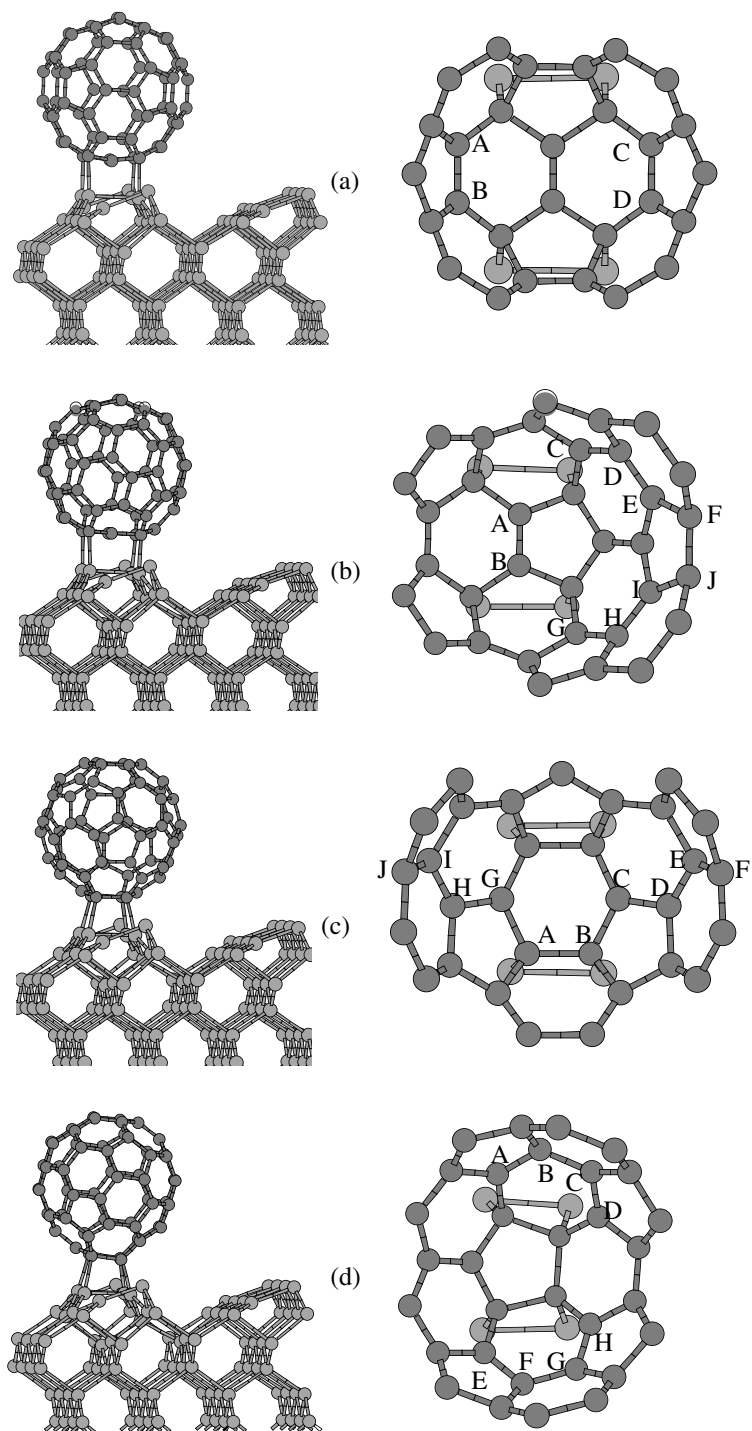
Fig. 3. Views and diagrams of four configurations of a fullerene bonded to the silicon surface, with the fullerene over the dimer row centred between two dimers.
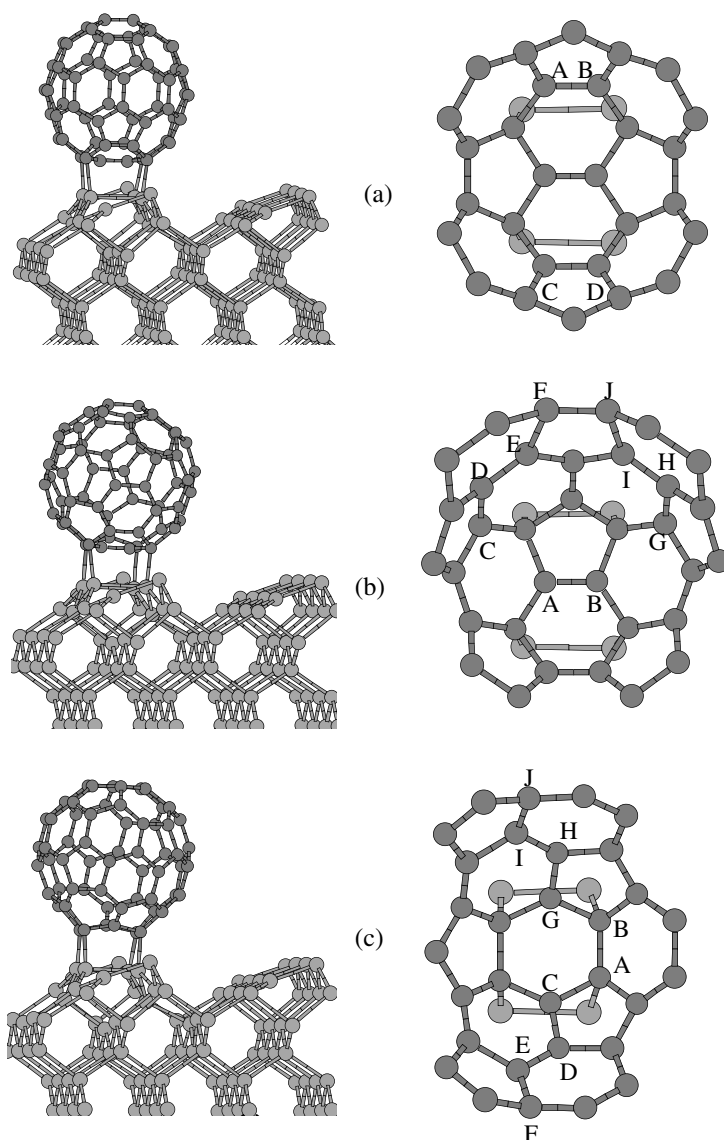
Fig. 4. Views and diagrams of the final three configurations of a fullerene bonded to the silicon surface, with the fullerene over the dimer row centred between two dimers. These three configurations correspond to the first three configurations of Fig. 3 rotated by a right angle.

with atoms C and D. With structure (b) the same bond breaking and remaking happens with atoms A and B but the rest of the rebonding is more complicated. Considering atoms C, D, E and F, a π-bond is broken leaving a π-radical on atom C. A π-bond already exists between atoms D and E and a delocalised chain forms along atoms C, D and E.

There is also some delocalisation across the bond to atom F which itself is one end of a π-bond. The symmetrically equivalent situation happens with atoms G, H, I and J. In structure (c), a π-bond is broken between atoms A and B allowing the bonding of one dimer. The other dimer bonds by breaking two π-bonds and leaving π-radicals on

atoms C and G. Considering atoms C, D, E and F, there is already a π-bond between atoms D and E. A new π-bond forms between atoms C and D and a weaker delocalised π-chain forms across atoms D, E and F. The symmetrically equivalent rebonding happens with atoms G, H, I and J. In structure (d) the rebonding is more straightforward. One dimer bonds to the fullerene by breaking two π-bonds

and leaving π-radicals on atoms A and D. There is a π-bond between atoms B and C which is broken, and two new π-bonds are formed, one between atoms A and B and the other between atoms C and D. The symmetrically equivalent rebonding happens with atoms E, F, G and H.

In the case of the three structures that are shown in Fig. 4 these are equivalent to the first
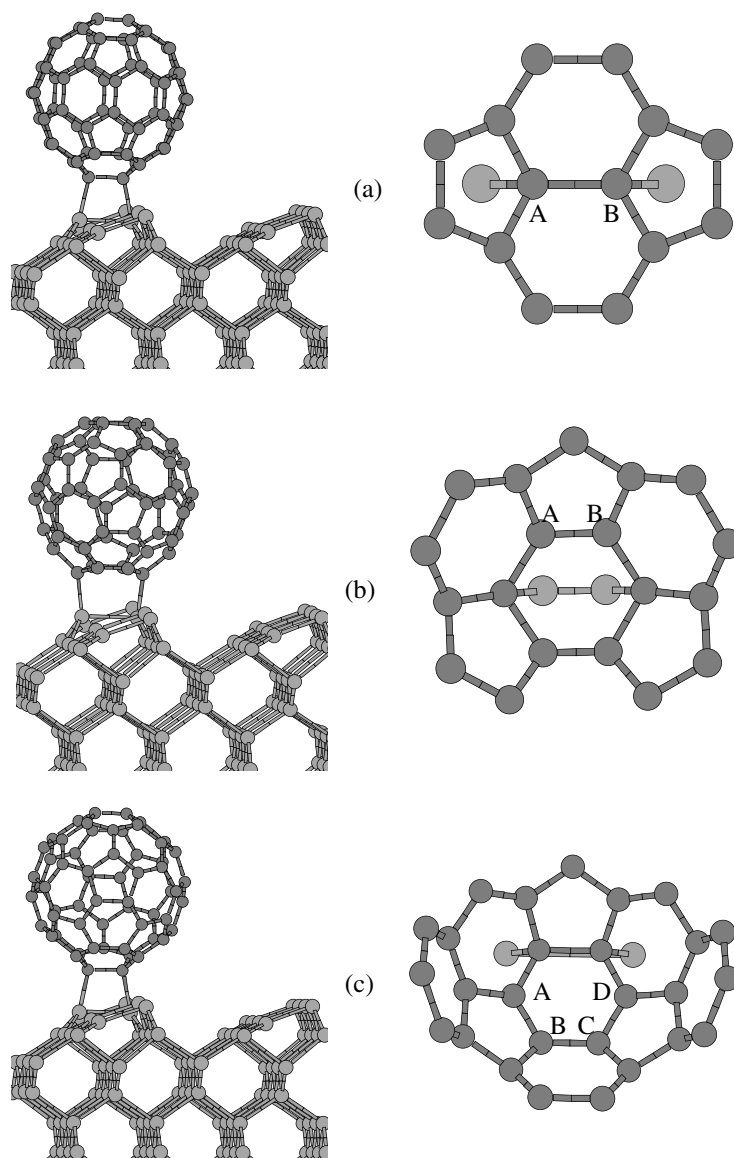

Fig. 5. Views and diagrams of a fullerene bonded to the silicon surface, with the fullerene over the dimer row centred on a single dimer.

three structures in Fig. 3 but with the molecule rotated by 90° about the vertical axis. The binding energies and Si–C bond lengths for these structures can be found in Table 1. The rebonding that takes place within these structures is equivalent to the corresponding structure in Fig. 3. These structures are energetically less favourable because the C–C bonds that form due to the rebonding are weaker, due to geometric constraints on the relaxation of the atoms. For structure (c) the Si–C bonds formed are also weaker than found in the corresponding structure in Fig. 3.

The sites with the C_{60}'s situated over the dimer rows are less favourable than the equivalent sites with C_{60}'s situated over the trenches. We find a dimer length of 2.16 Å and the distance between adjacent dimers along the dimer row is 3.84 Å, however the distance across the trench between dimers is 5.53 Å. This means that the C–Si bond angles are less favourable when the C_{60} molecules are situated above the dimer rows, than in the case of the trench, and that the C–C and Si–Si bonds are placed under strain when the C_{60} is placed on the dimer rows. If we compare the Si–C bond lengths found in the row 2 structures with those for the trench 4 structures we find that they are longer on average.

3.4. Row 1

With the fullerene placed over the dimer row, centred over a single dimer we found three stable configurations, which are shown in Fig. 5. The binding energies of these three structures are given in Table 1 along with the Si–C bond lengths. Referring to Fig. 5, in structure (a) the π-bond between atoms A and B is broken, allowing bonding to both ends of the dimer. In structure (b), two π-bonds are broken when the dimer bonds to the fullerene. This leaves π-radicals on atoms A and B which then form a new π-bond. In structure (c), again two π-bonds are broken leaving π-radicals on atoms A and D. There is already a π-bond between atoms B and C, this bond is broken and new π-bonds are formed between atoms A and B and C and D. There is some delocalisation across the single bond between atoms B and C.

4. Conclusions

We found the C_{60} molecule bonded to the Si(1 0 0) surface in all of the stable structures studied, implying that C_{60} chemisorbs onto the Si(1 0 0) surface. Rebonding takes place within the C_{60} molecule so as to leave no π-radicals. This can be seen from both the Muliken spin analysis and also by studying the rebonding that takes place in terms of the bond lengths and bond energies.

A set of simple rules can be formed which describe the majority of the cases for the adhesion of C_{60} onto Si(1 0 0). Sites where four Si–C bonds can be formed are more stable than those for which only two can be formed. The simpler the bond rearrangement within the C_{60} molecule, the more stable the site is. This is illustrated very clearly in the results for the row 1 case. In this the rebonding that occurs by a Si atom bonding to either end of a C–C double bond is most stable, as it breaks one C–C double bond. The arrangement that breaks two C–C double bonds and forms one new one is the next most stable and the least stable site is the arrangement that breaks three double bonds and forms two new ones. For the other surface sites where there is far more extended bond rearrangements we see that these are the least energetically favourable.

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