PHYSICAL REVIEW B VOLUME 50, NUMBER 15 15 OCTOBER 1994-I

Single-monolayer ordered phases of C_{60} molecules on Si(111)-(7×7) surfaces

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(Received 27 June 1994)

We report on ultrahigh-vacuum scanning tunneling microscopy of submonolayers of C_{60} molecules adsorbed on a Si(111)-(7×7) surface and the statistics of their bonding sites. The images reveal that as the submonolayer coverage increases, the adsorbate-adsorbate interaction becomes larger than that of the adsorbate-substrate interaction. For a full monolayer coverage of adsorbates, the adsorbate-adsorbate interaction becomes strong enough and they form two ordered structural phases registered with those pinned on the substrate corner holes. This result is in contrast to a previous report [Phys. Rev. Lett. **70**, 1850 (1993)] stating that several monolayers of adsorbates are required for the formation of the ordered structural phases.

Scanning-tunneling-microscopy (STM) studies of the adsorption of C_{60} molecules on silicon surfaces has been conducted by several groups in recent years.[1–7] The purpose of these investigations was to understand the interaction of fullerene materials with semiconductor surfaces and to explore the potential applications of these carbon molecules. In particular, several STM studies of C_{60} molecules adsorbed on Si(111)-(7×7) surfaces led to the conclusion that, for submonolayer coverages, C_{60} molecules adsorb randomly on the substrates and form no ordered structures.[2,3,5] Recently, Xu and coworkers[1,8] studied the growth of C_{60} crystalline islands on a Si(111)-(7×7) surface using STM. They observed that the grown C_{60} islands are oriented primarily in two distinct directions. Based on their STM observations, and assuming that the registry of the C_{60} molecules on the Si(111) surface is random, they proposed a model of the interfacial disorder-to-order transition, which occurs only after the growth of several layers of C_{60} molecules. They argued that the proposed interfacial phase transition is due to interlayer molecular interactions, and that the ordered interfacial structure can be stabilized only in the presence of additional ordered layers of C_{60} molecules.

Our studies show, however, that the ordering of the C_{60} monolayer on the Si(111)-(7×7) surface already takes place at near monolayer coverage and does not involve, therefore, interfacial disorder-to-order transition processes. We find that the ordering of a near monolayer, which consists of two-dimensional unit cells registered on the substrate (7×7) structure, results from (a) the pinning of C_{60} molecules at the substrate corner holes, and (b) the decrease in the strength of the adsorbate-substrate interaction relative to that of the adsorbate-adsorbate interaction.

The experiments in this study were conducted in an ultrahigh-vacuum chamber with a base pressure of 5.0×10^{-11} torr, using commercial *n*-type Si(111) wafers as sample substrates. The clean Si(111)-(7×7) surface was prepared by heating the sample to 1200 °C with electron-beam bombardment at the back of the sample, rapidly cooling to 900 °C, and then slowly cooling to room temperature. Pure (>99.8%) C_{60} powder, outgassed at 300 °C for more than 24 h, was deposited with a Knudsen cell equipped with a BN crucible that was mounted 5 cm away from the sample. During the C_{60} deposition, the maximum chamber pressure was kept below 5.0×10^{-10} torr. Typically, for a substrate at room temperature and a C_{60} source at 300 °C, a 15-min deposition will give approximately 1 ML of coverage. All the STM images in this study were acquired *in situ* with the constant current mode.

Figure 1(a) shows a 200×500 Å^2 STM image of a Si(111)-(7×7) surface following a deposition of approximately 1 ML of C_{60} molecules. Here, the sample bias and tunneling current were −4.0 V and 0.5 nA, respectively. Note that the presence of an atomic step on the sample surface, at the left-hand side of the image, together with the smaller apparent height of those C_{60} molecules adsorbed on the corner hole (highlighted by circles in the lower part of the image), clearly indicates that the adlayer is indeed *a single monolayer* of adsorbates. One observes that as a result of the pinning of the C_{60} molecules at corner holes, the C_{60} molecules form an ordered two-dimensional structure, which is registered with the substrate. A careful inspection of the image shows that the ordering contains two domains, which are oriented in two distinct directions. Several of these two domains are labeled, respectively, as *A* and *B*, and two of the boundaries between these domains are outlined. Scanning a larger area of the surface of the sample reveals no growth of a second molecular layer. This indicates that while the diffusion of C_{60} molecules on the Si(111)-(7×7) surface is minimal, the diffusion of the C_{60} molecules on the C_{60} adlayer should be quite large even at room temperature. Therefore, the second C_{60} layer will grow only after the first C_{60} molecules entirely cover the surface of the substrate.

The pinning of the C_{60} molecules at the corner holes fixes the two-dimensional unit cells of the C_{60} adlayer so that they have the same size as that of a unit cell of the substrate. Figure 1(b) is a zoomed image of Fig. 1(a) in

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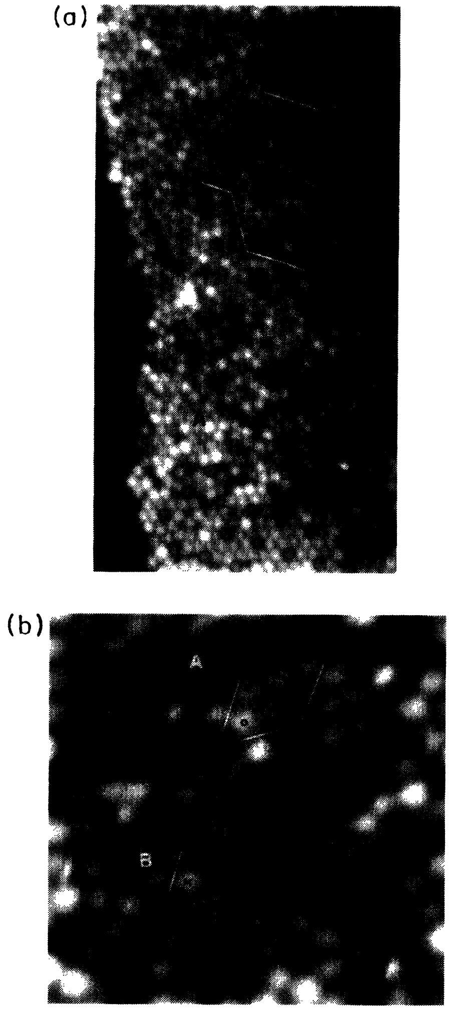

FIG. 1. (a) An STM image (−4.0 V, 0.5 nA) of a Si(111)-(7×7) surface following a deposition of approximately 1 ML of C_{60} molecules at room temperature. One observes two-domains of ordered molecular structures (marked by *A* and *B*, respectively) with two distinct orientations. Some of the C_{60} molecules pinned at corner holes are highlighted by circles in the lower part of the image, and two domain boundaries are also shown in the upper part of the image. (b) A zoomed image of (a), where two unit cells of the C_{60} monolayer on the Si(111)-(7×7) are outlined, one from domain *A* and the other from domain *B*.

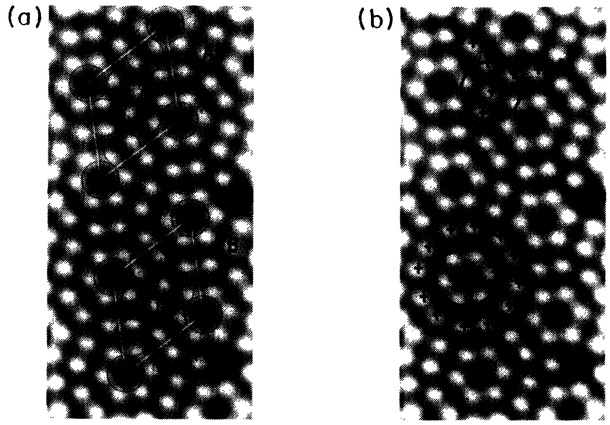

FIG. 2. (a) A schematic of the molecular arrangement of the C_{60} molecules superimposed on an STM image of a Si(111)-(7×7) surface. Two sets of equivalent adatom bridge sites (○ and ×) within a 7×7 unit cell give two possible molecular arrangements. (b) A schematic of two isolated C_{60} molecules superimposed on an STM image of a Si(111)-(7×7) surface, one is at a corner hole (*C*) and the other is within a unit cell (*M*). The midatoms interacting with the adsorbates are labeled with +.

which two unit cells of the C_{60} adlayer are depicted, one for domain *A* and the other for domain *B*. Here, each unit cell contains seven C_{60} molecules, one at the center of the corner hole and three in each triangular half cell.

Figure 2(a) is a schematic of the molecular arrangement of the C_{60} molecules, superimposed on an STM image of the Si(111)-(7×7) surface. Note that the 7×7 unit cell consists of 19 dangling bonds; 12 from the adatoms (shown as white protrusions), 6 from the rest atoms, and one deep at the center of the corner hole. The short diagonal of the unit cell is 26.9 Å, the spacing between the adatoms is 7.68 Å within one triangular subunit, and 6.65 Å across the boundary of the triangle, while the diameter of the corner hole is 13.3 Å.[9−11] Now, the three C_{60} molecules in one triangular half cell are each bonded to an adatom bridge site within the half cell. The six adatoms in a triangular half cell provide two sets of possible bonding sites [see the sites labeled as "○" and "×" in Fig. 2(a)], and give rise, therefore, to the formation of two distinctly ordered phases on the substrate. It is clear that the ordered molecular arrangements shown in Fig. 2(a) correspond to a coverage of one full monolayer of C_{60} molecules on the Si(111)-(7×7) surface, yielding 9.7×10^{13} molecules/cm^2. It is interesting to note that the distance from the center of a corner hole to its nearest "○" site or "×" site is 10.3 Å, and the distance between two nearest "○" or "×" sites is 10.2 Å. These spacings fit the C_{60} molecules quite well indeed!

It appears that the pinning of the C_{60} molecules at corner holes is the key factor in the ordering of the structures, indicating that the bonding of a C_{60} molecule to a corner hole differs in strength from the bonding to other sites. Indeed, Fig. 3 shows an adsorbate-induced modification of the local density of states (LDOS) around the C_{60} molecules at the corner holes. The figure shows two STM images (170×170 Å^2) obtained from the same area on a Si(111)-(7×7) surface, following a deposition of a submonolayer of C_{60} molecules at room temperature. Figures 3(a) and 3(b) were acquired with a sample bias of −2.0 and +2.0 V, respectively, and with a tunneling current of 0.5 nA. Note that the gray-scale discontinuity around the C_{60} adsorbates is an artifact due to image processing used to enhance the contrast of the background of the substrate. As shown in Fig. 3(a), the surface electronic structure in the vicinity of the C_{60} molecules depends on the adsorption sites of the C_{60} molecules. Around the molecule labeled *C*, which is at the center of a corner hole, the occupied LDOS of the 12 nearest midadatoms is reduced significantly, as evidenced by the dark ring around it.

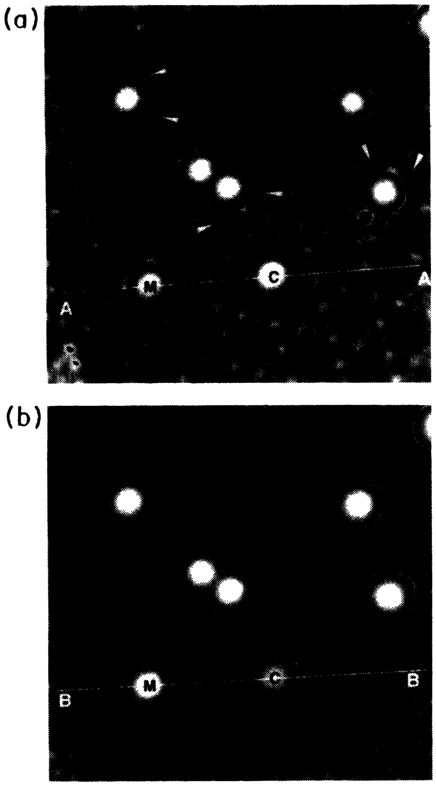

FIG. 3. Two STM images of a Si(111)-(7×7) surface following a deposition of a submonolayer of C_{60} molecules at room temperature. Both images are acquired from the same area (170×170 Å^2) of the surface, one representing an occupied state image with a sample bias of -2.0 V (a) and the other representing an unoccupied state image with a sample bias of 2.0 V. Both tunneling currents were 0.5 nA.

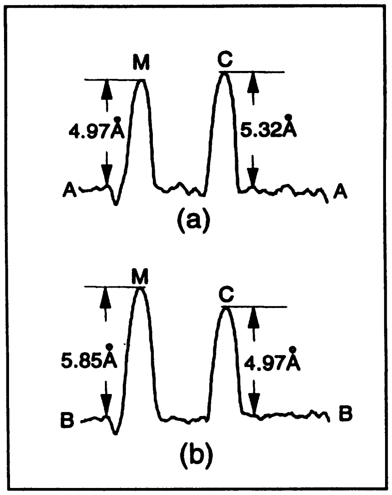

FIG. 4. Two cross sections of the line *A*-*A* in Fig. 3(a) and the line *B*-*B* of Fig. 3(b), showing the relative heights of the two isolated C_{60} molecules on a Si(111)-(7×7) surface. (a) An occupied state image and (b) an unoccupied state image, where one molecule is bonded at a corner hole (C) and the other within a unit cell (M). The heights were calibrated against that of an atomic step of the Si.

For the C_{60} molecules adsorbed within a triangular half cell, however, two small dark triangles are typically found around each of them, corresponding to the locations of two midadatoms [pointed by arrows in Fig. 3(a)]. Figure 2(b) schematically shows two isolated C_{60} molecules superimposed on a Si(111)-(7×7) STM image, one at a corner hole (C) and the other within a unit cell (M). The midadatoms marked by + are those whose occupied LDOS was reduced by the adsorbates. Note that there is no observable occupied LDOS change of the corner adatoms [see Fig. 3(a)]. On the other hand, as shown in Fig. 3(b), no visible unoccupied LDOS changes were observed around the adsorbates, with this sample bias, at either corner-hole sites or within the half cell. These observations indicate that the C_{60} molecules interact mainly with the substrate surface states of the midadatoms. The observed reduction of the occupied, rather than the unoccupied, LDOS at midadatoms around the adsorbates indicates that the interaction is characterized by a charge transfer from the midadatoms to the lowest unoccupied molecular orbital of the C_{60} molecules.

Displayed in Fig. 4 are two cross sections along the line *A*-*A* of Fig. 3(a) (occupied state image) and the line *B*-*B* of Fig. 3(b) (unoccupied state image), both relating to isolated C_{60} molecules. For the occupied state, the relative height of the C_{60} molecule at the corner hole (labeled *C*) is larger than for the one within the triangular half cell (labeled *M*). For the unoccupied state, these relative heights are reversed. This indicates again that the occupied LDOS of a C_{60} molecule at a corner hole is larger relative to the one within the triangular half cell. For a monolayer coverage, however, in contrast to the isolated C_{60} molecules case, the occupied LDOS of the C_{60} molecules at the corner holes appears smaller than the LDOS of the surrounding molecules (see Fig. 1). This result implies that the adsorbate-substrate interaction of an isolated corner hole C_{60} molecule is different from that of a corner hole C_{60} molecule in a monolayer. The measured heights of the C_{60} molecules shown in Fig. 4 were calibrated with the atomic step height (3.1 Å) of the silicon substrate. While the molecule labeled *M* shows a similar apparent height as compared with the results reported by Wang *et al.*,[3] the molecule labeled *C* is approximately 1.4 Å higher than their result. This discrepancy is probably due to different imaging conditions used in the two experiments (the imaging conditions of the results reported in Ref. 2 were not reported).

As observed in Fig. 3(a), the interaction of the molecule labeled *C* with the substrate extends to an area containing 18 adatoms (6 corner hole adatoms and 12 midadatoms). In the case of a monolayer coverage, however, the number of surface states interacting with a single C_{60} molecule is smaller, since each molecule occupies an area that on the average contains only 1.7 adatoms (7 C_{60} per 12 adatoms). Therefore, one expects that as the C_{60} coverage increases, the adsorbate-substrate interaction will be reduced and the adsorbate-adsorbate interaction will play a larger role, causing the two-dimensional disorder-

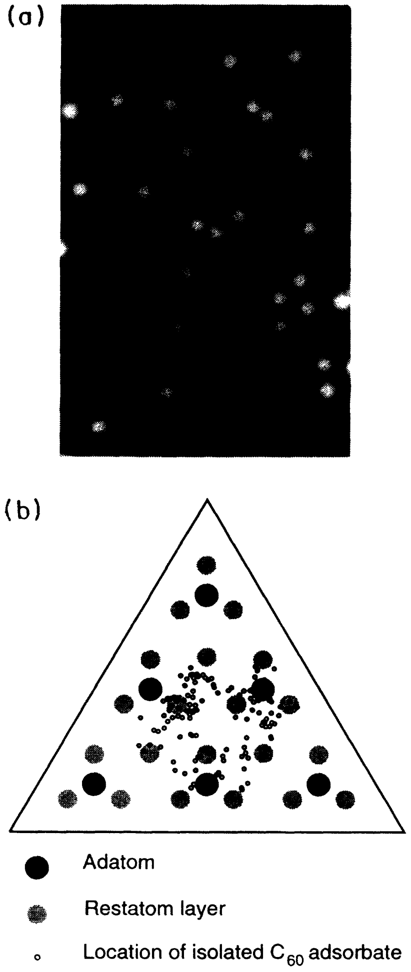

FIG. 5. (a) An STM image of individual C_{60} molecules adsorb on a Si(111)-(7×7) surface at room temperature. (b) A statistical distribution of the adsorption sites of isolated C_{60} molecules on the Si(111)-(7×7) surface. The computed positions of 116 adsorbates relative to their three nearest corner holes superimposed on a triangular half cell of the (7×7) symmetry, showing that the low-energy adsorption sites are those close to the three midadatoms of the substrate unit cell.

to-order transition. Note that for a monolayer coverage the intermolecular spacing is 10.2 to 10.3 Å, which is very close to their van der Waals interaction distance.

To show the significant difference between the low-coverage case and the near monolayer coverage, we conducted a statistical study of bonding sites of individual C_{60} molecules adsorbed on the Si(111)-(7×7) surface at room temperature. Figure 5(a) is an STM image of a submonolayer of C_{60} molecules on a Si(111)-(7×7) surface. A computerized search program identified the locations of each C_{60} molecule in the STM image relative to its three nearest corner holes. Figure 5(b) shows the locations of 116 C_{60} adsorbates superimposed on a triangular half cell of the Si(111)-(7×7) symmetry. One observes that the isolated C_{60} molecules bond predominantly to sites close to the three *midadatoms* in either half of a triangular cell. As shown earlier for monolayer coverage, however, the six C_{60} molecules in a (7×7) unit cell bond to the *adatom bridge sites.* These results again show that the higher coverage causes an increase in the adsorbate-adsorbate interaction, which drives the adsorbates away from the low-energy bonding sites (midadatom sites) to the higher energy bonding sites (adatom bridge sites). In fact, due to the limited surface mobility of the first layer of the C_{60} adsorbates and the low-energy bonding sites on the surface, we do not expect the ordered structure of the adlayer to form at a low coverage, in contrast to the case of C_{60} molecules adsorbed, for example, on a GaAs(110) surface.[12] Only when the local density of adsorbed molecules approaches a full monolayer coverage will an ordered structure form. This can also be observed in Fig. 1(a) where ordered areas are found in full molecular coverage, while the disordered areas are found at a lower coverage. For the near monolayer coverages, the C_{60} molecules that are pinned by the substrate corner holes serve as registration points for the rest of the C_{60} molecules. The adsorbate-adsorbate interaction will then rearrange the molecules locally, forming an ordered structure. The registry of the ordered adlayer structure on the substrate is manifested as a long-range coherent interaction, resulting in a two-dimensional polycrystalline structure having two distinct crystallites separated by disordered domain boundaries. Note also that in our sample, the percentage of surface covered with ordered domains is estimated to be around 75%.

In conclusion, we have observed an ordering of C_{60} molecules already taking place at a single monolayer coverage on a Si(111)-(7×7) surface, and explained the mechanism that gives rise to the formation of this ordered structure. We found that while the adsorbate-substrate interaction dominates at low molecular coverages, the adsorbate-adsorbate interaction plays the dominant role in the formation of the ordered structure at near-monolayer coverages.

This research is supported by the Ballistic Missile Defense Initiative, the National Science Foundation, the Office of Naval Research, and the Air Force Office of Scientific Research.

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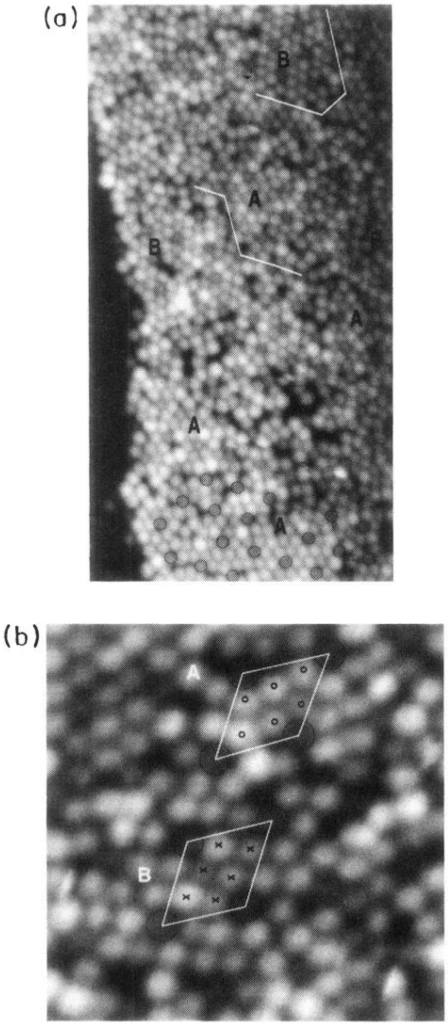
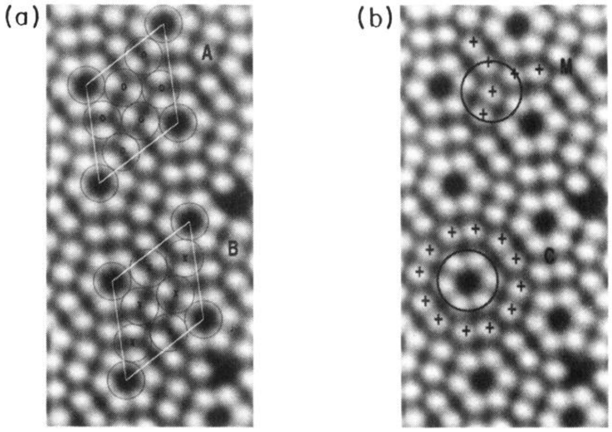


FIG. 1. (a) An STM image (−4.0 V, 0.5 nA) of a Si(111)-(7×7) surface following a deposition of approximately 1 ML of C_{60} molecules at room temperature. One observes two-domains of ordered molecular structures (marked by *A* and *B*, respectively) with two distinct orientations. Some of the C_{60} molecules pinned at corner holes are highlighted by circles in the lower part of the image, and two domain boundaries are also shown in the upper part of the image. (b) A zoomed image of (a), where two unit cells of the C_{60} monolayer on the Si(111)-(7×7) are outlined, one from domain *A* and the other from domain *B*.



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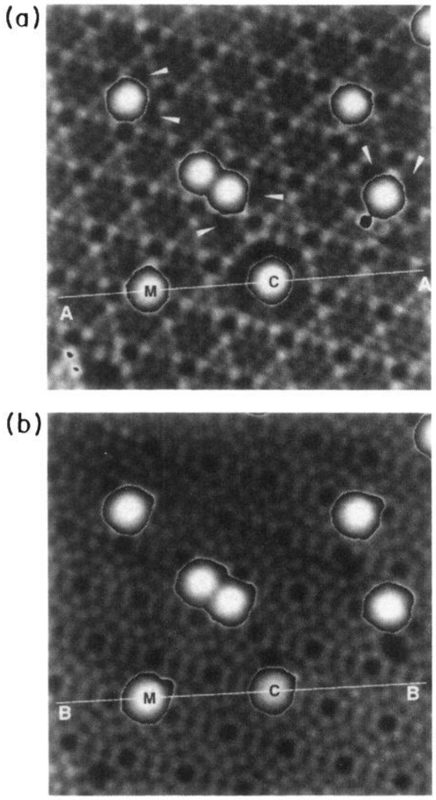

FIG. 3. Two STM images of a Si(111)-(7×7) surface following a deposition of a submonolayer of C_{60} molecules at room temperature. Both images are acquired from the same area (170×170 Å^2) of the surface, one representing an occupied state image with a sample bias of -2.0 V (a) and the other representing an unoccupied state image with a sample bias of 2.0 V. Both tunneling currents were 0.5 nA.

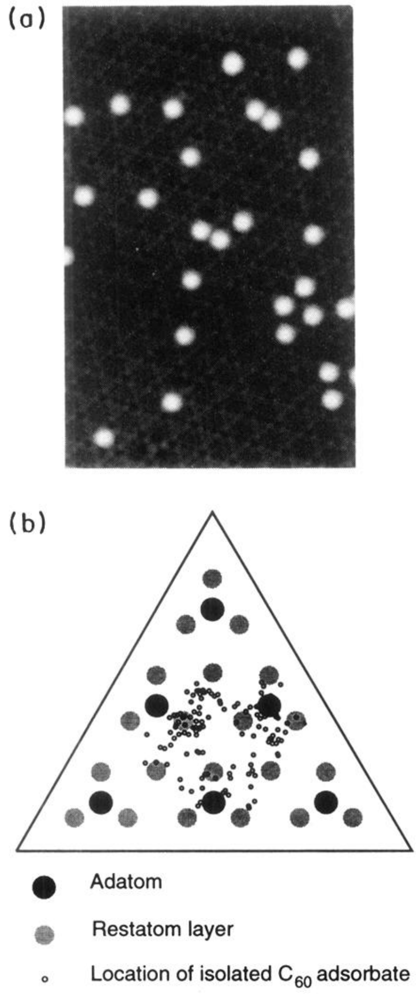

FIG. 5. (a) An STM image of individual C_{60} molecules adsorb on a Si(111)-(7×7) surface at room temperature. (b) A statistical distribution of the adsorption sites of isolated C_{60} molecules on the Si(111)-(7×7) surface. The computed positions of 116 adsorbates relative to their three nearest corner holes superimposed on a triangular half cell of the (7×7) symmetry, showing that the low-energy adsorption sites are those close to the three midadatoms of the substrate unit cell.