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Intramolecular Structures of C₆₀ Molecules Adsorbed on the Cu(111)-(1×1) Surface

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The structure of C₆₀ molecules adsorbed on the Cu(111)-(1×1) surface has been investigated by scanning tunneling microscopy (STM). Bias voltage dependent STM images of individual C₆₀ molecules in the monolayer film showed unique intramolecular structures with a threefold symmetry. The observed images agree well with those calculated using the local density approximation. With charge transfer from the Cu(111) substrate to the monolayer film, the C₆₀ molecule ratchets to threefold hollow sites.

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The investigation on carbon fullerenes discovered by Kroto *et al.* [1] has been a growing exciting field, since Krätschmer *et al.* [2] succeeded in the extraction and purification of C₆₀ and other fullerenes. Discovery of superconductivity by Hebard *et al.* [3] in a K-doped fullerene sample, K₃C₆₀, added further excitement with promising practical applications [4]. Scanning tunneling microscopy (STM) has been successfully used to reveal the geometric and electronic structure of the fullerenes with molecular resolution. The nucleation and growth of C₆₀ film and its structure on various substrates, such as Au(100) [5], (111) and (110) [6], Ag(111) [7], highly oriented pyrolytic graphite (0001) [8], GaAs(110) [9], and Si(111) [10], and (100) [11] have been major interests in STM studies. Investigations on other fullerene films, such as C₇₀ [12], C₈₄ [13], and ScC₇₄/Sc₂C₇₄ [14], and Sc₂C₈₄ [15] on the Si(100)-(2×1) surface have been reported using the FI-STM (field ion scanning tunneling microscope), elucidating the growth kinetics and geometric structures.

The Cu(111) surface is one of the ideal surfaces for the growth of C₆₀ film similar to the bulk [16], since the lattice mismatch is small (2%) between the nearest neighbor (nn) distance (10.0 Å) of the bulk C₆₀ crystal and 4 times of the Cu-Cu nn distance (10.2 Å). A recent study of C₆₀ adsorption on the Cu(111), (110), and (100) surfaces using x-ray photoemission spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS) and other techniques [17] concluded the following: (1) The Cu substrate donates charge to the lowest unoccupied molecular orbital (LUMO) band of C₆₀ as K does in K_xC₆₀ films and (2) single-domain epitaxy with a (4×4) superlattice and successive layer-by-layer growth can be achieved on the Cu(111) surface.

In this Letter, we report the intramolecular structure of C₆₀ molecules on the Cu(111)-(1×1) surface using the FI-STM [18]. C₆₀ molecules ratchet to hollow sites and are ordered due to the substrate-C₆₀ and C₆₀-C₆₀ interactions. Observed intramolecular structure with a unique threefold symmetry agrees well with the charge density around the molecule calculated using the local density approximation (LDA). It was confirmed in the STM im-

ages and calculated charge density that excess charge on the molecule is present on top of the pentagonal rings.

The experimental details of the extraction and purification of high-purity C₆₀ powder (purity of 99.95%, the rest being C₇₀) [19], and its deposition on Si and Cu surfaces in the UHV-STM have been described previously [10–16]. The base pressure of the FI-STM chamber was below 3×10^{-11} Torr and the background pressure during the deposition was kept below 6×10^{-11} Torr. At low coverages, C₆₀ molecules were mobile on the Cu(111) surface and easily diffused toward the step edges running along the $\langle \bar{1}10 \rangle$ direction, similar to the case of C₆₀ on Ag surfaces [20]. After all sites were occupied along the step edges with increasing C₆₀ coverage, two-dimensional islands grew with a close-packed arrangement from the step edges toward the upper terraces and eventually formed a C₆₀ monolayer. A well-ordered close-packed C₆₀ overlayer could be formed upon annealing the C₆₀ covered surface above 250°C. This surface exhibited a (4×4) low energy electron diffraction pattern, suggesting a commensurate C₆₀ monolayer on the Cu(111) surface. The C₆₀ monolayer, once formed on the Cu(111) surface, is rather stable and remains as the (4×4) structure with up to 380°C annealing. The height of the C₆₀ monolayer film on the Cu surface ranged from 4.2 to 5.0 Å, at the bias voltage of -3.0–3.0 V, and is smaller than the height of the second layer (8.2 Å), reflecting the difference in the local density of states between the Cu surface and C₆₀ molecules [5].

Figure 1 shows a STM image of C₆₀ monolayer film formed after annealing at 290°C, with the bias voltage of $V_b = 2.0$ V (sample bias voltage with respect to its Fermi level). Individual C₆₀ molecules could be imaged at the tunneling voltage of -3.0–3.0 V even within the HOMO-LUMO (HOMO denotes highest occupied molecular orbital) gap. In the case of the Si substrate, the STM image of C₆₀ could not be obtained at small bias voltages [10]. Our tunneling microscopy and spectroscopy results suggest that the gap states induced by electron charge transfer from the substrate to the overlayer enable us to image the molecule at the tunneling voltage within the HOMO-LUMO gap. The presence of

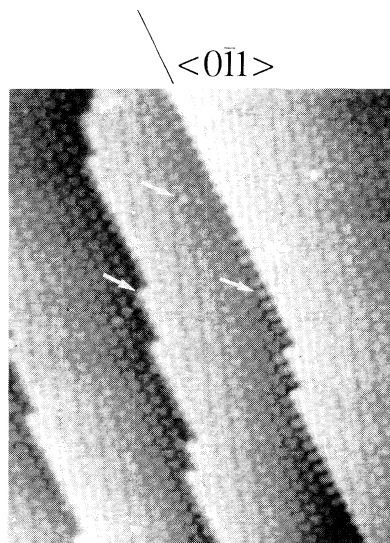


FIG. 1. A STM image of the Cu(111) surface covered completely with a monolayer C_{60} film prepared by annealing at 290°C (area: $300 \times 380 \text{ \AA}$, $V_b = 2.0 \text{ V}$, $I_t = 20 \text{ pA}$). Individual C_{60} molecules are imaged in a three-lobe clover shape. The step edges realign in the $\langle 0\bar{1}1 \rangle$ direction during formation of the C_{60} film. One lobe of each clover-shaped C_{60} molecule points upward along the $\langle 0\bar{1}1 \rangle$ direction on the lower left terrace, while it points downward on the rest of the terraces. Arrows indicate the low symmetry point where the molecule is rotating.

these states was also suggested by a photoemission study on the same system [17]. The existence of the gap states is evidence of the strong interaction between the Cu(111) substrate and the C_{60} molecules.

As discussed in the following, C_{60} molecules appear as a three-lobe clover shape at $V_b = 2 \text{ V}$. There are four terraces with the $\langle 0\bar{1}1 \rangle$ directional step edges in Fig. 1, and each terrace is covered with highly ordered, hexagonal close-packed C_{60} molecules. In all terraces, one of the three symmetric lobes representing the individual C_{60} is pointing downward (in the $\langle 0\bar{1}1 \rangle$ direction), except in the lowest terrace (in the lower left corner) where it points upward. It has been known that C_{60} molecules rotate even in the bulk crystal at room temperature. But the molecules ratchet to a specific direction (cease to rotate) on terraces of the Cu(111) surface in the monolayer film. Interestingly the C_{60} molecules appear to rotate at the step edge and at defect sites (shown by arrows in Fig. 1) as well as domain boundaries, most likely due to broken symmetry and weaker interaction with the substrate. The molecules may be aligned by the intermolecular interaction or indirectly through substrate Cu back bondings [21].

When this surface was imaged as a function of V_b , uniquely different images were obtained (Fig. 2). It may well be that the C_{60} image varies, influenced by tip properties and the tunneling gap. However, the general shape and symmetry remained intact and were consistent under

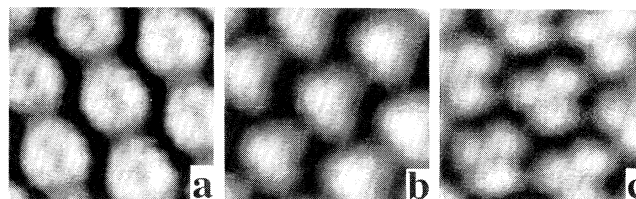


FIG. 2. Magnified ($22 \times 22 \text{ \AA}$) STM images of the C_{60} molecules uniformly adsorbed on the Cu(111) surface at bias voltages of (a) -2.0 V , (b) -0.10 V , and (c) 2.0 V . STM images reveal strong dependence on the bias voltage, but all exhibit the threefold symmetry.

various experimental conditions. In Fig. 2(a) ($V_b = -2.0 \text{ V}$), each C_{60} molecular image appears in a doughnut shape, almost round with a hole at the center, but it still maintains a weak threefold symmetry. The threefold symmetry is more evident in Fig. 2(c) ($V_b = 2.0 \text{ V}$). The unoccupied (LUMO) state image [Fig. 2(c)] should resemble t_{1u} symmetry in a free molecule. Since the molecule is known to rotate in the bulk and on most surfaces, the threefold symmetry has not been observed so far. If the observed threefold symmetry is due to that of the substrate, it should be observed even on rotating molecules near defects. Therefore, this symmetry must be originated from the intramolecular structure of the molecule. This symmetry can also be explained if there exist excess states localized at three pentagonal rings which consist of five sp^2 bonds. Though the occupied (HOMO) state image with h_u symmetry appears in a spherical shape for the rotating molecules on other surfaces, it appears in a doughnut shape on the Cu(111). If the localized states between the substrate and molecule decay rapidly, it cannot influence this symmetry.

Based on these STM images, an adsorption model of the C_{60} molecule on the Cu(111) surface can be derived. In order to reveal the threefold symmetry of C_{60} molecule, one of the *hexagonal rings* in the molecule should face down on the Cu(111) surface. If one of the pentagonal rings in the molecule faced the Cu(111) surface, the molecule would reveal a fivefold symmetry instead of the observed threefold symmetry. If either a single carbon atom or carbon double bond of a C_{60} molecule contacted the Cu substrate, the C_{60} molecule would exhibit a twofold symmetry, which is indeed the case of the C_{60} adsorption on the Si(100)- 2×1 surface [11].

For the registry site of the C_{60} molecule resulting in the Cu(111)- $(4 \times 4)C_{60}$, there are only two possible adsorption geometries, considering the symmetry of the STM images: (1) atop site and (2) threefold hollow site. Since the size of the hexagonal carbon ring is almost identical to the Cu-Cu distance and that each carbon atom takes up the position of the hollow site around the center Cu atom, the sixfold symmetry "atop" site actually can accommodate a C_{60} molecule quite well. Because of the threefold symmetry of the C_{60} molecule itself, there are

two orientationally nonequivalent configurations for the C_{60} molecule; each is equivalent except for the 60° rotational freedom.

On the other hand, if a C_{60} molecule occupies the threefold hollow site, there are two adsorption sites, site a and site c (type I and type II of Fig. 3) with respect to the Cu substrate [the regular stacking of the fcc (111) surface; $abcabc \dots$]. This difference can be reflected in the STM image as the displacement of $\frac{1}{3}$ of the Cu-Cu interatomic distance in the $\langle 0\bar{1}1 \rangle$ direction. There are three possible adsorption geometry based on the symmetry argument: The angle between the $\langle 0\bar{1}1 \rangle$ direction and one of the carbon double bonds of the hexagonal ring facing the Cu(111) surface is (i) 0° , (ii) 30° or (iii) -30° . The present STM images rule out the possibility of configuration (i) since none of the lobes of the clover-shaped C_{60} images points in the $\langle \bar{2}11 \rangle$ direction. The difference between configurations (ii) 30° and (iii) -30° arises from the 60° rotation.

Therefore, there should be four domains expected if a C_{60} molecule occupies the hollow site and two domains if it does the atop site. In the present data, *four domains* were observed, two of which were displaced from each other by $\frac{1}{3}$ of the unit Cu-Cu distance in the $\langle 0\bar{1}1 \rangle$ direction. Based on these arguments, the hollow site (shown in Fig. 3) is the proper registry site of the C_{60} molecule.

In order to interpret the intramolecular structures ob-

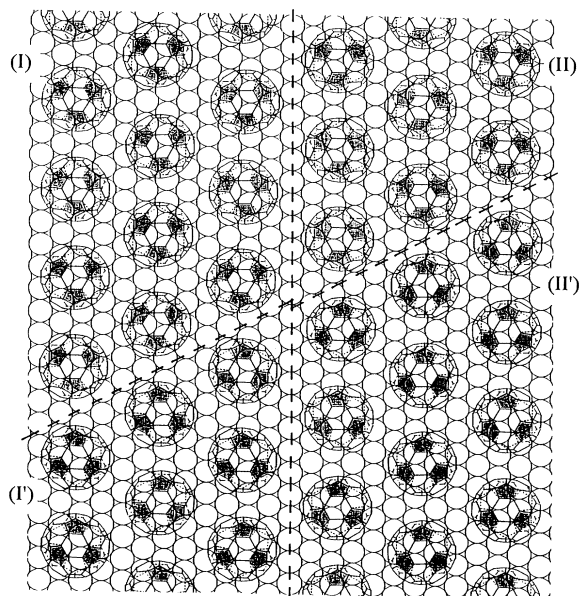


FIG. 3. Proposed adsorption model of the C_{60} overlayer on the Cu(111) with a 4×4 superlattice. The intermolecular distance (C_{60} - C_{60}) is 10.2 \AA , equal to 4 times the Cu-Cu nearest neighbor distance. Three pentagonal rings located in the upper portion of the C_{60} molecules are shaded for better viewing of the rotational freedom of each C_{60} molecule. Four domains are shown in (I), (I'), (II), and (II') where each C_{60} occupies the hollow site.

served by the STM, the calculation of the voltage-dependent local charge density around the molecule was carried out. The details of the theoretical calculation on Si(100) were reported previously [22]. Band structure calculations of three-dimensional C_{60} crystal structures based on the pseudopotential (thus, pseudocharge) formalism [23] were reported. In the present approach, a two-dimensional band structure was calculated for a fcc (111) layer of C_{60} molecules using the local density approximation in the framework of the density functional theory. The mixed basis including $1s$ and $2p$ atomic orbitals was used to examine the spatial locality and symmetry. After solving the pseudo eigenfunction, it was transferred to the nondiagonal frame to evaluate the charge density. Fixed exponential damping rates were used for $1s$ and $1p$ atomic wave functions. Further details will be published elsewhere [24].

Since the main aim of the calculation is the spatial charge density around the C_{60} molecule, the C_{60} molecular structure was treated as accurately as possible using a full-potential algorithm. For the Cu(111) substrate we used a model in which the substrate effect is incorporated only by assuming a triangular lattice and a charge transfer from the Cu atoms. The previous theoretical calculation showed that the charge density on top of the C_{60} molecule are insensitive to the interactions between the bottom of C_{60} molecule and the substrate [22]. With this approximation for the substrate, the spatial variation of the charge density around the C_{60} molecule can be calculated. As for the interaction between the C_{60} molecules and the Cu(111) surface, the assumptions of weak adlayer-substrate interaction and resulting Fermi level pinning in the C_{60} band structure were used.

The two-dimensional energy band for the hexagonal close-packed C_{60} monolayer film was calculated (Fig. 4). The local charge density can be mapped out easily from

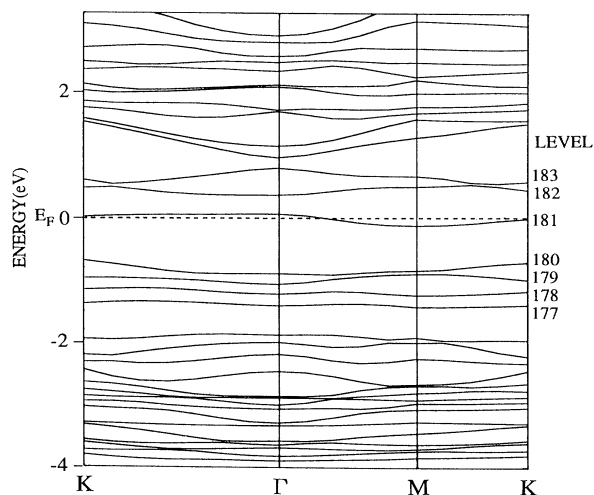


FIG. 4. Two-dimensional energy band structure of the C_{60} triangular lattice.

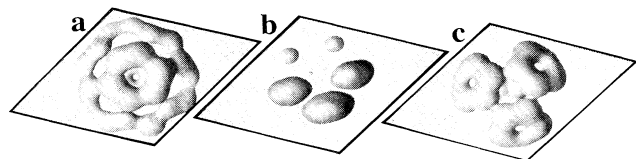


FIG. 5. Top views of the local density of the states at $E - E_f =$ (a) -2.0 eV, (b) 0 eV, and (c) 2.0 eV.

this dispersion. The calculation shows that charge distributions of levels 177, 178, and 179 are of a doughnut shape in the HOMO-derived states, round with a center hole and very similar to those observed in STM. The charge distribution of level 180 is round without a center hole. Levels 181, 182, and 183 all show a threefold symmetry representing three pentagonal C rings in the LUMO-derived states. Since the exact amount of charge transfer from the Cu substrate to the C_{60} monolayer is difficult to calculate, the absolute energy level may not be determined unambiguously. In the present study, the theoretical result was shifted by 0.5 eV upward in the energy scale for the best fit with the experimental results. In this energy scale, the Fermi level is positioned at the center of molecular level 181 (Fig. 4). This energy level shift amounts to ~ 1 electron/ C_{60} charge transfer, and appears to be in good agreement with Rowe's XPS-HREELS results [17] as well as that in the case of C_{60} adsorption on the Si(100)-(2 \times 1) surface [25].

Under this energy scheme, the STM image at $V_b = -2.0$ V [corresponding to image of Fig. 2(a)] should be the mixed charge density resulted from levels 177, 178, 179, and 180 and to a lesser extent from level 181. The STM image at $V_b = -0.1$ V [image in Fig. 2(b)] should be compared with level 181. The STM image at $V_b = +2.0$ V [image in Fig. 2(c)] should be from levels 181, 182, and 183. The STM images were simulated and are shown in Fig. 5. The simulated images, Figs. 5(a) and 5(c), are the mixture of levels 178, 179, and 180, and levels 181, 182, and 183 with equal weight, respectively. The simulated STM images agree well with the observed ones in Fig. 2.

There have been several papers lately reporting STM observations of intramolecular structures of C_{60} adsorbates. However, the present study demonstrates for the first time an excellent agreement of the STM images with the calculated charge density around the C_{60} molecules on a metal surface. The present results also conclusively demonstrate that the C_{60} molecule in the epitaxial film on

the Cu(111) ratchets to a hollow site even at room temperature in the presence of charge transfer from the substrate to the molecule.

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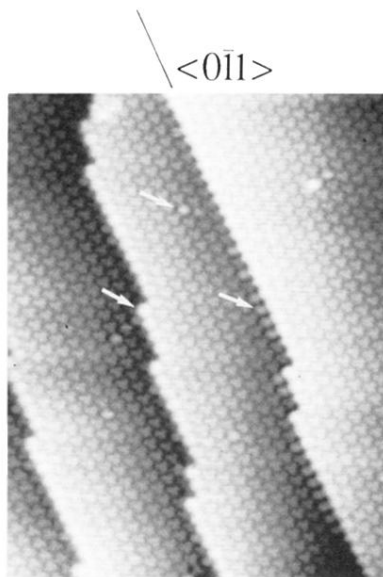


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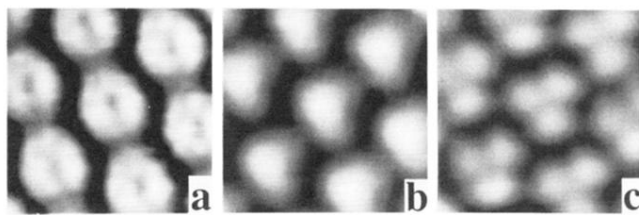


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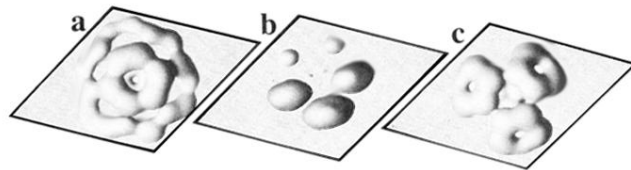


FIG. 5. Top views of the local density of the states at $E - E_f =$ (a) -2.0 eV, (b) 0 eV, and (c) 2.0 eV.