Adsorption and motion of C_{60} molecules on the Pb-covered Si(111) surface

Shih-Hsin Chang,[*] Ing-Shouh Hwang,[†] Chung-Kai Fang, and Tien T. Tsong

Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan, Republic of China 115

Adsorption and diffusion of C_{60} molecules at a monolayer Pb-covered Si(111) surface is studied with a scanning tunneling microscope (STM). At room temperature, C_{60} molecules stably adsorb with two configurations: one with a hexagonal ring and the other with a pentagonal ring bonded to the Si(111) substrate. We can manipulate the molecules out of the stable states with a STM tip by decreasing the tunneling gap. The molecules would then randomly diffuse at the surface and momentarily stop at some metastable states. Eventually, they settle down at a stable state and become immobile again. Through monitoring the change in the intramolecular features during the entire motion processes, we believe that random thermal rolling may occur during the diffusion process of C_{60} molecules at the surface. A possible schematic potential diagram for the diffusion of this spherelike molecule at the Pb-covered surface is proposed.

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I. INTRODUCTION

Understanding how three-dimensional (3D) nano-objects (clusters, particles, or molecules) diffuse at solid surfaces has drawn an increasing research interest from both the scientific and technologic points of view. Scientifically, most studies of surface diffusion are focused on single atoms.[1–5] There are also some studies of surface diffusion of single molecules or clusters.[6–14] Up until now, a number of diffusion mechanisms have been proposed, such as shearing motion,[10] periphery diffusion, collective gliding,[11,12] Brownian motion,[13] or rotational motion.[14] Recently, there were several reports of surface diffusion of large molecules.[15–19] Even though these molecules have 3D features, their structures are mainly planar, i.e., one dimension is significantly smaller than the other two dimensions. It is much more energetically favorable for them to adsorb with the plane of the molecules parallel to the surface than other configurations. Thus, rotation of a cluster or a molecule about an axis that is not perpendicular to the substrate surface, which we define here as the random thermal rolling,[20] is very unlikely to occur. One can expect that random thermal rolling at surfaces is more likely to occur for polyhedron or spherelike nano-objects because there are more than four facets that are energetically favorable for their attachment to the substrate and that neighboring facets are separated by an angle much smaller than 180°. The change of adsorption between neighboring facets of a molecule would not require a high energy barrier. For polyhedron or spherelike nano-objects, there are also many other motions besides random thermal rolling because of their high degrees of freedom in motions.[21] These molecules can also rotate about an axis perpendicular to the substrate surface, just like rotation of planar molecules on surfaces. In addition, they can glide (or translate) without rotation. Moreover, there can be many different adsorption sites on a substrate surface. This would lead to many possible bonding configurations between a polyhedron or spherelike nano-object and a crystalline surface. Therefore, it would be of great scientific interest to study these complicated processes.

Technologically, self-assembly of 3D nano-objects has been widely applied to form many kinds of nanometer-scale patterns with good uniformity at the samples of macroscopic sizes.[22] Understanding detailed diffusion mechanisms of these nano-objects can help our controlling these fine patterns, which also determine the function of the surface.

Previous studies of dynamic behavior of individual polyhedron or spherelike molecules focuses only on their manipulations. For example, molecules are pushed, pulled, or rolled by following the tips' trajectory one step after another.[23–25] However, direct observation of diffusion of individual polyhedron or spherelike molecules on solid surfaces is still lacking.

A C_{60} molecule can be a model polyhedron or spherelike molecule for the study of surface diffusion because the fullerene structure is well understood.[26] Moreover, the C_{60} molecule is very stable and does not react with most substrates. The model of the C_{60} molecule is illustrated in Fig. 1(a). This cage-structured molecule consists of 12 pentagonal rings and 20 hexagonal rings. The diameter of the C_{60} molecule is 0.71 nm and its shape and the structure closely resemble a soccer ball. Owing to its spherical shape and very stable structure, it would not require a high temperature to observe the diffusion process of the molecule at a surface. Also, the molecule can be easily manipulated with a tip, as demonstrated in several previous studies.[24,27]

In this work, we study C_{60} molecules at a Pb/Si(111) surface at room temperature with a scanning tunneling mi-
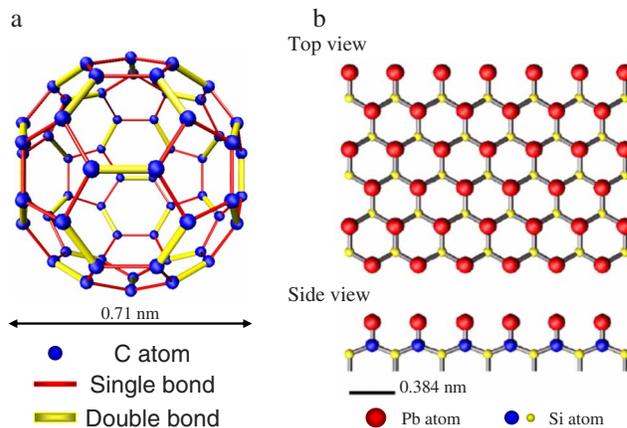

FIG. 1. (Color online) Atomic model of the C_{60} molecule (a) and of the Pb/Si(111)-(1 × 1) structure (b).

croscope (STM). Two stable adsorption states are identified, and the adsorption configurations are proposed based on STM images of their intramolecular features. A stable C_{60} molecule can be kicked out of its stable adsorption site with an STM tip and starts to diffuse at the surface. From our observations, the diffusion of the molecule at the surfaces is not only through translation but probably also through random thermal rolling.

II. EXPERIMENT PROCEDURES

Our experiments are carried out using a commercial STM (Omicron VT-STM) in an ultrahigh vacuum chamber with a base pressure of 4×10^{-11} torr. We start with a clean Si(111)-(7×7) surface.[28] Submonolayer Pb (99.999% pure Pb) is evaporated from an effusion cell onto the Si(111)-(7 ×7) surface at room temperature. The sample is then annealed at 400 °C for ~2 s. The deposited Pb atoms destroy the Si(111)-(7×7) structure locally and form the Pb-covered regions surrounded by Si(111)-(7×7).[29–31] In the Pb-covered region is mainly a two-dimensional 1×1-Pb structure on top of a bulk-truncated Si(111) substrate and its Pb coverage has been determined to be about 1 ML.[32,33] The model of the (1×1) structure is shown in Fig. 1(b). In this model, Pb atoms are located on the T_1 sites and bind to Si atoms underneath. The (1×1) structure appears flat with no atomic corrugation at most tunneling conditions, but a hexagonal (1×1) atomic structure can be resolved at low biases for both polarities if the tip is good.[29–31] After the above preparations, high-purity C_{60} molecules are deposited onto the surface from an effusion cell. The sample is then transferred to the STM stage for imaging. The substrate is kept at room temperature during the deposition and STM imaging.

We find that C_{60} molecules randomly distribute in both the Pb-covered (1×1) and Si(111)-(7×7) regions. C_{60} molecules on the Si(111)-(7×7) are immobile, and this subject was previously investigated with STM.[34] In this study, we focus on C_{60} molecules in the Pb-covered (1×1) region only.

In our STM imaging, we usually use the sample bias of +2 V and the tunneling current of 0.15 nA. At this condition, we can obtain reliable images and the tip has little influence on the surface structure and on the adsorption of C_{60} molecules due to the relatively large tip-surface spacing. Even though we can achieve atomic resolution on the Pb-covered regions at low biases (<1 V), there is a risk of crashing the tip to the surface or moving the C_{60} molecules. In addition, we have obtained many STM images of the Pb-covered regions at low biases previously,[29–31] so we know very well about the relation between the atomic structures and the patterns of surface corrugation obtained at high sample biases (around +2 V). Thus, we can propose atomic models based on STM images taken at high biases.

III. RESULTS AND DISCUSSION

Figure 2(a) shows a STM image of several C_{60} molecules at a Pb-covered region. In our normal imaging conditions, C_{60} molecules do not move with time. They usually appear as round spheres, but the internal structure can be resolved
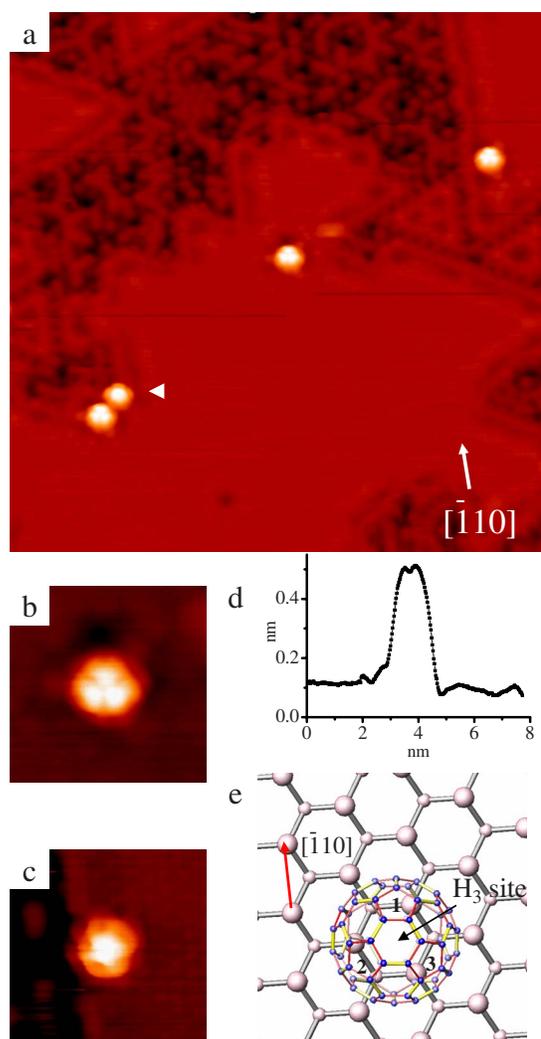

FIG. 2. (Color online) (a) Room-temperature STM topograph showing adsorption of C_{60} molecules at the Pb/Si(111)-(1×1) surface, taken at a sample bias of +2 V and a tunneling current of 0.15 nA. (b) High-resolution image of a three-lobe-type C_{60} molecule. (c) High-resolution image of a pentagon type. (d) Line profile across a three-lobe-type C_{60} molecule. (e) Atomic model illustrating a C_{60} molecule occupying a H_3 site. Three pentagonal rings marked with 1, 2, and 3 correspond to the three lobes seen in STM images.

for some tips, indicating that they are not rotating at this surface at room temperature. In Fig. 2(a), C_{60} molecules exhibit two distinctive appearances at the surface. One appears with a three-lobe clover shape (three-lobe type). A close-up of this molecule, as shown in Fig. 2(b), clearly reveals its threefold symmetry, and each lobe is approximately pointed toward a $\langle \bar{1}10 \rangle$ direction. By triangulating from a nearby Si(111)-(7×7) reconstruction region, we determine that this type of C_{60} molecules are adsorbed on the H_3 site [Figs. 3(a) and 3(b)]. We also find another three-lobe-type C_{60} molecules, which are 60° rotated relative to the previous type. They are determined to occupy the T_4 site [Fig. 3(c)]. The ratio of these two adsorption sites is very close to 1:1. A height profile across a three-lobe-type C_{60} molecule is shown in Fig. 2(d), which is ~0.37 nm higher than the Pb-covered
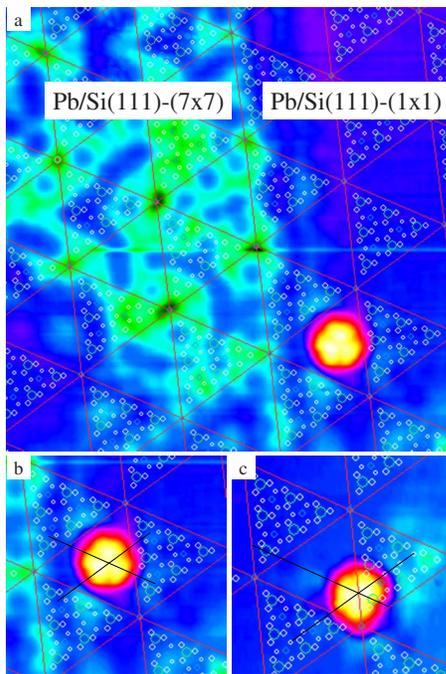
FIG. 3. (Color online) Determination of the adsorption site of C$_{60}$ molecules by triangulation from the Si(111)-(7×7) region. Grid intersections correspond to corner holes in the Si(111)-(7 ×7) region and the atomic model in the unfaulted halves of Si(111)-(7×7) are extended to the Pb-covered region (Ref. 46). In the entire Pb-covered region, the underlying Si(111) substrate is the bulk-terminated structure, i.e., the same as that in the unfaulted halves. If a C$_{60}$ molecule happens not to occupy a part showing the atomic model, its site is determined through triangulation from the atomic model in neighboring half cells. (a) and (b) illustrate our determination of a three-lobe-type C$_{60}$ molecule occupying a H_3 site. (b) is only a section of (a) around the C$_{60}$ molecule. (c) illustrates our determination of another three-lobe-type C$_{60}$ molecule occupying a T_4 site. The part with the Si(111)-(7×7) region is not shown here in order to reduce the figure size.

flat region. Our measurement over several three-lobe-type C$_{60}$ molecules shows that the height difference between the C$_{60}$ molecule and the Pb layer is 0.38 ± 0.01 nm from +2 V to +1 V and 0.35 ± 0.01 nm from −2 V to −1 V. We do not see any appreciable height difference for the two adsorption sites. Clearly, these height values are significantly smaller than the diameter of the C$_{60}$ molecule, i.e., 0.71 nm. Here, we use single Si(111) atomic step height as a reference to calibrate all the height measurements.

The observation that the three-lobe-type C$_{60}$ molecule is only ~0.38 nm above the Pb overlayer suggests that the molecule may not sit directly on top of the Pb overlayer but probably binds to the Si(111)-(1×1) substrate directly. The latter is reasonable if one considers the Pb-Si bond length of ~0.29 nm. Even though the surface electronic structure can affect the height measurement in STM topographic images, this effect rarely exceeds 0.15 nm. We note that the height of C$_{60}$ molecules have been measured at Ag(001),[35] Au(110),[36] and Pt(110) (Ref. 37) surfaces. The measured values range from 0.57 to ~0.7 nm, which are also much larger than the height we have obtained here.

It is not surprising that the C$_{60}$ molecule can attach to the Si(111) substrate by replacing the Pb-Si bonds. It has been demonstrated that surfactant-mediated epitaxial growth of Ge at monolayer Pb-covered Si(111) surface can occur at room temperature.[38] Deposited Ge atoms should be able to exchange with the Pb overlayer in order to form an epitaxial layer on the Si(111) substrate. This indicates that the activation energy for the exchange process is low. Another observation is that thermal desorption of Pb atoms from Si(111) substrate occurs at temperatures below 400 °C,[32] suggesting the weak Pb-Si bond strength. Thus, the attachment of C$_{60}$ molecules to the Si(111) substrate in this case may also has a low activation energy.

The specific orientations of the three-lobe-type C$_{60}$ molecule shown in Fig. 2(a) also support a stable and specific bonding between the molecule and the Si substrate with no Pb layer in between. Previous experimental and theoretical results have shown that C$_{60}$ molecules can form Si-C covalent bonds on Si(111) and Si(001).[24,34,39] In addition, theoretical calculations have shown that locations of lobes seen in empty-state STM images correspond to pentagonal rings in the C$_{60}$ cage structure.[40,41] Therefore, the three-lobe-type C$_{60}$ molecule is probably adsorbed with a hexagonal ring facing down with the Si(111) substrate. An atomic model for the adsorption configuration at the H_3 site is shown in Fig. 2(e). The three pentagonal rings surrounding the top hexagon correspond to the three lobes 1, 2, and 3.

In Fig. 2(a), the white triangle indicates another type of C$_{60}$ molecule, which exhibits a pentagon on the top and less bright curved stripes surrounding the pentagon edges (pentagon type). A close-up is shown in Fig. 2(c). In many cases, the curved stripes are not present on one side of the pentagon. This could be due to the effect of an asymmetric tip shape or due to a small angular tilt of the adsorbed molecule from the surface normal. The height of the pentagon-type C$_{60}$ molecules is measured to be ~0.38 nm at +2 V and ~0.33 nm at −2 V. As to the adsorption configuration of the pentagon-type C$_{60}$ molecule, probably the molecule is adsorbed with a pentagonal ring facing down with the Si(111) substrate. No specific correlation between the orientations of the pentagons with that of the Si substrate is found. We find that the pentagon-type C$_{60}$ molecules are seen only at defect sites or at phase boundaries of the Pb-covered region. Our statistics shows that the ratio of the pentagon to the three-lobe-type C$_{60}$ molecules is 3:7. However, we believe that this ratio should vary with the defect density.

There is another interesting observation. The three-lobe-type C$_{60}$ molecules can induce a subtle atomic rearrangement in the surrounding Pb-covered region. An example is shown in Fig. 4(a). In this image, there are two adsorbed C$_{60}$ molecules. The upper one is the three-lobe type [upper inset of Fig. 4(a)] and the other is the pentagon type. At this tunneling condition, the (1×1) appears flat with no atomic corrugation. However, a weak corrugation with a local order mainly in $\sqrt{3} \times \sqrt{3}$ (a unit cell is outlined) can be seen in the Pb overlayer around the three-lobe-type C$_{60}$ molecule. The pattern is evident within 1.5 nm around the molecule, but the intensity of the corrugation gradually decays into a flat (1 ×1) region as the distance moves away from the molecule. We have checked many three-lobe-type C$_{60}$ molecules and
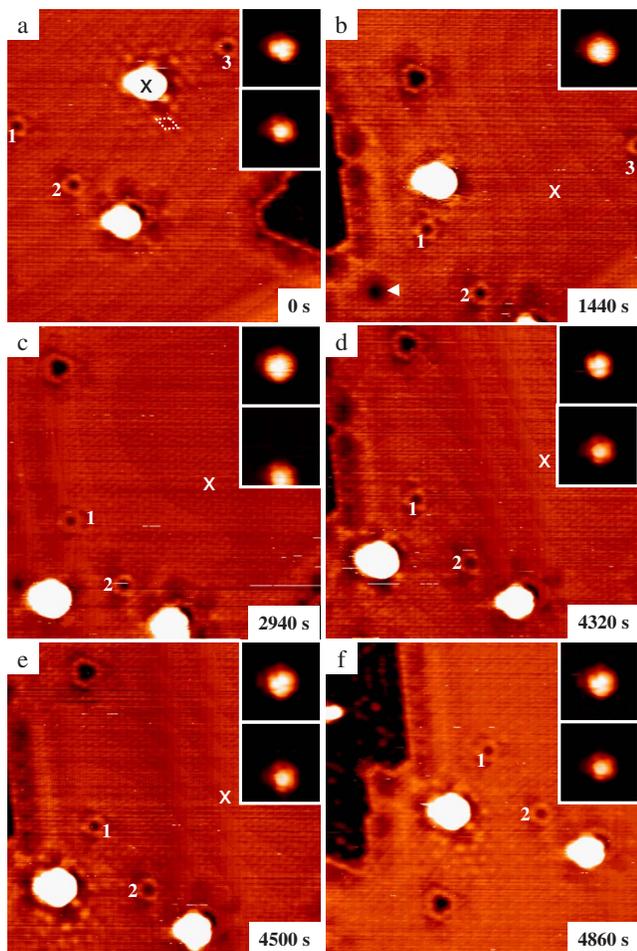
FIG. 4. (Color online) Observation of diffusion of a C_{60} molecule. The scan size is 15×15 nm^2. All images are taken at a sample bias of +2 V and a tunneling current of 0.15 nA. (a) Image before manipulation. (b)–(f) are images chosen from our consecutive images taken every $\sim$3 min. The time for each image is indicated at the lower right-hand corner. Three defects indicated with 1, 2, and 3 can serve as markers for identifying the motions of the C_{60} molecule. In (b)–(e), an $\times$ marks the original site of the C_{60} molecule before manipulation. Since the image contrasts for the small corrugations in the Pb layer (0.1–0.2 Å) and for the fine feature on top of the C_{60} molecules cannot be simultaneously shown, we choose enhanced contrast of the former for each major image and that of the latter in the two insets at the upper right-hand corner. The C_{60} molecule that is manipulated is shown in the upper inset and the other immobile pentagon-type C_{60} molecule is shown in the lower inset. We note that STM images of the internal structure for the immobile pentagon-type C_{60} molecule do not show any change throughout the entire observation, indicating that the tip does not change.

find that the pattern always appears around them. In contrast, no surface atomic rearrangement has been observed surrounding any pentagon-type C_{60} molecule.

The monolayer Pb-covered Si(111) surface has been found to exhibit many subtle and interesting reconstruction.[31,32,42,43] Certain point defects, phase boundaries, or Si islands can affect the pattern of the atomic rearrangement near them. Away from these imperfections, the Pb

atoms tend to form a hexagonal (1×1) pattern with a long-ranged order at room temperature. However, the (1×1) pattern gradually evolves into a pattern with a $\sqrt{3} \times \sqrt{3}$ short-ranged order near these imperfections. Because the local atomic rearrangement of the Pb layer is very sensitive to imperfections or perturbations, this monolayer Pb-covered Si(111) structure was called a "soft reconstruction."[42,43] In these patterns, it was also found that Pb atoms tended to be laterally displaced from the T_1 site to form small trimer domains with a $\sqrt{3} \times \sqrt{3}$ order inside each domain.[31,42,43] It was thought that the easy atomic rearrangement might be related to the vertical Si-Pb bonds, which resulted in very low activation energies for lateral displacements of the Pb adatoms.

A similar induced rearrangement (a hexagonal ringlike pattern) was recently reported for the adsorption of atomic H at the Pb-covered Si(111) surface.[31] The phenomena were found to be not purely electronic because the periodicity of the induced pattern was not bias dependent. Thus, it was attributed to an intricate interplay between electronic and atomic interactions as perturbed by the adsorbed hydrogen atoms. The pattern that appears around the three-lobe-type C_{60} molecule also does not vary with the sample bias. Therefore, we believe that these two patterns at the Pb-covered region have a very similar origin. However, it remains unclear why the atomic rearrangement is seen around the three-lobe-type C_{60} molecule only, but not around the pentagon-type molecule. This would be an interesting subject for further experimental and theoretical investigation.

The diffusion behavior of C_{60} molecules at surfaces is unique and interesting. As we have shown above, the C_{60} molecules at the two stable states are not mobile and do not rotate either. However, a C_{60} molecule can start to diffuse after manipulation with the scanning tip by decreasing the spacing between the tip and the molecule.[44] One method is to reduce the tunneling bias while maintaining the same tunneling current. An example is shown in Fig. 4. By changing the sample bias from +2.0 to +0.39 V right before the tip scans across the molecule, there is a good chance that the C_{60} molecule can be moved out of its stable state. The upper three-lobe-type C_{60} molecule (its site is marked with an "$\times$") in Fig. 4(a) is manipulated this way. After the tip has scanned over the molecule, the bias is changed back to +2.0 V to track the motion of the molecule.

Figures 4(b)–4(f) show several STM images selected from our continuous-time images, which are taken every 3 min after the manipulation. The molecule seen in Figs. 4(b) and 4(c) appears as a round sphere with no clear intramolecular features [upper insets of Figs. 4(b) and 4(c)], suggesting rapid rotation of the molecule. In addition, the induced corrugation originally seen around the molecule [Fig. 4(a)] disappears in Figs. 4(b) and 4(c). Note that no defect is left after the molecule is moved out of its original adsorption site (marked with an $\times$ in Fig. 4(b)). This indicates that the molecule does not occupy a defect site. The molecule shown in both Figs. 4(b) and 4(c) is not mobile for at least 20 s (52 scan lines) so that the images of the molecule can be clearly taken with the appearance of a single round sphere. The molecule seems to stop at a metastable site momentarily and make a long hop again to another metastable state. It finally settles down at another stable adsorp-

tion site [Fig. 4(d)], which is indicated with a white triangle in Fig. 4(b). As shown in the inset of Fig. 4(d), the three-lobe feature of the molecule can be seen again, indicating that the molecule ceases to move or rotate. Notice that the induced corrugated pattern cannot be seen around the molecule now. However, the pattern gradually appears, as shown in Figs. 4(e) and 4(f). We note that this new stable adsorption site appears darker than the normal (1×1) in Fig. 4(b), but the (1×1) periodicity can still be resolved inside this darker region (not shown). We think it is not a surface defect and the image contrast may be caused by a charged impurity atom (probably a dopant) located a few layers underneath. We note that the tunneling tip does not change during the entire observation process because the immobile pentagon-type C$_{60}$ molecule maintains the same appearance, as shown in the lower inset for each image in Fig. 4, except for that in Fig. 4(b).

Our height measurement of the C$_{60}$ molecule during the motion reveals something interesting. After manipulation, the C$_{60}$ molecule in the metastable states exhibits a slightly larger height, i.e., 0.40 nm.[45] The height maintains throughout the entire motion with variation smaller than 1% of the height. It eventually changes back to 0.38 nm when the induced corrugation in the surrounding Pb layer starts to occur [Fig. 4(e)]. A surprising observation is that the height of the molecule remains at 0.40 nm for the image shown in Fig. 4(d), when the three-lobe feature has appeared and the molecule ceases to move or rotate.

Figure 5 shows a different case that a three-lobe-type C$_{60}$ molecule is moved away from a nondefect adsorption site and eventually settles down with the pentagon type at a defect site. Figure 5(a) shows the STM image taken before the manipulation. The molecule exhibits a three-lobe shape [inset of Fig. 5(a)] and an induced corrugated pattern can be seen in the Pb layer around it. The sample bias is then changed from +2 to +0.27 V when the tip is about to scan across the molecule. After that, the tunneling bias is changed back to +2 V for imaging the motion of the molecule. The molecule seen in Figs. 5(b) and 5(c) also does not exhibit any intramolecular feature and no induced pattern is seen in the Pb layer around it. The height of the molecule in Figs. 5(b) and 5(c) is ~0.40 nm. The diffusion behavior of this molecule is very similar to that shown in Fig. 4. It finally settles down at a defect site marked with a "2" in Fig. 5(d). Notice that a pentagon is seen on top of the molecule [inset of Fig. 5(d)], and no induced corrugation is found around the molecule. This is consistent with our observations about the pentagon-type C$_{60}$ molecule.

The C$_{60}$ molecules usually appears as single round spheres in most images, as shown in Figs. 4 and 5, indicating that they do not displace in position when the scan lines are covering the molecule. For the case in Fig. 5, there are 67 scan lines to cover an entire molecule and each scan line takes ~0.4 s. Note that the C$_{60}$ molecule in Fig. 5(b) exhibits a sudden displacement of ~2.1 nm between scan lines 163 and 164, resulting in two separated incomplete round spots. The height profiles taken before (line 163) and after (line 164) the displacement are shown in Fig. 5(e). Notice that the two line scans trace the entire height profile of the molecule with no discontinuity, indicating that the displacement does
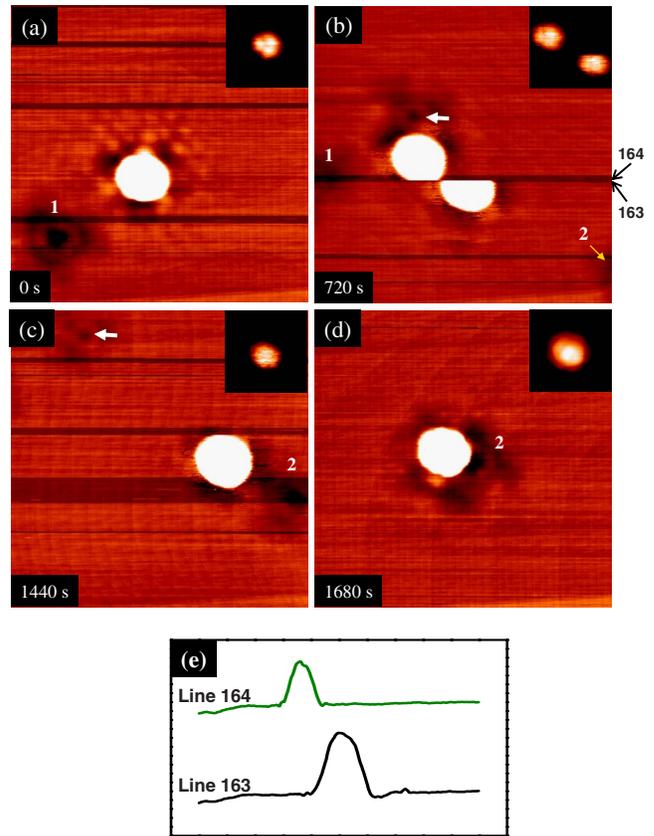

FIG. 5. (Color online) Observation of diffusion of a C$_{60}$ molecule. The scan size is 10×10 nm^2. All images are taken at a sample bias of +2 V and a tunneling current of 0.15 nA. (a) Image before manipulation. (b)–(d) are images chosen from our consecutive images taken every 134 s. The time for each image is indicated at the lower left-hand corner. Defects 1 and 2 can serve as markers for identifying the motions of the C$_{60}$ molecule. Since the image contrasts for the small corrugations in the Pb layer $(0.1-0.2 \text{ Å})$ and for the fine feature on top of the C$_{60}$ molecule cannot be simultaneously shown, we choose enhanced contrast of the former for each major image and that of the latter in the inset. In (b) and (c), an arrow indicates the position of the original site of the C$_{60}$ molecule before manipulation. In (b), a sudden translation of the C$_{60}$ molecule occurs when the tip is scanning over the region, resulting in an image of two noncomplete circles for the molecule. The stripes seen in these images may be due to motion of some unknown molecule onto or away from the tip end. (e) Height profiles of lines 163 and 164 for the image shown in (b). The slow scan direction is from the bottom to the top.

not occur while the tip is directly on the molecule. Our statistics over 2253 scan lines (only part of our data) covering C$_{60}$ molecules in such states show that there are only 11 hops, corresponding to an average hopping probability of ~0.5% within the duration of a scan line, ~0.4 s. The average displacement distance is 1.38 nm, which is much larger than the spacing between two neighboring T_4 sites, i.e., 0.38 nm. We note that none of the 11 hops occur while the tip is directly on the molecule. This indicates that the tip has almost no influence on the molecular jumps and that the C$_{60}$ molecules make long hops during the displacements.
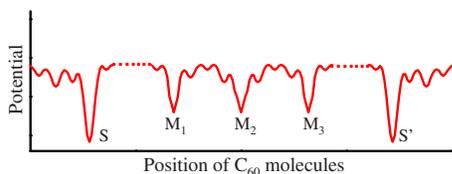
FIG. 6. (Color online) Schematic potential diagram for the diffusion of a C_{60} molecule at the Pb-covered surface. The horizontal axis is the one-dimensional representation of the position of the molecule at the surface. S and S' represent stable adsorption states and M_i represents a metastable adsorption state.

As seen in Figs. 5(a) and 5(d), the change of the top intramolecular feature after motions suggests that the molecule may rotate around an axis not perpendicular to the surface. We cannot totally rule out the possibility that the three-lobe type is rotated to the pentagon type by the initial tip manipulation and that the molecule only glides, without making random thermal rolling, on the surface with the pentagonal ring always on the top and at the bottom. However, this scenario is less likely because the motion behavior of this C_{60} molecule before stopping at a stable adsorption site is not distinguishable from that of C_{60} molecules which start with a three-lobe type and end also with a three-lobe type. We note that random thermal rolling does not necessarily lead to the change in the intramolecular feature, as observed for the rolling of a molecular wheel by Grill *et al.*[23]

Moriarty *et al.*[24] also observed a change of the intramolecular feature of C_{60} molecules before and after manipulation on Si(001)-2×1. The rolling mechanism was proposed to explain the motion. Later experimental and theoretical results also showed that the rolling process of C_{60} molecules could minimize the number of broken bonds through a pivot mechanism and was expected to have a minimum energy barrier for translation.[21]

We believe that a C_{60} molecule is locked to a stable adsorption state only when it moves to a certain adsorption site with a certain orientation relative to the substrate. Then, the C_{60} molecule may form relatively strong chemical bonds with the Si substrate and no rotation can occur. If the molecule is moved out of the stable state with a tip, it can undergo many degrees of freedom in motion, including rotations and translation. Thus, it may not be easy to fit to the special relative position and orientation of the stable adsorption state.

Figure 6 illustrates a schematic potential diagram for the diffusion of a C_{60} molecule at the Pb-covered surface. Due to the weak bonding between the substrate and the molecule for most of the relative orientations and positions, the molecule can diffuse with low activation energies. These motions are probably too fast for STM imaging. Only in some occasions when it happens to stop at a metastable adsorption state for a period of time can we image the molecule. The molecule is probably rotating very rapidly at these metastable states, resulting in the loss of detailed intramolecular features as seen in STM images in Figs. 4(b), 4(c), 5(b), and 5(c). The average lifetime for a metastable state depends on its bonding strength with the substrate. At this moment, we cannot tell whether there is only one or several metastable states. Ap-

parently, their heights are the same and there is no intramolecular feature. Our observations show that for some metastable state, the molecule can stay longer than 3 min before it starts to translate again. This scenario can explain why the molecule often makes long jumps between metastable sites. The translation, random thermal rolling, and rotation motions stop only when the molecule happens to occupy stable adsorption states again, which are indicated with an S or S' in Fig. 6. This schematic is also similar to the concept of "lock-and-key" recently proposed.[18]

The role of the Pb overlayer in the motions of the C_{60} molecule is an interesting subject to study. Since the height of the C_{60} molecule remains much smaller than the diameter of the molecule during the entire diffusion process, the molecule may move on the Si(111) substrate, rather than on the Pb overlayer. When a C_{60} molecule moves out of a site, a vacancy can be expected to appear. No vacancy is seen in our imaging probably due to the weak Pb–Pb and Pb–Si bondings. The Pb atoms may move away readily when a C_{60} molecule hops in and they can also rearrange in a short time to fill up the vacancy left behind. We even suspect that the Pb atoms may reduce the activation energies for the translation motion of the C_{60} molecule because diffusion of the C_{60} molecule on pure semiconductor surfaces at room temperature had not been reported before.

It remains a question why the three-lobe-type C_{60} molecule can induce a corrugated pattern in the surrounding Pb-covered region and why the pentagon-type C_{60} molecule does not. Also, it is very surprising that the pattern does not appear right after a diffusing C_{60} molecule stops at a three-lobe-type stable state, as seen in Fig. 4(d). We suspect that some kind of subtle bond-formation processes among the C_{60} molecule, the Si substrate and the surrounding Pb atoms cause such a gradual appearance of the induced pattern. The subtle change in height of the C_{60} molecule in Figs. 4(d) and 4(e) seems to support such a scenario.

IV. CONCLUSION

Here, we report our study of the dynamic behavior of C_{60} molecules at a Pb-covered Si(111) surface with a scanning tunneling microscope. There are two stable adsorption states, at which the molecules do not move or rotate. The C_{60} molecules can be moved out of their stable adsorption states with a tip and then start to diffuse randomly at the surface. They rapidly diffuse at most sites but may momentarily stop at some metastable states. Eventually, the motion will be stopped when the molecules happen to lock at the stable adsorption states. The motions seem to indicate that the molecules can rotate with many degrees of freedom, including random thermal rolling at the surface. We hope this can be a model system for further theoretical and experimental studies of diffusion mechanisms of polyhedron or spherelike nano-objects.

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*Present address: Institute of Applied Physics and Microsctructure Research Center Hamburg, University of Hamburg, Jungiusstrasse 11, D-20355 Hamburg, Germany.

†Corresponding author; ishwang@phys.sinica.edu.tw

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[44] We can also manipulate the motion of C_{60} by approaching the tip to one side of C_{60} molecule with zero bias.

[45] The height of a nearby immobile C_{60} molecule is also measured and does not show any variation in these images. Thus, we can conclude that the small height change ($\sim$0.02 nm) between the stable states and the metastable states is not caused by any tip change. This measured height change might result from either a real height change of the C_{60} molecule or electronic effects. We cannot distinguish between them at this moment.

[46] This image processing was performed with WSXM software (http://www.nanotec.es).